WATTS'

DICTIONARY OF CHEMISTRY

REVISED AND ENTIRELY REWRITTEN (189[illegible])

BY
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ASSISTED BY EMINENT CONTRIBUTORS

IN FOUR VOLUMES

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INTRODUCTION

TO THE ARTICLES ON INORGANIC CHEMISTRY.

It has been thought advisable to include in an ADDENDA brief accounts of the chief work done in descriptive inorganic chemistry since the publication of Vols. I., II., and III., and the printing off the final proofs of Vol. IV.

Nothing bearing on organic chemistry has been included in the ADDENDA, as to give an account of what has been done in this department since the various volumes were published would occupy many hundred pages.

Dates are attached to the references made to original memoirs in the ADDENDA; and references are frequently made to abstracts of the memoirs in the *Journal of the Chemical Society.*

M. M. PATTISON MUIR.

INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

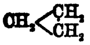
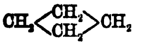
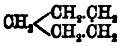
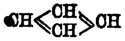
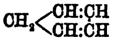
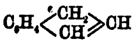
THE names used to denote ring formulæ are given below for convenience of reference.

Since the publication of the last volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs. T. Cooksey, T. A. Lawson, Samuel Rideal, Messrs. J. Wilkie, G. N. Huntly, and J. T. Norman. I have also been assisted by Mr. Arthur G. Green and Mr. Cecil W. Cunnington in the work of revising the proof-sheets. I have great pleasure in thanking these gentlemen for the energetic and efficient manner in which they have carried out their share of the work.

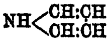
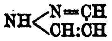
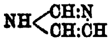
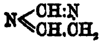
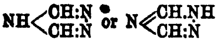
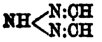
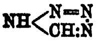
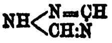
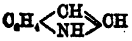
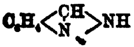
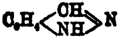
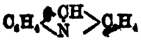
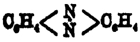
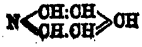
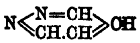
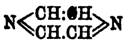
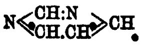
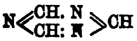
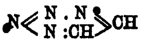
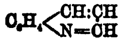
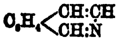
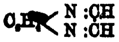
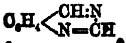
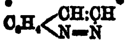
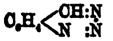
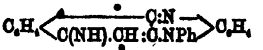
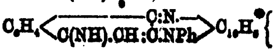
H. FORSTER MORLEY.

Nomenclature of Ring Formulæ.

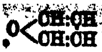
Hydrocarbons.

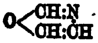
 $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}$	*Trimethylene.*
 $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2$	*Tetramethylene.*
 $CH_2<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}$	*Pentamethylene.*
 $CH<\begin{matrix}CH\\CH\end{matrix}>CH$	*Tetramethenyl.*
 $CH_2<\begin{matrix}CH:CH\\CH:CH\end{matrix}$	*Pentamethenyl hydride.*
 $C_6H_4<\begin{matrix}CH_2\\CH\end{matrix}>CH$	*Indonaphthene.*

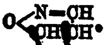
Nitrogen compounds.

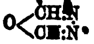
 $NH<\begin{matrix}CH:CH\\CH:CH\end{matrix}$	*Pyrrole.*
 $NH<\begin{matrix}N=CH\\CH:CH\end{matrix}$	*Pyrazole.*
 $NH<\begin{matrix}CH:N\\CH:CH\end{matrix}$	*Glyoxaline.*
 $N\ll\begin{matrix}CH:N\\CH.CH_2\end{matrix}$	*Metapyrazole.*
 $NH<\begin{matrix}CH:N\\CH:N\end{matrix}$ or $N\ll\begin{matrix}CH.NH\\CH:N\end{matrix}$	*Triazole.*
 $NH<\begin{matrix}N:CH\\N:CH\end{matrix}$	*Osotriazole.*
 $NH<\begin{matrix}N=N\\CH:N\end{matrix}$	*Tetrazole.*
 $NH<\begin{matrix}N=CH\\CH:N\end{matrix}$	*Pyrrodiazole.*
 $C_6H_4<\begin{matrix}CH\\NH\end{matrix}>CH$	*Indole.*
 $C_6H_4<\begin{matrix}CH\\N\end{matrix}>NH$	*Indazine.*
 $C_6H_4<\begin{matrix}CH\\NH\end{matrix}>N$	*Pseudo-indazine.*
 $C_6H_4<\begin{matrix}CH\\N\end{matrix}>C_6H_4$	*Acridine.*
 $C_6H_4<\begin{matrix}N\\N\end{matrix}>C_6H_4$	*Phenazine.*
 $N\ll\begin{matrix}CH:CH\\CH.CH\end{matrix}\gg CH$	*Pyridine.*
 $N\ll\begin{matrix}N=CH\\CH.CH\end{matrix}\gg CH$	*Pyridazine.*
 $N\ll\begin{matrix}CH:CH\\CH.CH\end{matrix}\gg N$	*Pyrazine.*
 $N\ll\begin{matrix}CH:N\\CH.CH\end{matrix}\gg CH$	*Pyrimidine.*
 $N\ll\begin{matrix}CH.\ N\\CH:\ N\end{matrix}\gg CH$	*Triazoline.*
 $N\ll\begin{matrix}N\ .\ N\\N\ :CH\end{matrix}\gg CH$	*Osotetrazole.*
 $C_6H_4<\begin{matrix}CH:CH\\N=CH\end{matrix}$	*Quinoline.*
 $C_6H_4<\begin{matrix}CH:CH\\CH:N\end{matrix}$	*Isoquinoline.*
 $C_6H_4<\begin{matrix}N\ :CH\\N\ :CH\end{matrix}$	*Quinoxaline.*
 $C_6H_4<\begin{matrix}CH:N\\N=CH\end{matrix}$	*Quinazoline.*
 $C_6H_4<\begin{matrix}CH:CH\\N=N\end{matrix}$	*Cinnoline.*
 $C_6H_4<\begin{matrix}CH:N\\N\ :N\end{matrix}$	*Phentriazine.*
 $C_6H_4<\begin{matrix}\overline{\qquad\qquad C:N}\\C(NH).CH:C.NPh\end{matrix}>C_6H_4$	*Rosinduline.*
 $C_6H_4<\begin{matrix}\overline{\qquad\qquad C:N.}\\C(NH).CH:C.NPh\end{matrix}>C_{10}H_6$	{ *Naphthoros induline.*

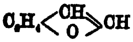
Oxygen compounds.

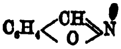

$O<\begin{matrix}CH:CH\\CH:CH\end{matrix}$ *Furfurane.*

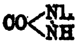

$O<\begin{matrix}CH:N\\CH:CH\end{matrix}$ *Oxazole.*

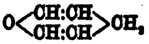

$O<\begin{matrix}N-CH\\CH:CH\end{matrix}$ *Iso-oxazole* or *Isoxazole.*

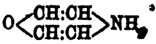

$O<\begin{matrix}CH:N\\CH:N\end{matrix}$ *Biazole.*

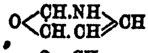

$C_6H_4<\begin{matrix}CH\\O\end{matrix}>CH$ *Coumarone.*

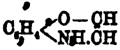

$C_6H_4<\begin{matrix}CH\\O\end{matrix}>N$ *Indoxazine.*

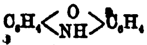

$CO<\begin{matrix}NH\\NH\end{matrix}$ *Carbizine.*


$O<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CH_2$ *Furidane.*

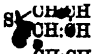

$O<\begin{matrix}CH:CH\\CH:CH\end{matrix}>NH$ *Pyroxazine.*

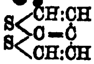

$O<\begin{matrix}CH.NH\\CH.CH\end{matrix}>CH$ *Pyroximidine.*

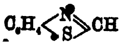

$C_6H_4<\begin{matrix}O-CH\\NH.CH\end{matrix}$ *Quinoxazine.*

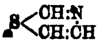

$C_6H_4<\begin{matrix}O\\NH\end{matrix}>C_6H_4$ *Phenoxazine* or *Phenazoxine.*

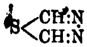
Sulphur compounds.

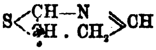

$S<\begin{matrix}CH:CH\\CH:CH\end{matrix}$ *Thiophene.*

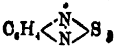

$\begin{matrix}S<\\S<\end{matrix}\begin{matrix}CH:CH\\C=C\\CH:CH\end{matrix}$ *Thiophthene.*

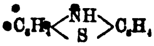

$C_6H_4<\begin{matrix}N\\S\end{matrix}>CH$ *Methenyl-amido-phenyl-mercaptan.*


$S<\begin{matrix}CH:N\\CH:CH\end{matrix}$ *Thiazole.*


$S<\begin{matrix}CH:N\\CH:N\end{matrix}$ *Diazthiole. Thiobiazole.*


$S<\begin{matrix}CH-N\\CH\ .\ CH_2\end{matrix}>CH$ *Penthiazole.*


$C_6H_4<\begin{matrix}N\\N\end{matrix}>S$ *Piazthiole.*


$C_6H_4<\begin{matrix}NH\\S\end{matrix}>C_6H_4$ *Imido-di-phenyl-sulphide.*

INITIALS OF SPECIAL CONTRIBUTORS.

S. A.	SVANTE ARRHENIUS, Ph.D., *Professor of Chemistry in Stockholm.* Contributes Solutions I.
J. W. C.	J. W. CAPSTICK, D.Sc., M.A., *Fellow of Trinity College, and Demonstrator in Physics in the University, Cambridge.* Contributes Capillarity, methods based on; and Viscosity of liquids.
G. G.	GEORGE GLADSTONE, Esq. Contributes Optical methods, *section* Refraction and Dispersion.
W. D. H.	W. D. HALLIBURTON, M.D., F.R.S., *Professor of Physiology at King's College, London.* Contributes Proteïds.
W. N. H.	W. N. HARTLEY, F.R.S., *Professor of Chemistry in the Royal College of Science Dublin.* Contributes Optical methods, *section* Spectroscopic methods.
E. A. L.	E. A. LETTS, Ph.D., *Professor of Chemistry at Queen's College, Belfast.* Contributes Phosphines.
R. M.	RAPHAEL MELDOLA, F.R.S., *Professor of Chemistry in the Finsbury Technical College.* Contributes Photographic chemistry.
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Articles by Mr. MUIR are initialed M. M. P. M.

Unsigned Articles are by Dr. MORLEY, except those in the *Addenda*, which are by Mr. MUIR.

ABBREVIATIONS

I. JOURNALS AND BOOKS.

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initial only.

A.	Liebig's Annalen der Chemie.
A. A.	Annales de la Sociedad Cientifica Argentina.
A. Ch. P.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
A. Ph. S.	Proceedings of the American Philosophical Society.
Ar. N.	Archives néerlandaises—The Hague.
Acad.	Mémoires de l'Académie des Sciences.
Ar. Ph.	Archiv der Pharmacie.
Ar. Sc.	Archives des Sciences phys. et nat.
B.	Berichte der deutschen chemischen Gesellschaft.
B. A.	Reports of the British Association.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
C. S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C. J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences—Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fr.	Fresenius' Zeitschrift für analytische Chemie.
G.	Gazzetta chimica italiana.
G. A.	Gilbert's Annalen der Physik und Chemie.
H.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
I.	Proceedings of the Royal Irish Academy.
J.	Jahresbericht über die Fortschritte der Chemie und verwa anderer Wissenschaften.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. de Ph.	Journal de Physique et des Sciences accessoires.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
J. Th.	Jahresbericht über Thierchemie.
J. R.	Journal of the Russian Chemical Society.
J. Z.	Jenaische Zeitschrift für Medicin und Naturwissenschaft.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
Mém. S. d'A.	Mémoires de la Société d'Arcueil.
Mém. B.	Mémoires couronnés par l'Académie de Bruxelles.

N.	Nature.
N.Ed.P.J.	New Edinburgh Philosophical Journal.
N. J. P.	Neues Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorff.
P. M.	Philosophical Magazine.
P.	Poggendorff's Annalen der Physik und Chemie.
P. B.	Beiblätter zu den Annalen der Physik und Chemie.
Pf.	Pflüger's Archiv für Physiologie.
Pr. E.	Proceedings of the Royal Society of Edinburgh.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Central-Blatt.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
P. Z.	Pharmaceutische Zeitschrift für Russland.
R. T. C.	Recueil des travaux chimiques des Pays-Bas
R. P.	Repertorium für die Pharmacie.
Q. J. S.	Quarterly Journal of Science.
S.	Schweigger's Journal der Physik.
Scher. J.	Scherer's Journal der Chemie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz.W.	Sitzungsberichte der K. Akademie zu Wien.
T. or *Tr.*	Transactions of the Royal Society.
T. E.	Transactions of the Royal Society of Edinburgh.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.
Z. B.	Zeitschrift für Biologie.
Z. f. d. g. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften.
Z. K.	Zeitschrift für Krystallographie und Mineralogie.
Z. P. C.	Zeitschrift für physikalische Chemie.
Bn.	Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.
E. P.	English Patent.
G. P.	German Patent.
Gm.	Gmelin's Handbook of Chemistry—English Edition.
Gm.-K.	Gmelin-Kraut: Handbuch der anorganischen Chemie.
Gerh.	Traité de Chimie organique: par Charles Gerhardt.
K.	Lehrbuch der organischen Chemie: von Aug. Kekulé.
G. O.	Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]
Stas. Rech.	Stas' Recherches, &c. — Aronstein's German translation is referred to as *Chem. Proport.*
Stas. Nouv. R.	Stas' Nouvelles Recherches, &c.
Th.	Thomsen's Thermochemische Untersuchungen.

II. Terms and Quantities, &c., frequently used.

Aq.	Water; e.g. NaOHAq means an aqueous solution of caustic soda.
aq.	18 parts by weight of water.
A' A'' A'''	Residues of mono-, di-, and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA', CaA'_2, AlA'_3 may be written, HA' standing for the acid. For a dibasic acid we should write Na_2A'', CaA'', $Al_2A''_3$ &c.
B' B'' etc.	Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be $B'HCl$ or $B''2HCl$, according as the base is monacid or diacid, &c.
conc.	Concentrated.
dil.	Dilute.
g.	gram.
mgm.	milligram.
mm.	millimetre.
mol.	molecule.
oil.	liquid, nearly, or quite, insoluble in water.
pp.	precipitate.
to ppt.	to precipitate.
ppg.	precipitating.
ppd.	precipitated.

ABBREVIATIONS.

[illegible]	soluble in.
insol.	insoluble in.
v. e. sol.	very easily
v. sol.	very
m. sol.	moderately } soluble in.
sl. sol.	slightly
v. sl. sol.	very slightly
v.	see.
cf.	compare.
c.	about.
[°]	a melting-point.
(°)	a boiling-point.
H.	Hardness (of minerals).
At. w.	Atomic weight.
Mol. w. or M. w.	Molecular weight.
D.	Density.
cor.	corrected.
uncor.	uncorrected.
i.V.	in vapour.
V.D.	vapour-density, *i.e.* density of a gas compared with hydrogen or air
S.G.	Specific gravity compared with water.
S.G. $\frac{10}{0}$	,, ,, at 10° compared with water at 0°.
S.G. $\frac{15}{4}$	,, ,, ,, 15° ,, ,, ,, ,, 4°.
S.G. ^{12}	,, ,, ,, 12°; compared with water of which the temperature is not given.
S.H.	Specific heat.
S.H. v.	,, ,, of a gas at constant volume.
S.H. p.	,, ,, ,, ,, ,, pressure.
H.C.	Quantity of heat, in gram-units, produced during the complete combustion of the mass of a solid or liquid body represented by its formula, taken in grams.
H.C. v.	Heat of combustion in gram-units of a gram-molecule of an element or compound, when gaseous, under constant volume.
H.C. p.	The same, under constant pressure.
H.F.	Quantity of heat, in gram-units, produced during the formation of the mass of a solid or liquid body represented by its formula, taken in grams, from the masses of its constituent elements expressed by their formulæ, taken in grams.
H.F. v.	Heat of formation of a gram-molecule of a gaseous compound from the gram-molecules of its elements under constant volume.
H.F. p.	The same, under constant pressure.
H.V.	Heat of vaporisation of a liquid, *i.e.* gram-units of heat required to change a gram-molecule of the liquid compound at B. P. into gas at same temperature and pressure.
T.C.	Thermal conductivity (unit to be stated).
S.V.	Specific volume; or the molecular weight of a gaseous compound divided by the S.G. of the liquid compound at its boiling-point compared with water at 4°.
S.V.S.	Specific volume of a solid; or the mass of the solid expressed by its formula, taken in grams, divided by its S.G.
E.C.	Electrical conductivity (the unit is stated in each case).
C.E. (10° to 20°)	Coefficient of expansion (between 10° and 20°).
S.	Solubility in water { of a gas = volume dissolved by 1 volume of water. of a liquid or solid = number of grms. dissolved by 100 grms. of water. In both cases the temperature is stated.
S. (alcohol)	,, ,, alcohol
μ_β	Index of refraction for hydrogen line β.
μ_D, &c.	,, ,, ,, sodium ,, ,, D, &c.
$R_D \frac{15}{0}$	Molecular refraction for sodium light, i.e. index of refraction for line D minus one, multiplied by molecular weight, and divided by S.G. at 15° compared with water at 0°.
R_D	The same; S.G. being determined at 15°–20° and referred to water at 4°.
R_∞	The same for line of infinite wave-length, index being determined by Cauchy's formula (Brühl's R_A).
$[\alpha]_D$	Specific rotation for sodium light.
$[\alpha]_j$	,, ,, ,, neutral tint. $[\alpha] = \frac{100}{p} \times \frac{a}{d}$. a = observed rotation for 100 mm. of liquid. d = S.G. of liquid. p = no. of grammes of active substance in 100 grammes of liquid.

M. M.	Molecular magnetic rotatory power $= \frac{m \times \alpha}{d \times \alpha' \times m'}$, where m = molecular weight of the body of S.G. = d, α = angle of rotation under magnetic influence, α' = angle of rotation of water under same influence, and m' = molecular weight of water (18).	
Ac	Acetyl C_2H_3O.	
Bz	Benzoyl C_7H_5O.	
Cy	Cyanogen CN.	
Et	Ethyl C_2H_5.	in formulæ.
Me	Methyl CH_3.	
Ph	Phenyl C_6H_5.	
Pr	Normal Propyl $CH_2.CH_2.CH_3$.	
Pr	Isopropyl $CH(CH_3)_2$.	
R, R' &c.	Alcohol radicles or alkyls.	
prim	primary.	
sec	secondary.	
tert	tertiary.	
n	normal.	
m, *o*, *p*	meta—ortho—para.	
c	consecutive.	
i	irregular.	
s	symmetrical.	
u	unsymmetrical.	
ψ	pseudo.	
ν	attached to nitrogen.	
α β γ	Employed to denote that the substituent is attached to a carbon atom which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined by the nature of the compound. Thus $CH_3.CHBr.CO_2H$ is α-bromo-propionic acid.	
ω	denotes that the element or radicle which follows it is attached to a terminal carbon atom.	
α, β, γ, &c.	indicate position in an open chain, only.	
1, 2, 3, &c.	indicate position in a ring only.	
(α), (β), &c.	Used when α, β, &c. are employed in a sense different from the above, *e.g.* (α)-di-bromo-camphor.	
	Baeyer's Nomenclature:	
(*B.*)	benzene ring.	
(*Py.*)	pyridine ring. Thus (*B.* 1:3) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring. While (*Py.* 1:3) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings, but both united to the same carbon atom.	
(*A.*)	denotes the central ring in the molecule of anthracene, acridines, and azines.	
eso-	means that the element or radicle it precedes is in a closed ring.	
exo-	„ „ „ „ „ not in a benzene ring.	
allo-	denotes isomerism that is not indicated by ordinary formulæ; thus maleic acid may be called *allo*-fumaric acid.	
thio-	denotes displacement of oxygen by sulphur.	
sulpho-	„ the group SO_3H, except in the word sulphocyanide.	
sulphydro-	„ the group SH.	
	Tribromonitrobenzene sulphonic acid [1:2:3:4:5] means that the three bromines occupy positions 1, 2, and 3; the nitro- group the position 4, and the sulpho- group the position 5.	

* Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulæ without this mark are those of analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated otherwise.

Wave-lengths are given in 10^{-7} mm.

Formulæ, when used instead of names of substances, have a qualitative meaning only.

Thomsen's notation is used in thermochemical data.

DICTIONARY OF CHEMISTRY

PHENYL-AZOXAZOLE $\begin{matrix}CH:N\\ CPh:N\end{matrix}\!\!>O$. [30°]. Formed by the action of CO_2 on an alkaline solution of the oxim of phenyl-glyoxal (Russanoff, *B.* 24, 3503). Needles, insol. water.

PHENYL-BENZAMIDINE $C_{13}H_{12}N_2$ *i.e.* $C_6H_5C(NH).NHPh$ or $C_6H_5.C(NPh).NH_2$ [112°]. Formed from benzonitrile and aniline hydrochloride at 230° (Bernthsen, *A.* 184, 348; 192, 33). Formed also from benzimido-ether and aniline, and from CPhCl:NPh and NH_3 (Kobbert, *A.* 265, 138). Nodules (from alcohol), sl. sol. water. Forms a crystalline nitrate.

Reactions.—1. Split up by heat into aniline and benzonitrile.—2. Dry H_2S at 130° forms $C_6H_5.CS.NHPh$ and some thio-benzamide.—3. CS_2 at 100° forms thio-benzanilide and phenyl-benzamidine sulphocyanide.—4. Reduced by sodium-amalgam to $C_6H_5.CH(NH_2).NHPh$.—5. *Nitrous* acid forms benzanilide (Mieran, *A.* 265, 141).

The derivatives $C_6H_5C(N.SO_2Ph).NHPh$ [139°] and $C_6H_4(SO_2N:C(NHPh).C_6H_5)_2$ [196°] have been prepared (Wallach, *A.* 214, 214; Jackson, *Am.* 9, 346).

s-**Di-phenyl-benzamidine** $C_{19}H_{16}N_2$ *i.e.* $C_6H_5.C(NPh).NHPh$. [144°].

Formation.—1. From benzanilide by treatment with PCl_5 and aniline (Gerhardt, *A.* 108, 219; Hofmann, *Z.* 1866, 161; Wallach, *A.* 184, 83).—2. From $Ph.CCl_3$ and aniline with or without $ZnCl_2$ (Limpricht, *A.* 135, 82; Döbner, *B.* 15, 233).—3. A product of the action of aniline hydrochloride at 250° on benzonitrile, thiobenzamide, or phenyl-benzamidine (Bernthsen, *A.* 184, 352).—4. By heating benzanilide with phenyl cyanate at 190° (Kühn, *B.* 18, 1476).—5. By heating the hydrochloride of benzimido-ether in alcohol with aniline for a long time (Kobbert, *A.* 265, 155).

Properties.—Needles (from alcohol), m. sol. benzene. Its alcoholic solution is neutral to litmus. Not affected by nitrous acid. Split up into aniline and benzanilide when boiled for a long time with alcohol.

Reactions.—1. Dry H_2S at 160° forms thio-benzanilide.—2. CS_2 at 140° forms PhCS.NHPh and NPhCS (Bernthsen, *A.* 192, 34).—3. Conc. HClAq at 1[illegible]° yields aniline and benzoic acid.

Salts.—B'HCl: v. sl. sol. water.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$: yellow needles.

u-**Di-phenyl-benzamidine** $C_6H_5.C(NH).NPh_2$. [112°]. Formed by heating diphenylamine hydrochloride with benzonitrile at [illegible] for 5 days (Bernthsen, *A.* 192, 5). Trimetric tablets, v. sol. alcohol and benzene.

Its alcoholic solution turns litmus blue. Conc. H_2SO_4 gives a violet-blue colour on warming.

Reactions.—1. Dilute HClAq at 150° forms NPh_2Bz.—2. The free base and its hydrochloride yield benzonitrile and diphenylamine on heating.—3. Nitrous acid forms NPh_2Bz (Klobbert, *A.* 265, 157).—4. H_2S at 130° forms $Ph.CS.NH_2$, diphenylamine, $PhCS.NPh_2$, and NH_3.—5. CS_2 at 140° forms $PhCS.NPh_2$ and HNCS.

Salts.—B'HCl. [c. 223°]. Monoclinic crystals, $a:b:c = {\cdot}529:1:{\cdot}507$; $\beta = 85°52'$. V. sol. water, sol. alcohol, insol. ether.—$B'_2H_2PtCl_6$.—B'HNCS. [203°]. Yellow prisms.

PHENYL-BENZAMIDOXIM $C_6H_5.C(NOH).NHPh$. [136°]. Formed by boiling $C_6H_5.CS.NHPh$ with an alcoholic solution of hydroxylamine (Müller, *B.* 19, 1669). Needles (from water). Yields B'HCl. $ClCO_2Et$ forms $C_{14}H_{10}N_2O_2$ [167°].

DI-PHENYL-BENZAZIDINE $C_{19}H_{18}N_4$ *i.e.* $C_6H_5C(N.NHPh).NH.NHPh$. [179°]. Formed by the action of phenyl-hydrazine on $PhCCl_3$ or on the hydrochloride of benz-imido-ether dissolved in absolute alcohol (Pinner, *B.* 17, 182; Marckwald, *C. C.* 1888, 1410). Dark-red needles.

PHENYL-BENZENE *v.* DIPHENYL.

p-**Di-phenyl-benzene** $C_{18}H_{14}$ *i.e.* $C_6H_4Ph_2$. Mol. w. 230. [207°]. (c. 405°).

Formation.—1. A product of the action of sodium on an ethereal solution of *p*-di-bromo-benzene, or, better, of a mixture of *p*-di-bromo-benzene with bromine (Riese, *Z.* [2] 6, 192, 785; *A.* 164, 168).—2. Together with its isomeride, and other products, by passing the vapour of benzene, or of a mixture of benzene and toluene, through a red-hot tube (G. Schultz, *B.* 6, 415; *A.* 174, 230; 203, 118; Carnelley, *C. J.* 37, 712).—3. Together with the isomeride and other products, by the action of $AlCl_3$ on a mixture of MeCl and diphenyl (Adam, *Bl.* [2] 49, 97; *A. Ch.* [6] 15, 241).

Properties.—Needles (from benzene), or iridescent laminæ (by sublimation); insol. alcohol, v. sl. sol. HOAc. Its solution in benzene shows blue fluorescence. Conc. H_2SO_4 gives a dirty-green solution changing to purple. CrO_3 in HOAc oxidises it to diphenyl *p*-carboxylic [216°] and terephthalic acids. Does not form a compound with picric acid. Not volatile with steam. Yields $C_{18}Cl_{14}$ on exhaustive chlorination with $SbCl_5$ (Merz a. Weith, *B.* 16, 2884).

References.—BROMO- and TRI-CHLORO-DI-PHENYL-BENZENES.

Iso-di-phenyl-benzene $C_{18}H_{14}$. [85°]. (c. 370°). Formed as above. Slender prisms, v. sol. al.

cohol. Yields benzoic acid on CrO_3.

s-Tri-phenyl-benzene $C_{24}H_{18}$ *i.e.* $C_6H_3Ph_3$. Mol. w. 306. [171°]. (above 360°). Formed from acetophenone by treatment with P_2O_5, with alcoholic NH_3, or with dry HCl (Engler, *B.* 6, 638; 7, 1123). Formed also by heating $C_6H_3(C_6H_4.CO_2H)_3$ with KOH (Gabriel a. Michael, *B.* 11, 1007). It is also a by-product in the action of acetophenone on dimethylaniline in presence of $ZnCl_2$ (Döbner a. Petschoff, *A.* 242, 338). Trimetric crystals; *a*:*b*:*c* = ·566:1:·766, sl. sol. alcohol. Yields benzoic acid on oxidation by CrO_3 in HOAc (Mellin, *B.* 23, 2533). By exhaustive chlorination with $SbCl_5$ it yields per-chloro-tri-phenyl-benzene (Merz a. Weith, *B.* 16, 2883). On heating with I and red P at 275° it yields the crystalline dodeca-hydride $C_{24}H_{30}$ and finally oily $C_{24}H_{42}$ (Mellin, *B.* 23, 2534). Fuming H_2SO_4 at 100° forms a disulphonic acid, which yields the Ba salt $C_{24}H_{16}S_2O_6Ba$ crystallising in needles.

PHENYL-BENZENE-SULPHAZIDE *v.* *Phenyl-hydrazide* of BENZENE SULPHONIC ACID.

DI-PHENYL-BENZENYL-DI-UREA NHPh.CO.NH.CPh:N.CO.NHPh. [172°]. Formed from benzamidine hydrochloride, phenyl cyanate, and NaOHAq (Pinner, *B.* 22, 1607). Needles, insol. water, v. sl. sol. hot alcohol.

PHENYL-BENZIMIDO-ETHER $C_{15}H_{15}NO$ *i.e.* CPh(NPh).OEt. A product of the action of aniline on benzimido-ether (Lossen, *A.* 265, 138). Oil. Decomposed by conc. HClAq into EtCl and benzanilide.

PHENYL BENZOATE *v.* *Benzoyl derivative* of PHENOL.

PHENYL-BENZOIC ACID *v.* DIPHENYL-CARBOXYLIC ACID.

PHENYL-BENZOPHENONE $C_{19}H_{14}O$ *i.e.* [1:4] $C_6H_5.C_6H_4.CO.C_6H_5$. [104°]. V.D. 9·0. Formed by oxidation of *p*-benzyl-diphenyl with chromic acid (Goldschmiedt, *M.* 2, 437; Köller, *M.* 12, 501). Formed also from diphenyl, BzCl, and $AlCl_3$ (Wolf, *B.* 14, 2032). Scales, sol. alcohol. Yields benzophenone-*p*-carboxylic acid on further oxidation by CrO_3.

Oxim. [194°]. Needles. When HCl is passed into its solution in HOAc containing Ac_2O and the mixture heated in sealed tubes at 100°, it is converted into the isomeric $C_6H_5.C_6H_4.CO.NHC_6H_5$ [224°]. The oxim is reduced by sodium-amalgam to the corresponding amine $C_6H_5.C_6H_4.CH(NH_2).C_6H_5$ [77°].

Benzoyl derivative of the *Oxim* [193°]. Needles (from alcohol).

Phenyl-hydrazide. [144°]. Yellow needles (from dilute alcohol).

Di-phenyl-benzophenone $(C_6H_5.C_6H_4)_2CO$. [229°]. Formed by the action of $COCl_2$ on diphenyl in presence of $AlCl_3$ (Adam, *Bl.* [2] 47, 689; *A. Ch.* [6] 15, 259). Got also by oxidising $CH_2(C_6H_4Ph)_2$ (Weiler, *B.* 7, 1188). White needles, sol. acetone, v. sl. sol. alcohol. Not attacked by fuming HNO_3 or by H_2SO_4 and HNO_3 at 100°. By adding Na to its solution in alcohol-benzene it is reduced to $(C_6H_5.C_6H_4)_2CH.OH$, [151°], S. (ether) 5; S. (alcohol) 1·25 at 15°. Potash-fusion gives diphenyl-*p*-carboxylic acid [218°].

PHENYL-BENZOPHENONE CARBOXYLIC ACID $C_6H_4Ph.CO.C_6H_4.CO_2H$. [220°]. Formed from diphenyl, phthalic anhydride, and $AlCl_3$ (Kaiser, *A.* 257, 96). Needles. Yields an oxim ether MeA' [85°-90°].

PHENYL-BENZOYL is BENZOPHENONE.

PHENYL-BENZOYL-ACETIC ACID $CHBzPh.CO_2H$. *Methyl ether* MeA'. Form from de-oxybenzoin, NaOEt, and $ClCO_2$ (Rattner, *B.* 21, 1316). Oil, decomposed by d tillation into $C_2H_2Ph_2$, CO_2, and HOBz.

PHENYL-BENZOYL-BUTYRIC ACID $CHBzPh.CH_2.CH_2.CO_2H$. (β)-*Desyl-propion* *acid*. [136°]. Formed from deoxybenzoi NaOEt, and β-iodo-propionic ether (Knoevenag *B.* 21, 1344). Needles. Yields MeA' [6 and EtA' [84°].

The isomeric acid CHBzPh.CHMe.CO [215°], formed from β-bromo-propionic acid, less sol. alcohol and ether.

PHENYL-BENZOYL-CARBINOL *v.* BENZOÏ

PHENYL-BENZOYL-PROPIONIC ACID $CHBzPh.CH_2.CO_2H$. [156°]. Formed from d oxybenzoin, NaOEt, and chloro-acetic eth (Meyer a. Oelkers, *B.* 21, 1295; Knoevenage *B.* 21, 1344). Small tables (from alcohol).

Di-phenyl-benzoyl-propionic acid $CH_2Bz.CPh_2.CO_2H$. [183°]. Got by the action alcoholic potash on the lactone of oxy-tri-pheny crotonic acid (Japp a. Klingemann, *B.* 22, 2882 Yields a phenyl-hydrazide $C_{28}H_{22}N_2O$ [185° and an oxim $C_{22}H_{19}NO_2$ [152°].

PHENYL-BENZYL ALCOHOL $C_{13}H_{12}O$ *i.* $C_6H_4Ph.CH_2OH$. Got from $C_6H_4Ph.CH_3$ by treatment with Br and alcoholic potash; the resultin syrupy $C_6H_4Ph.CH_2OEt$ being treated with H (Adam, *Bl.* [2] 49, 97). Syrup.

PHENYL-BENZYL-AMIDO-DI-PHENYL-METHANE $C_{26}H_{23}N$ *i.e.* $CH_2Ph.C_6H_4NPh.C_7H$ Formed by heating NPh_2H (1 mol.) with benzy chloride (2 mols.) and $ZnCl_2$ at 210° (Meldola *C. J.* 41, 200). Solid; *v.* sol. ether, insol. alcoho and HOAc.

PHENYL-BENZYL-AMINE *v.* BENZYL-ANILINE.

Nitrosamine $C_7H_7NPh.NO$. [58°]. Needle (Antrick, *A.* 227, 360). Yields benzyl-anilin and benzylidene-aniline on treatment wit alcoholic HCl (O. Fischer, *A.* 241, 328).

Phenyl-di-benzyl-amine *v.* DI-BENZYL-ANILINE.

Di-phenyl-benzyl-amine $NPh_2.CH_2Ph$. [87°] Got from $C_6H_5.CSNPh_2$, zinc-dust, and HClAq (Bernthsen a. Trompetter, *B.* 11, 1761; *cf.* Wilm a. Girard, *B.* 8, 1196). Needles, sl. sol. cold alcohol. Yields a green dye on heating with HClAq and arsenic acid (Meldola, *B.* 14, 1385).

DI-PHENYL-DI-BENZYL-TETRAZONE $NPh(CH_2Ph).N:N.NPh(CH_2Ph)$. [109°]. Formed from (α)-phenyl-benzyl-hydrazine, $CHCl_3$, and HgO (Michaelis a. Philips, *A.* 252, 290). Needles.

PHENYL-BENZYL-CARBINOL $C_{14}H_{14}O$ *i.e.* $CH_2Ph.CH(OH).C_6H_5$. *Toluylene hydrate.* [42°]. Formed by reducing deoxybenzoin, and by the action of alcoholic potash on the same body (Limpricht a. Schwanert, *A.* 155, 62; Goldenberg, *A.* 174, 332; Zagoumenny, *A.* 184, 163; Anschütz, *A.* 261, 298). Formed also [62°] by the action of nitrous acid on $CH_2Ph.CHPh.NH_2$ (Leuckart, *B.* 22, 1410). Long slender needles (from alcohol), insol. water. Reduced by HIAq to dibenzyl. Yields a liquid acetyl derivative.

PHENYL BENZYL ETHER *v.* *Phenyl ether* of BENZYL ALCOHOL.

[illegible]-PHENYL-THIO-UREA [illegible] [91°]. Formed from ethyl-thiocarbimide and benzyl-aniline in alcohol (Dixon, *C. J.* [illegible], 566). Rectangular prisms, insol. cold water, v. e. sol. boiling alcohol.

An isomeride [91° uncor.] formed from benzyl-thiocarbimide and ethyl-aniline crystallises in oblique prisms grouped in rosettes.

PHENYL-BENZYL-HYDRAZINE $C_{13}H_{14}N_2$ *i.e.* $CH_2Ph.NPh.NH_2$. [26°]. Formed from sodium phenyl-hydrazine and benzyl chloride, and got also by reduction of phenyl-benzyl-nitrosamine (Antrick, *A.* 227, 361; Michaelis a. Philips, *A.* 252, 286). Needles (containing aq), decomposed by heat. Benzoic aldehyde forms $CH_2Ph.NPh.N{:}CHPh$. [111°]. In benzene solution it gives with $SOCl_2$ the thionyl compound $C_7H_7NPh.N{:}SO$ [65°] (Michaelis a. Ruhl, *A.* 270, 122). $C_6H_5PCl_2$ forms $C_7H_7NPh.N{:}PC_6H_5$ [141°], crystallising from ether in needles.—B'HCl. [167°]: colourless needles. Benzene phosphinate $B'C_6H_5PH_2O_2$ [108°] (Michaelis, *A.* 270, 135).

Acetyl derivative. [121°]. Scales.

Benzylo-chloride $(C_7H_7)_2NPhCl.NH_2$. [154°].

PHENYL-BENZYLIDENE-ALLYL-HYDRAZINE $NPh(C_3H_5).N{:}CHPh$. [52°]. Formed from phenyl-allyl-hydrazine and benzoic aldehyde (Michaelis a. Claesson, *B.* 22, 2237). Needles, v. sol. ether and hot alcohol.

PHENYL-BENZYLIDENE-AMINE *v.* BENZYLIDENE-ANILINE.

Phenyl-benzylidene-diamine $C_6H_5.CH(NH_2)(NHPh)$. [115°]. Formed by reduction of phenyl-benzamidine with zinc and HCl (Bernthsen a. Szymanski, *B.* 13, 917). Small crystals.—B'HCl. [224°]. Thick prisms.—$B'_2H_2PtCl_6$: spikes or plates.

DI-PHENYL-BENZYLIDENE-ETHYLENE-DIAMINE $CHPh{<}\substack{NPh\\NPh}{>}C_2H_4$. [137°]. Formed from benzoic aldehyde and di-phenyl-ethylene-diamine (Moos, *B.* 20, 732). Needles, split up by dilute HCl into the parent bodies.

PHENYL-BENZYLIDENE-ETHYL-HYDRAZINE $PhNEt.N{:}CHPh$. [59°]. Formed from benzoic aldehyde and phenyl-ethyl-hydrazine (Michaelis a. Philips, *A.* 252, 272).

PHENYL-BENZYLIDENE-HYDRAZINE *v.* *Phenyl-hydrazide* of BENZOIC ALDEHYDE.

DI-PHENYL-BENZYLIDENE-DI-INDOLE $CHPh(C_{14}H_{10}N)_2$. [268° uncor.]. Formed from benzoic aldehyde and $C_6H_4{<}\substack{CH\\NH}{>}CPh$ (E. Fischer a. Schmidt, *B.* 21, 1074). Slender leaflets, v. sl. sol. hot alcohol.

PHENYL-BENZYL-INDOLE $C_{21}H_{17}N$ *i.e.* $C_6H_4{<}\substack{C(C_7H_7)\\NH}{>}CPh$. [101°]. Formed by heating the phenyl-hydrazide of di-benzyl ketone with alcoholic HCl (Trenkler, *A.* 248, 112). Hexagonal prisms (from hot ligroin). Does not give the pine-wood reaction.

PHENYL BENZYL KETONE $C_{14}H_{12}O$ *i.e.* $C_6H_5.CH_2.CO.C_6H_5$. *Desoxybenzoin. Deoxybenzoin.* Mol. w. 196. [60°]. (322° cor.). (177·6° at 12 mm.) (Anschütz a. Berns, *B.* 20, 1392).

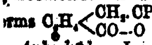
Formation.—1. By the action of zinc and HCl on benzoin (Zinin, *A.* 119, 179; 126, [illegible]; [illegible] 4, 718; V. Meyer, *B.* 21, 1296; Wachter, *B.* 25, 1728).—2. By passing benzoin over heated zinc-dust (Limpricht a. Schwanert, *A.* 155, 59).—3. By heating bromo-di-phenyl-ethylene with water at 190° (L. a. S.).—4. By distilling a mixture of calcium benzoate and calcium phenyl-acetate (Radziszewski, *B.* 6, 489; 8, 756).—5. By the action of $AlCl_3$ on a mixture of phenyl-acetyl chloride and benzene (Graebe a. Bungener, *B.* 12, 1079).—6. From phenyl-acetic acid, benzene, and P_2O_5 (Zincke, *B.* [illegible], 1771).—7. By the action of alcoholic ammonium sulphide (or KHS) on benzil (Zinin, *J. pr.* 33, 35; Jena, *A.* 155, 87).—8. By dissolving s-di-phenyl-acetylene in H_2SO_4 and adding water (Béhal, *Bl.* [2] 49, 387).

Properties.—White plates (from alcohol); sl. sol. hot water, volatile with steam.

Reactions.—1. On heating with *alcoholic potash* it yields phenyl-benzyl-carbinol and 'di-ethyl carbobenzonic' acid $C_{18}H_{18}O_2$ [100°], which gives EtA' (209° at 11 mm.) (Zagoumenny, *A.* 184, 163; Anschütz, *A.* 261, 298). The acid $C_{18}H_{18}O_2$ is converted by P and HI into an isomeric acid [184°], by HNO_3 (S.G. 1·18) into $C_{18}H_{16}O_3$ [128°], by conc. HNO_3 into $C_{18}H_{16}(NO_2)_2O_2$ [156°], and by potash-fusion into β-benzyl-isobutyric acid.—2. KOH in *propyl alcohol* at 150° forms $C_{20}H_{22}O_2$ [90°] and also an isomeride [139°] which yields $C_{20}H_{20}(NO_2)_2O_2$ [176°].—3. KOH in *isobutyl alcohol* at 140° forms 'di-isobutyl-carbobenzonic' acid $C_{22}H_{26}O_2$ [148°], S. (alcohol) 5. The homologous isoamyl compound $C_{24}H_{30}O_2$ [160] may be got in like manner.—4. Reduced by HI to di-phenyl-ethylene and di-phenyl-ethane.—5. *Sodium-amalgam* reduces it to $C_{28}H_{26}O_2$ and finally to phenyl-benzyl-carbinol.—6. *Nitric acid* (S.G. 1·2) yields benzil, nitro-benzil, and *p*-nitro-benzoic acid. Conc. HNO_3 (S.G. 1·475) at 0° forms $C_{14}H_{11}(NO_2)O$ [142°], whence $C_{14}H_{11}(NH_2)O$ [95°]. The nitro- and amido-compounds yield oxims melting at 107° and 141° respectively. Fuming HNO_3 (S.G. 1·51) at 0° forms three isomeric di-nitro- derivatives [116°], [126°] and [155°] (Golubeff, *B.* 18, 2403; *J. R.* 18, 23).—7. *Bromine* forms $C_{14}H_{11}BrO$ [55°] (Knoevenagel, *B.* 21, 1355) and $C_6H_5.CO.CBr_2.C_6H_5$ [112°].—8. PCl_5 yields $CHPh{:}CClPh$.—9. *Alcoholic potash* and *benzoic* aldehyde form benzamarone $C_{35}H_{28}O_3$ [315°] (Japp a. Klingemann, *B.* 21, 2934; *cf.* Zinin, *Z.* 1871, 127).—10. NaOEt and nitrous acid yield the mono- oxim of benzil.—11. NaOEt and $CSCl_2$ yield golden $(C_6H_5.C(CS).CO.C_6H_5)_x$ [286°] (Bergreen, B. 21, 350).—12. NaOEt and MeI yield phenyl phenyl-ethyl ketone $C_6H_5.CO.CHMePh$. Other alkyl iodides act in like manner (V. Meyer, *B.* 21, 1295).—13. Sodium acting on a benzene solution in absence of air forms $C_6H_5.CO.CHNa.C_6H_5$, a very hygroscopic yellow substance converted by CO_2 into an acid, whence hydroxylamine forms $\substack{CPh\ {:}N\\CHPh.CO}{>}O$ [160°] (Beckmann a. Paul, *A.* 266, 22).—14. $CSCl_2$ or CS_2 forms desaurin [illegible] which is fiery yellow, sparingly soluble, and yields a violet solution in H_2SO_4 (Bergreen a. Meyer, *B.* 21, 353; Meyer a. Wege, *B.* 24, 3535; Wachter, *B.* 25, 1727). HNO_3 and H_2SO_4 convert desaurin into $C_{14}H_9SN_3O_7$? [60°]. Fuming HNO_3 forms $C_{14}H_9SN_2O_{10}$ [60°] and *m*-nitro-benzoic acid. Desaurin when heated for a long time with aniline yields phenyl benzyl ketone, tri-phenyl-guanidine, and H_2S.

Oxim $C_6H_5.CH_2.C(NOH).C_6H_5$. [98°].

Phenyl-hydrazide $CH_2Ph.C(N_2HPh).Ph$. [106°]. Needles (from alcohol) (Ney, *B.* 21, 2447).

PHENYL BENZYL KETONE-*o*-CARBOXYLIC ACID $C_{15}H_{12}O_3$ *i.e.* $C_6H_5.CO.CH_2.C_6H_4.CO_2H$. *Deoxybenzoïn-carboxylic acid.* [168]. Formed by heating isobenzylidene-phthalide with NaOH (Gabriel, *B.* 18, 2446). Needles, v. sol. alcohol. Reduced by sodium-amalgam to $C_6H_5.CH(OH).CH_2.C_6H_4.CO_2H$. Ammonia forms isobenzylidene-phthalimidine. Hydroxylamine hydrochloride in alcoholic solution at 100° forms  $C_6H_4<{CH_2.CPh \atop CO-O}>N$ [189°]. AgA′: pp.

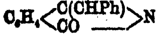
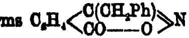
Anhydride v. Isobenzylidene-phthalide.

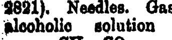
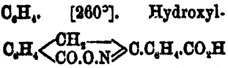
Methylamide $CH_2Bz.C_6H_4.CO.NHMe$. 44°]. Formed from isobenzylidene-phthalide nd methylamine in alcohol at 100° (Gabriel, . 20, 2866). White needles.

Phenyl benzyl ketone *o*-carboxylic acid $H_5.CH_2.CO.C_6H_4.CO_2H$. *Deoxybenzoïn-carboxylic acid.* [75°]. Formed by boiling benzidene-phthalide with KOHAq (Gabriel a. ichael, *B.* 11, 1018). Prisms (containing aq). AgA′: crystalline pp.

Anhydride v. Benzylidene-phthalide.

Amide $CH_2Ph.CO.C_6H_4.CO.NH_2$. [166°]. ormed from benzylidene-phthalide and alcolic NH_3 at 100° (Gabriel, *B.* 18, 2434). eedles, sol. hot water, converted into benzylidene-phthalimidine by boiling with HOAc.

Ethylamide $CH_2Ph.CO.C_6H_4.CO.NHEt$. [140°]. Formed from benzylidene-phthalide and alcoholic $NEtH_2$ at 100° (Gabriel, *B.* 18, 1258, 2434). Converted by boiling HOAc into  $C_6H_4<{C(CHPh) \atop CO}>NEt$. [77°]. Hydroxylamine forms  $C_6H_4<{C(CH_2Ph) \atop CO-O}>N$ [177°], which is also formed by the action of hydroxylamine on phenyl benzyl ketone carboxylic acid.

Phenyl benzyl ketone dicarboxylic acid $C_6H_4(CO_2H).CO.CH_2.C_6H_4.CO_2H$. [239°]. Formed together with an isomeride [250°] by heating phenyl-acetic-*o*-carboxylic acid with phthalic anhydride and NaOAc at 190° (Ephraim, *B.* 24, 2821). Needles. Gaseous HCl acting on its alcoholic solution forms the anhydride  $C_6H_4<{CH_2\ .CO \atop CO.O.CO}>C_6H_4$. [260°]. Hydroxylamine yields  $C_6H_4<{CH_2- \atop CO.O.N}>C.C_6H_4.CO_2H$ [280°] crystallising in needles. Alcoholic NH_3 forms crystalline $C_{16}H_{11}NO_3$.

PHENYL-BENZYL-METHYL-AMINE $C_{14}H_{15}N$ *i.e.* $NMePh.CH_2Ph$. [306°] (Nölting, *M. S.* [3] 13, 89).

Methylo-chloride B′MeClaq. [110°]. Formed from di-methyl-aniline and benzyl chloride (Michler, *B.* 10, 2079). Tables, v. sol. water and alcohol. Converted by successive treatment with Ag_2SO_4 and baryta into a syrupy hydroxide, which is split up on distillation into benzyl alcohol and di-methyl-aniline.

PHENYL-BENZYL-METHYL-THIO-UREA $C_{15}H_{16}N_2S$ *i.e.* $NPhMe.CS.NHC_7H_7$. [85°]. Formed from benzyl-thiocarbimide and methyl-aniline (Dixon, *C. J.* 59, 568). Prisms.

Isomeride $NHMe.CS.NPhC_7H_7$. [illegible]. Formed by boiling methyl-thiocarbimide with benzyl-aniline in alcoholic solution (D.). Tufts of white prisms, v. sl. sol. hot water.

PHENYL-BENZYL-METHYL-UREA $CH_2Ph.NH.CO.NPhMe$. [84°]. Formed from $CH_2Ph.NH.COCl$ and methyl-aniline (Kühn a. Riesenfeld, *B.* 24, 3817). V. sol. alcohol.

BENZYL-PHENYL-NITROSAMINE $C_7H_7NPh(NO)$. *Nitrosamine of benzyl-aniline.* [58°]. Formed from benzyl-aniline (10 g.), alcohol (125 c.c.), H_2SO_4 (6 c.c.), and $NaNO_2$ in the cold, the product being poured into water (500 c.c.) (Antrick, *A.* 227, 360). Pale-yellowish needles, v. sol. alcohol and ether.

PHENYL-BENZYL-OXIDE *v. Phenyl ether* of Benzyl alcohol.

PHENYL-BENZYL-PHOSPHINE? $CH_2Ph.PHPh$ or $C_{25}H_{24}P_2$. [171°]. Formed by heating $C_6H_5PCl_2$ with benzyl chloride and zinc (Michaelis a. Gleichmann, *B.* 15, 1961). Needles, converted by successive treatment with chlorine and alkalis into $C_{13}H_{13}PO$ or $C_{25}H_{24}P_2O_2$ [155°].

Di-phenyl-benzyl-phosphine dichloride $C_7H_7PCl_2(C_6H_5)_2$. [187°]. Formed from $(C_6H_5)_2PCl$ and benzyl chloride at 180° (Dörken, *B.* 21, 1506; *cf.* Michaelis, *B.* 18, 2117). Prisms.

Di-phenyl-benzyl-phosphine oxide $C_7H_7PO(C_6H_5)_2$. [196°]. Formed by decomposing the preceding body with water. Yields a tri-nitro- derivative [206°].

DI-PHENYL-DI-BENZYL-SUCCINIC ACID. *Nitrile.* $CN.CPh(CH_2Ph).CPh(CH_2Ph).CN$. [235°]. Formed from $CN.CNaPh(CH_2Ph)$ and I (Chalanay a. Knoevenagel, *B.* 25, 290). White crystalline powder, sl. sol. alcohol.

PHENYL BENZYL SULPHONE $C_{13}H_{12}SO_2$ *i.e.* $C_6H_5.SO_2.CH_2Ph$. [148°]. Formed from $C_6H_5.SO_2Na$ and benzyl chloride (Knoevenagel, *B.* 21, 1344). Sl. sol. ether, m. sol. alcohol.

DI-PHENYL-BENZYL-THIOSEMICARBAZIDE $NPh(C_7H_7).NH.CS.NHPh$. [150°]. Formed from phenyl-benzyl-hydrazine in alcohol and phenyl-thiocarbimide (Michaelis a. Philips, *A.* 252, 289). Crystals, v. sol. hot alcohol.

PHENYL-BENZYL-THIO-UREA $C_{14}H_{14}N_2S$ *i.e.* $NHPh.CS.NHCH_2Ph$. [154°]. Formed by mixing alcoholic solutions of benzylamine and phenyl-thiocarbimide (Dixon, *C. J.* 55, 300). Prisms (from alcohol), sl. sol. CS_2.

Phenyl-di-benzyl-thio-urea $C_{21}H_{20}N_2S$ *i.e.* $NPh(C_7H_7).CS.NH.C_7H_7$. [103°]. Formed from phenyl-thiocarbimide and benzyl-aniline (D.). White prisms, v. sl. sol. hot water.

PHENYL-BENZYL-*p*-TOLYL-BIURET $C_{22}H_{21}N_3O_2$. [95°–104°]. Needles (from dilute alcohol) (Kühn a. Henschel, *B.* 21, 504).

PHENYL-BENZYL-UREA $C_{14}H_{14}N_2O$ *i.e.* $NHPh.CO.NHCH_2Ph$. [168°]. Formed by mixing benzyl cyanate with aniline (Letts, *C. J.* 25, 448). Needles, v. sol. alcohol.

Phenyl-di-benzyl-urea $C_{21}H_{20}N_2O$. [128°]. Got from $(C_7H_7)_2N.COCl$ and aniline (Hammerich, *B.* 25, 1819). Silky needles (from alcohol).

PHENYL-BISMUTHINE *v.* vol. i. p. 517.

PHENYL-BIURET $C_8H_9N_3O_2$ *i.e.* $NHPh.CO.NH.CO.NH_2$. Formed from phenyl-urea and PCl_5 (Weith, *B.* 10, 1744). Crystals.

s-Di-phenyl-biuret $NH(CO.NHPh)_2$. [210°]. Formed by boiling allophanic ether, biuret, or [illegible] ether, with aniline (Hofmann, *B.* [illegible] 250; Leuckhart, *J. pr.* [2] 21, 27). Formed also by the action of phenyl cyanate on phenyl-urea (Kühn a. Henschel, *B.* 21, 504). Needles.

u-Di-phenyl-biuret NH$_2$.CO.NPh.CO.NHPh. [165°]. Got from di-phenyl dicyanate and alcoholic NH$_3$ (Hofmann). Prisms, sol. alcohol.

s-Tri-phenyl-biuret NPh(CO.NHPh)$_2$. [148°]. Formed from di-phenyl dicyanate and aniline (H.) and by heating phenyl cyanate with di-phenyl-urea at 150°. Prisms (from alcohol). An isomeride [105°] was got by Schiff (*B.* 8, 651) by distilling phenyl-carbamic ether.

References.—Di-bromo-di- and Oxy- phenyl-biuret.

PHENYL-BORATE $C_6H_5BO_2$. Formed by heating phenol (3 pts.) with B_2O_3 (2 pts.), or, better, by heating tri-phenyl borate with alcohol at 150° (Schiff, *A. Suppl.* 5, 202). Sticky mass.

Tri-phenyl borate $(C_6H_5)_2B_2O_5$. Formed by boiling phenol with B_2O_3. Glassy mass, decomposed by hot water.

Tetra-phenyl diborate $(C_6H_5)_4B_2O_5$. S.G. [illegible] 1·124. Formed, with the preceding body, by heating $C_6H_5BO_2$ at 350°. Thick oil, quickly decomposed by water.

Phenyl-boric acid $C_6H_5.B(OH)_2$. [204°]. Formed from $C_6H_5BCl_2$ and water (Michaelis a. Becker, *B.* 15, 181). Needles, sol. alcohol, ether, and hot water. Powerful antiseptic, with but slight physiological action. With $HgCl_2$ it gives a pp. of PhHgCl. Reduces ammoniacal $AgNO_3$, forming a mirror. On heating, it yields the oxide C_6H_5BO [190°] (above 360°), which forms crystals, sol. alcohol.

Salts.—NaA″: dimetric tables.—$CaH_2A''_2$: crystals.—AgHA″: yellow pp.

Ethyl ether Et_2A''. (176°). Oil.

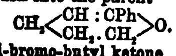
Chloride v. vol. i. p. 531.

PHENYL BROMIDE *v.* Bromo-benzene.

PHENYL BROMO-ALLYL OXIDE *v. Bromo-allyl derivative* of Phenol.

PHENYL BROMO-BENZYL KETONE $C_6H_5.CO.CHBrPh$. [55°]. Got by brominating phenyl benzyl ketone (Knoevenagel, *B.* 21, 1355).

PHENYL BROMO-BUTYL KETONE $C_6H_5.CO.CH_2.CH_2.CH_2.CH_2Br$. [61°]. Formed from phenyl oxy-butyl ketone anhydride or its carboxylic acid and conc. HBrAq (W. H. Perkin, jun., *C. J.* 51, 732; *B.* 19, 2559). Six-sided plates, v. sol. alcohol. Converted by warm alcoholic potash into the parent



$$CH_2{<}{\begin{matrix}CH:CPh\\CH_2.CH_2\end{matrix}}{>}O.$$

Phenyl di-bromo-butyl ketone $C_6H_5.CO.CH_2.CH_2.CHBr.CH_2Br$. Formed from allyl-acetophenone and Br (Perkin, *C. J.* 45, 188). Oil. Bromine yields $C_{11}H_{11}Br_3O$ [122°] crystallising from dilute alcohol in prisms.

PHENYL BROMO-ETHYL KETONE $C_6H_5.CO.C_2H_4Br$. Formed from phenyl ethyl ketone and Br in CS_2 (Pampel a. Schmidt, *B.* 19, 2897). Oil with pungent odour.

PHENYL BROMO-ETHYL OXIDE *v. Bromo-ethyl derivative* of Phenol.

PHENYL BROMO-ETHYL SULPHONE $C_6H_5.SO_2.CHMeBr$. [50°]. Formed by boiling an aqueous solution of the Na salt of the acid $C_6H_5.SO_2.CMeBr.CO_2H$ [184°], which is got by bromination of $C_6H_5.SO_2.CMeH.CO_2H$ (Otto, *J. pr.* [2] 40, 550). Rectangular tables.

PHENYL BROMO-IMESATIN *v.* Isatin.

PHENYL-BROMO-METHENYL-DI-ETHYL TRI-SULPHONE $C_6H_5.SO_2.CBr(SO_2.C_2H_5)_2$. [135°]. Formed by bromination of the sulphone $CH(SO_2Ph)(SO_2Et)_2$ (Laves, *B.* 25, 354). Plates (from alcohol) or needles (from Aq).

TRI-PHENYL-BROMO-METHENYL TRI-SULPHONE $CBr(SO_2Ph)_3$. [255°]. Got by brominating $CH(SO_2Ph)_3$ (Laves, *B.* 25, 351). Amorphous insoluble pp.

PHENYL BROMO-METHYL KETONE *v.* ω-Bromo-acetophenone.

PHENYL BROMO-METHYL SULPHONE $C_6H_5.SO_2.CH_2Br$. [48°]. Formed, together with $C_6H_5.SO_2.CHBr_2$ [75°], from $C_6H_5.SO_2.CH_2.CO_2H$ and Br (Otto, *J. pr.* [2] 40, 542). Both compounds form monoclinic tables, v. sol. hot alcohol.

PHENYL BROMO-(α)-NAPHTHYL KETONE $C_6H_5.CO.C_{10}H_6Br$. [98°]. Formed by bromination of phenyl (α)-naphthyl ketone (Elbs a. Steinike, *B.* 19, 1966). Yields a crystalline di-nitro- derivative decomposing at about 90°. Yields $C_{17}H_{10}Br(SO_3H)$ [116°] on sulphonation.

PHENYL-BROMO-NITRO-METHANE *v.* Bromo-nitro-toluene.

PHENYL-BROMO-DI-NITRO-PHENYL-AMINE *v.* Bromo-di-nitro-di-phenyl-amine.

PHENYL-BROMO-NITRO-PHENYL-HYDRAZINE $C_6H_5.N_2H_2.C_6H_3Br(NO_2)$. [3:1:4], [165°]. Formed from phenyl-hydrazine and $C_6H_3Br(NO_2)_2$ (Willgerodt, *J. pr.* [2] 37, 458). Red needles (from alcohol).

PHENYL-p-BROMO-PHENYL-HYDRAZINE $C_6H_5.N_2H_2.C_6H_4Br$. [115°]. Formed by reduction of $C_6H_5.N_2.C_6H_4Br$ by alcoholic ammonium sulphide (Janovsky, *B.* 20, 364). Tables.

PHENYL BROMO-PHENYL KETONE *v.* Bromo-benzophenone.

DI-PHENYL BROMO-PROPYLENE DISULPHONE $C_3H_5Br(SO_2Ph)_2$. [160°]. Got from $CH_2Br.CHBr.CH_2Br$ and NaSPh in alcohol (Stuffer, *B.* 23, 1411). Needles.

PHENYL BROMO-PROPYL KETONE $C_6H_5.CO.CH_2.CH_2.CH_2Br$. [39°]. Formed from 'benzoyl-trimethylene carboxylic' acid and fuming HBr (W. H. Perkin, jun., *C. J.* 47, 844). Crystalline mass, v. sol. alcohol.

PHENYL-BUTANE *v.* Butyl-benzene.

Di-phenyl-butane $CH_2Ph.CH_2.CH_2.CH_2Ph$. [52°]. Formed by heating di-phenyl-butylene with HI and P at 250° (Freund a. Immerwahr, *B.* 23, 2858). Crystals, v. sol. alcohol.

Di-phenyl-butane CHMePh.CHMePh. [123·5°]. Formed by the action of zinc-dust or Na on CHMePhBr (Radziszewski, *B.* 7, 142; Engler, *B.* 7, 1127). Needles (from ether).

Di-phenyl-butane CPh_2MeEt. [128°]. Formed from $CPh_2Me.CO.CH_3$, phosphorus, and HI (Zincke a. Thörner, *B.* 11, 1990). Tables or prisms, m. sol. alcohol.

Di-phenyl-butane $CH_3.CH(CH_2Ph)_2$. (300°). Formed by heating acetophenone with HIAq and P at 180° (Graebe, *B.* 7, 1627). Oil.

References.—Amido-, Tri-chloro-, and Tri-chloro-di-nitro- and Oxy- phenyl-butanes.

PHENYL-BUTANE TRICARBOXYLIC ACID. *Ethyl ether* $C_6H_5.CH_2.C(CO_2Et)_2.CHMe.CO_2Et$. (338° cor.). S.G. [illegible] 1·1008. μ_D 1·4850 at 20°. Formed from sodium-propane tri-carboxylic ether and benzyl chloride (Bischoff a. Mintz, [illegible]). The free acid gives benzyl-methyl-succinic acid on heating.

Di-phenyl-butane dicarboxylic acid $C_6H_4(CO_2H).CH_2.CH_2.CH_2.CH_2.C_6H_4.CO_2H$. [193°]. Formed by heating $C_2H_4(CO.C_6H_4.CO_2H)_2$ with HIAq and P at 160° (Gabriel a. Michael, *B.* 10, 2208). Nodules, insol. water.—Ag_2A'': pp.

PHENYL-BUTENYL ALCOHOL $C_{10}H_{12}O$ *i.e.* $C_6H_5.C_2H(OH).C_2H_3$. (225°). S.G. 12 ·985. Got from its acetyl derivative (228°-230°), formed from CPh:CEt by successive treatment with HBr and AgOAc (Morgan, *C. J.* 29, 162). Liquid.

PHENYL-BUTENYL KETONE $CH_2:CH.CH_2.CH_2.CO.Ph$ (235°-238°) at 710 mm. Obtained from allyl-benzoyl-acetic acid and boiling dilute alcoholic potash (W. H. Perkin, jun., *C. J.* 45, 187). Oil, smelling like camphor. Insol. water. Combines with Br. Excess of Br added to a glacial acetic acid solution forms bromo-phenyl-butenyl ketone dibromide, [122°].

PHENYL-BUTINENE $C_{10}H_{10}$ *i.e.* CPh:CEt. *Phenyl-ethyl-acetylene.* (202°). S.G. 21 ·923. Formed from sodium phenyl-acetylene and EtI (Morgan, *C. J.* 29, 162). Liquid.

Phenyl-butinene $C_{10}H_{10}$. (185°-190°). Got from $CH_2Ph.CH_2.CHBr.CH_2Br$ and alcoholic potash at 180° (Aronheim, *A.* 171, 231). Liquid.

Di-phenyl-butinene CHPh:CH.CH:CHPh. [148°]. (320°-340°). Obtained by heating $CHPh:CH.CH:CPh.CO_2H$ (Rebuffat, *G.* 15, 107; 20, 154). Micaceous plates.

References.—AMIDO- and OXY-PHENYL-BUTINENES.

PHENYL-BUTINENE DICARBOXYLIC ACID $CHPh:CH.CH:C(CO_2H)_2$. [208°]. Formed by heating cinnamic aldehyde with malonic acid and HOAc at 100° (Stuart, *C. J.* 49, 366). Needles; gives off CO_2 when melted.

DI-PHENYL-DI-BUTINYL KETONE $CO(CH:CH.CH:CHPh)_2$. [142°]. Formed from cinnamic aldehyde, acetone, and NaOHAq (Diehl a. Einhorn, *B.* 18, 2325). Needles.

PHENYLBUTINYL METHYL KETONE $CH_3.CO.CH:CH.CH:CHPh$. [68°]. Formed from cinnamic aldehyde, acetone, and NaOHAq (Diehl a. Einhorn, *B.* 18, 2321). Plates (from ether). Yields a dibromide [174°] and a phenyl-hydrazide [180°] crystallising in plates.

DI-PHENYL-BUTONENE $C_{16}H_{12}$. *Phenyl naphthalene?* [101°]. (346°). Formed from di-oxy-ethyl-benzene (styrolene alcohol) by treatment with H_2SO_4 (16 pts.) and water (9 pts.) (Zincke a. Breuer, *A.* 226, 23). Plates, v. sol. alcohol. Oxidised by $K_2Cr_2O_7$ and HOAc to $C_{16}H_{10}O_2$ [110°], which crystallises in golden needles, m. sol. alcohol, and is readily polymerised by exposure of its solution to light, yielding two polymerides [207°] and [225°-229°]. The quinone $C_{16}H_{10}O_2$ is reduced by $SnCl_2$ to the hydroquinone $C_{16}H_{10}(OH)_2$ [93°] which gives $C_{16}H_{10}(OAc)_2$ [152°]. The quinone $C_{16}H_{10}O_2$ is reduced by aqueous SO_2 at 120° to the quinhydrone $C_{32}H_{22}O_4$ [133°]. On heating the quinone with NaOHAq it is converted into the oxy-quinone $C_{16}H_9(OH)O_2$ [144°], which gives $C_{16}H_9(OAc)O_2$ [111°], and may be reduced to the oxy-quinhydrone [1[illegible]°], and the oxy-hydroquinone [73°]. The oxyquinone is oxidised by alkaline $KMnO_4$ to an acid $C_9H_8O_4$ [177°-197°] whence $BaA''2aq$, K_2A'', $Cu_2(OH)_2A''6aq$, and Ag_2A''. Alcoholic NH_3 converts the quinone into [illegible] while ethylamine, aniline, *o-* and *p-* toluidine, and naphthylamine form compounds melting at [130°], [158°], [108°], [155°], and [148°] respectively. The compound $C_{16}H_{11}NO_2$ forms an acetyl derivative [201°], and on treatment with aqueous SO_2 at 140° gives the oxyquinone and a substance $C_{32}H_{22}O_5$ [187°].

PHENYL-*sec*-BUTYL-ALCOHOL $C_{10}H_{14}O$ *i.e.* $C_6H_5.CH_2.CH_2.CH(OH).CH_3$. [68°]. Formed by reducing styryl methyl ketone with sodium-amalgam (Engler a. Leist, *B.* 6, 255). Crystals.

Phenyl-*tert*-butyl alcohol $C_{10}H_{14}O$ *i.e.* $C_6H_5.CH_2.CMe_2.OH$. [22°]. (220°-230°). Got from phenyl-acetyl chloride and $ZnMe_2$ followed by water (Popoff, *B.* 8, 768). Needles.

Tri-phenyl-*tert*-butyl-alcohol $CPh_3.CMe_2OH$. (above 260°). Formed from $CCl_3.CMe_2.OH$, benzene, and $AlCl_3$ (Willgerodt a. Genieser, *J. pr.* [2] 37, 368).

DI-PHENYL-DI-ISOBUTYL-TETRAZONE $C_4H_9NPh.N:N.NPh.C_4H_9$. [107°]. Got from phenyl-isobutyl-hydrazine in ether by treatment with HgO (Michaelis a. Philips, *A.* 252, 284).

PHENYL-BUTYLENE $C_{10}H_{12}$ *i.e.* $C_6H_5.CH_2.CH:CH.CH_3$ or $C_6H_5.CH_2.CH_2.CH:CH_2$. (177°). S.G. 15·5 ·915. Formed from benzyl chloride, allyl iodide, and Na (Aronheim, *B.* 5, 1068; *A.* 171, 219). The same hydrocarbon appears to be formed by distilling the lactonic acid of γ-oxy-γ-phenyl-s-di-methyl-succinic acid (Penfield, *A.* 216, 125). Oil, yielding a liquid dibromide. KNO_2 and HOAc form $C_{10}H_{12}N_2O_3$, which gives on reduction a base $C_{10}H_{15}NO$, whence B'HCl and $B'_2H_2PtCl_6$ (Tönnies, *B.* 11, 1511).

(α)-Phenyl-butylene $C_6H_5.CH:CH.CH_2.CH_3$. (186°). Formed by distilling $C_{10}H_{11}Br$ obtained by bromination of *n*-butyl-benzene (Radziszewski, *B.* 9, 260). Forms a dibromide $C_{10}H_{12}Br_2$ [71°] crystallising in white needles. Probably identical with the phenyl-butylene (187°) obtained by Perkin (*C. J.* 32, 667; 35, 140) from phenyl-angelic acid by successive treatment with HBr and Na_2CO_3Aq or with HI and KOH. Perkin's phenyl-butylene forms a crystalline dibromide [67°] converted by alcoholic potash into oily $C_{10}H_{11}Br$, which forms oily $C_{10}H_{11}Br_3$.

(β)-Phenyl-butylene $C_6H_5.CH:CMe_2$. (185°). Formed by heating benzoic aldehyde with sodium isobutyrate and isobutyric anhydride for 8 hours with inverted condenser (Perkin, *C. J.* 35, 138), and by distilling β-oxy-phenyl-valeric acid (Fittig a. Jayne, *A.* 216, 113). Oil. Forms an oily dibromide converted by alcoholic potash into $C_{10}H_{11}Br$, which forms crystalline $C_{10}H_{11}Br_3$ [63·5°]. Yields benzoic and acetic acids on oxidation. Nitrous acid forms $C_{10}H_{12}N_2O_3$ [112°] (Angeli, *B.* 25, 1962).

DI-PHENYL-BUTYLENE $C_{16}H_{16}$ *i.e.* $C_6H_5.CH:CH.CH_2.CH_2.C_6H_5$. [39°]. Formed by reduction of the nitrile of α-phenyl-β-styryl-acrylic acid (Freund a. Immerwahr, *B.* 23, 2858). Crystals, v. sol. alcohol. Yields a dibromide [83°].

DI-PHENYL-BUTYLENE-DIAMINE $C_4H_8(NHPh)_2$. Formed from isobutylene dibromide and aniline (Colson, *C. R.* 105, 1014; *Bl.* [2] 48, 800). Oil. Yields a nitrosamine [90°].—$B''H_2Cl_2$ [98°]. S. 10 at 15°.—$B''H_2Br_2$ [122°]. S. 10 at 15°; 20 at 100°.

DI-PHENYL-ISOBUTYL-GLYOXALINE [illegible] *i.e.* $\begin{matrix}CPh.NH\\CPh.N\end{matrix}\!\!>C.CH_2Pr$. [223°]. Formed from benzil, isovaleric aldehyde, and NH_3Aq (Japp a. Wynne, *C. J.* 49, 468).—$B'H_2PtCl_6$: crystalline.

PHENYL-ISOBUTYL-HYDRAZINE $C_4H_9NPh.NH_2$. (240°-245°). Formed from isobutyl bromide and sodium phenyl-hydrazine (Michaelis a. Philips, *B.* 20, 2485; *A.* 252, 282; 270, 122). Liquid, which reduces hot Fehling's solution. Converted by thionyl-aniline into oily $C_4H_9NPh.N{:}SO$—$B'H_2SO_4$: plates.

Acetyl derivative $C_4H_9NPh.NHAc$. [114°].

PHENYL BUTYL KETONE $C_6H_5.CO.CH_2Pr$. Mol. w. 162. (237°) at 720 mm. Got by boiling propyl-benzoyl-acetic ether with alcoholic potash (Perkin a. Calman, *C. J.* 49, 162). Oil.

Phenyl isobutyl ketone $C_6H_5.CO.CH_2Pr$. (228°) at 720 mm. S.G. $^{17·5}$ ·993. Formed from isopropyl-benzoyl-acetic ether (P. a. C.) and also by distilling a mixture of calcium benzoate and calcium isovalerate (Popoff, *A.* 162, 153). Liquid. Does not combine with $NaHSO_3$. Yields benzoic, isobutyric, and acetic acids on oxidation.

PHENYL BUTYL KETONE CARBOXYLIC ACID $C_6H_5.CO.CH_2.CHEt.CO_2H$. *Ethyl-benzoyl-propionic acid.* [83°]. Formed by heating the dicarboxylic acid. Small needles.—CaA'_2 aq.

Ethyl ether EtA'. Oil.

Phenyl butyl ketone carboxylic ether $C_6H_5.CO.CHPr.CO_2Et$. *Propyl-benzoyl-acetic acid* (251° at 300 mm.). Formed from benzoyl-acetic ether, NaOEt, and PrI at 100° (Perkin a. Calman, *C. J.* 49, 160). Liquid.

Phenyl isobutyl ketone carboxylic ether $C_6H_5.CO.CHPr.CO_2Et$. (237° at 225 mm.). Formed in like manner, using isopropyl iodide.

Phenyl butyl ketone dicarboxylic acid $C_6H_5.CO.CH_2.CEt(CO_2H)_2$. *Benzoyl-ethyl-isosuccinic ether.* Got by saponifying its ether, which is formed from sodium-malonic ether and ω-bromo-acetophenone (Dittrich a. Paal, *B.* 21, 3453). Crystalline mass.—$(NH_4)_2A''$: amorphous.—K_2A'': pearly plates, v. sol. water.—CaA'' aq.—Ag_2A'': plates. *Hydrazine salt.* [103°].

Phenyl hydrazide $C_{25}H_{26}N_4O_3$. [132°].

PHENYL BUTYL METHYLENE DIKETONE $C_6H_5.CO.CH_2.CO.CH_2Pr$. *Valeryl-acetophenone.* (184° at 30 mm.). Oil. Got from acetophenone, isovaleric ether, and NaOEt (Stylos, *B.* 20, 2181).

PHENYL-BUTYL METHYL KETONE CARBOXYLIC ETHER $CH_3.CO.CEt(CH_2Ph).CO_2Et$. (c. 297°). Formed from sodium benzyl-acetoacetate and EtI (Conrad, *B.* 11, 1057).

PHENYL BUTYL OXIDE *v. Butyl derivative* of PHENOL.

PHENYL-ISOBUTYLPHENYL-THIO-UREA $C_6H_5NH.CS.C_6H_4.CH_2Pr$. [152°]. Formed from $C_6H_4(NH_2).CH_2Pr$ and phenyl-thiocarbimide (Mainzer, *B.* 16, 2023). Plates, sol. alcohol.

DI-PHENYL-ISOBUTYL-QUINOXALINE $C_6H_3(CH_2Pr)\!<\!\begin{matrix}N{:}CPh\\N{:}CPh\end{matrix}$ [144°]. Formed from benzil and isobutylphenylene-diamine (Gelzer, *B.* 20, 3257). Needles, v. sol. alcohol.—B'_2HCl.

PHENYL-BUTYL-THIO-ALLOPHANIC ACID $NHPh.CS.N(C_4H_9).CN$. [139°]. Formed from sodium cyanamide, phenyl thiocarbimide, and isobutyl iodide (Hecht, *B.* 25, 822). Slender needles, v. sl. sol. hot water.

DI-PHENYL-ISOBUTYL-THIO-SEMI-CARBAZIDE $NHPh.CS.NH.NPh(CH_2Pr)$. [140°]. Formed from phenyl-isobutyl-hydrazine and phenyl-thiocarbimide (Michaelis a. Philips, *A.* 252, 284). White crystals.

PHENYL-ISOBUTYL-THIO-UREA $NHPh.CS.NHC_4H_9$ [82°]. Formed from phenyl-thiocarbimide and isobutylamine (Hecht, *B.* 25, 815). Needles, m. sol. hot water.

PHENYL-BUTYL-THIOHYDANTOÏN $CS\!<\!\begin{matrix}NPh.CO\\NH.CH(C_4H_9)\end{matrix}$. [179° uncor.]. Formed by fusing phenyl thiocarbimide with leucine (Aschan, *B.* 17, 426). Minute colourless prisms.

PHENYL-BUTYRIC ACID $C_{10}H_{12}O_2$ *i.e.* $CH_3CH_2.CHPhCO_2H$. [42°]. (272°). Formed by saponifying the nitrile which is made by the action of EtI and solid NaOH on benzyl cyanide (Neure, *A.* 250, 153). Crystalline mass.—CaA'_2 2aq; groups of needles.—AgA'.

Methyl ether MeA'. (228°).

Nitrile PhCHEt.CN. (245°).

γ-Phenyl-*n*-butyric acid $CH_2Ph.CH_2.CH_2.CO_2H$. [47·5°]. (290°). Formed from oxy-phenyl-butyric acid and HI (Burcker, *A. Ch.* [5] 26, 459) and from phenyl-isocrotonic acid by protracted treatment with sodium-amalgam (Jayne, *A.* 216, 107). Long flat plates (from water).—CaA'_2: amorphous mass.

Phenyl-isobutyric acid $CH_2Ph.CHMe.CO_2H$. *Benzyl-methyl-acetic acid.* [37°]. (272°). S. ·31 at 15°.

Formation.—1. By heating benzyl-methyl-malonic acid (Conrad, *B.* 13, 598).—2. By heating benzyl-methyl-acetoacetic ether with conc. KOHAq.—3. By reduction of the phenyl-crotonic acid obtained from benzoic aldehyde, sodium propionate, and propionic anhydride.—4. By reducing phenyl-angelic (methyl-cinnamic) acid with sodium-amalgam (von Miller, *B.* 23, 1888).

Properties.—Plates. Converted by H_2SO_4 at 150° into oxy-methyl-indonaphthene.

Salt.—AgA'. S. ·248 at 20°.

Ethyl ether EtA'. (287°). S.G. $\frac{22}{17}$ 1·05. Oil (Conrad a. Bischoff, *A.* 204, 177).

Benzyl ether C_7H_7A'. (320°-325°). S.G. $^{16·5}$ 1·046. A product of the action of sodium on benzyl propionate (Conrad a. Hodgkinson, *A.* 193, 312).

Amide $CH_2Ph.CHMe.CONH_2$. [109°]. Formed by heating the NH_4 salt (Edeleano, *B.* 20, 618). Needles, v. sol. alcohol and ether.

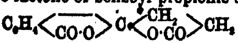
Di-phenyl-butyric acid $CH_2Ph.CMePh.CO_2H$. [126°]. Got from its nitrile, which is obtained from α-phenyl-propionitrile and benzyl chloride (Janssen, *A.* 250, 137). Needles, v. sol. ether and alcohol.—NaA'7aq: long thin needles.—CaA'_2.—BaA'_2.—CuA_2'. [78°].—AgA': white insoluble powder.

Nitrile $C_{16}H_{15}CN$. (337°). Oil.

Isomeride *v.* DI-BENZYL-ACETIC ACID.

References.—BROMO-, NITRO-, NITRO-AMIDO-, and OXY- PHENYL-BUTYRIC ACID.

PHENYL-ISOBUTYRIC ALDEHYDE $CH_3.CH(CH_2Ph).CHO$. (227°). Formed by distilling the corresponding lime salt with calcium formate (Miller a. Rohde, *B.* 23, 1080). Oil.

γ-PHENYL-BUTYRIC-*o*-CARBOXYLIC ACID $C_{11}H_{12}O_4$ *i.e.* $C_6H_4(CO_2H).CH_2.CH_2.CH_2.CO_2H$. [139°]. Formed by heating at 180°–190° the double-lactone of benzoyl-propionic-*o*-carboxylic acid  $C_6H_4\left\langle\begin{matrix}\text{——}\\CO\cdot O\end{matrix}\right\rangle C\left\langle\begin{matrix}CH_2\\O\cdot CO\end{matrix}\right\rangle CH_2$ with HI and P (Roser, *B.* 18, 3118). Small plates. V. sol. alcohol, sl. sol. cold water.—A″Ba: very soluble in water.

PHENYL-BUTYRO-LACTONE *v.* *Lactone* of OXYPHENYL-BUTYRIC ACID.

PHENYL-CACODYL *v.* vol. i. p. 320.

PHENYL-CAMPHORAMIC ACID *v.* CAMPHORIC ACID.

PHENYL-CAMPHYL-THIO-UREA *v.* CAMPHYL-THIO-UREA.

PHENYL CARBAMATE $NH_2.CO_2Ph$. [143°]. Formed by the action, in ethereal solution, of NH_3 on $ClCO_2Ph$ or of $NH_2.COCl$ on phenol (Kempf, *B.* 2, 740; Gattermann, *A.* 244, 43). Formed also, together with Et_2CO_3, by heating phenyl ethyl carbonate at 300° (Bender, *B.* 19, 2268). Needles (from water), sol. alcohol and ether. Decomposed by NaOHAq into NH_3, phenol, and Na_2CO_3. NH_3Aq at 150° forms phenol and urea.

PHENYL-CARBAMIC ACID $NHPh.CO_2H$. *Carbanilic acid.* The ethers of this acid are got by the action of aniline on the chloroformic ethers Cl.CO.OR, and also by the action of phenyl cyanate on alcohols. They are decomposed by potash into CO_2, aniline, and alcohols.

Acetyl derivative $NPhAc.CO_2H$. The Na salt is formed by passing CO_2 over sodium acetanilide in the cold (Seifert, *B.* 18, 1358). It is decomposed by water into acetanilide and $NaHCO_3$. By heating at 140° under pressure it is converted into $NPhH.CO.CH_2.CO_2Na$.

Methyl ether NHPh.CO.OMe. [47°] (Hentschel, *B.* 18, 978). Prisms. Converted by HNO_3 (S.G. 1·48) into $C_6H_3(NO_2)_2NH.CO_2Me$ [127°] and [6:4:2:1]$C_6H_2(NO_2)_3.NH.CO_2Me$ [192°] (Van Romburgh, *R. T. C.* 10, 135). H_2SO_4 forms $SO_3H.C_6H_4.NH.CO_2Me$ which is converted by bromine into $C_6H_3Br_2NH.CO_2Me$ [96·5°] (Hentschel, *J. pr.* [2] 34, 423). Distillation with lime at 260° gives aniline, methyl-aniline, di-methyl-aniline, and di-phenyl-urea (Nölting, *B.* 21, 3154).

Ethyl ether $NHPh.CO_2Et$. [52°]. (238°) (Wilm a. Wischin, *C. J.* 21, 192). Formed as above and also by boiling the product of the action of phenyl-urea on aceto-acetic ether with conc. HCl (Behrend, *A.* 233, 6) and by the action of sodium acetanilide on chloro-formic ether (Paal a. Otten, *B.* 23, 2590). Needles (from water). Not affected by boiling conc. HClAq, but decomposed by HClAq at 150° into CO_2, aniline, and EtCl. Boiling alcoholic KOH gives aniline and K_2CO_3. Yields a bromo-derivative [81°], a di-nitro- derivative [110°], and a tri-nitro- derivative [144°]. When distilled with NaOPh at 220° it gives phenol and di-phenyl-urea [235°] (Hentschel, *J. pr.* [2] 27, 498). — $NKPh.CO_2Et$. Formed by dissolving phenyl-carbamic ether in alcoholic potash. Hygroscopic needles, decomposed by water.

Chloro-ethyl ether $NHPh.CO_2.CH_2.CH_2Cl$. [51°]. Formed from aniline and $Cl.CO.OC_2H_4Cl$ (Nemirowsky, *J. pr.* [2] 31, 174; Otto, *J. pr.* [2] 44, 15). Needles, sl. sol. hot water. When boiled alone and afterwards with conc. KOH it yields $NPh\left\langle\begin{matrix}CO\\CH_2\end{matrix}\right\rangle CH_2$ [124°], which is converted by HClAq at 170° into chloro-ethyl-aniline.

Ethylene ether C_2H_4A''. [158°]. Formed from ethylene glycol and phenyl cyanate (Snape, *B.* 18, 2430; *C. J.* 47, 773). Prisms.

Propyl ether PrA′. [59°]. Slender needles, v. sol. alcohol (Römer, *B.* 6, 1101).

Isopropyl ether PrA′. [90°] (Gumpert, *J. pr.* [2] 31, 119; 32, 278); [43°] (Spica, *G.* 17, 165). Needles (from dilute alcohol).

Di-chloro-propyl ether (Otto, *J. pr.* [2] 44, 22) $CH_2Cl.CHCl.CH_2A'$. [74°]. Prisms.

Isobutyl ether C_4H_9A'. [80°]. (216°). Needles, v. sol. alcohol (Mylius, *B.* 5, 972).

Heptenyl ether $C_7H_{13}A'$. [85°]. Formed by the action of phenyl cyanate on the heptenyl alcohol got by reducing suberone (Markownikoff, *C. R.* 110, 466). Prisms (from alcohol).

Glyceryl ether v. GLYCERYL-TRI-PHENYL-TRI-CARBAMATE.

Phenyl ether $NHPh.CO_2Ph$. [126°]. Formed from phenyl cyanate and phenol (Gumpert; *cf.* Hofmann, *B.* 4, 249). Needles (from benzene). With NH_3Aq it forms phenyl-urea.

Phenylene ethers. The *o* [165°], *m* [164°], and *p* [207°] compounds are got by heating pyrocatechin, resorcin, and hydroquinone respectively with phenyl cyanate (Snape, *B.* 18, 2428).

Phenylphenyl ether $C_6H_5.C_6H_4A'$. [110°]. Formed from *p*-amido-diphenyl and $ClCO_2Et$ (Zimmermann, *B.* 13, 1965).

(α)-*Naphthyl ether* $C_{10}H_7A'$. [178·5°]. Slender needles (Leuchart a. Schmidt, *B.* 18, 2340; Snape, *C. J.* 47, 776). Decomposed by heat into (α)-naphthol and phenyl cyanate.

(β)-*Naphthyl ether* $C_{10}H_7A'$. [230°]. (L. a. S.); [155°] (S.). Thick prisms. The tetrahydride $C_{10}H_{11}O.CONPhH$ [98·5°] is formed from (β)-naphthol *ac*-tetrahydride and phenyl cyanate.

Di-phenyl-carbamic acid.

Chloride $NPh_2.COCl$. [85°]. Formed from $COCl_2$ and diphenylamine in $CHCl_3$ (Michler, *B.* 9, 396). White scales (from alcohol).

Ethyl ether $NPh_2.CO_2Et$. [72°]. (above 360°). Formed by heating diphenylamine with $ClCO_2Et$ (Merz a. Werth, *B.* 6, 1511; Hager, *B.* 18, 2573). Large prisms (from benzene).

Phenyl ether PhA′. [104°]. Formed from the chloride and KOPh (Lellmann a. Bonhöffer, *B.* 20, 2122). The compound $C_6H_4(NO_2)A'$ [114°], made in like manner from *o*-nitrophenol, may be reduced to $C_6H_4(NH_2)A'$ [191°]. The *m*- and *p*- nitro-phenyl ethers [90°] and [116°] yield *m*- and *p*- amido-phenyl ethers [133°] and [146°] (Lellmann a. Benz, *B.* 24, 2111).

p-Tolyl-ether C_7H_7A'. [81°]. (L. a. B.).

References.—AMIDO-, BROMO-, DI-BROMO-NITRO-, NITRO-, NITRO-AMIDO-, NITRO-OXY-, OXY-, OXY-AMIDO-, and NITRO- PHENYL-CARBAMIC ACID and ETHER.

PHENYL-CARBAMINE C_6H_5NC. Mol. w. 103. (167°). S.V. 121·6 (Lossen, *A.* 254, 73). Formed by distilling aniline with chloroform and alcoholic potash (Hofmann, *A.* 144, 117). Stinking liquid, quickly decomposed by acids into aniline and formic acid. Changes into the isomeric benzonitrile by heating at 210° (Weith, *B.* 6, 210). Yields phenyl-thiocarbimide on heating with sulphur. Mixed with propionitrile and ether, it yields, by successive treatment with sodium and water, the compound $CPh(NH).CHMe.CN$ [97°] (Von Meyer, *J. pr.* [2] 39, 189).

Chloride $NPh.CCl_2$ (212°). Formed from phenyl-thiocarbimide and Cl (Sell a. Zierold, *B.* 7, 1228). Pungent liquid, with nasty smell, yielding *s*-di-phenyl-urea when heated with water at 100°.

PHENYL-CARBAZIC ACID. The crystalline salt $N_2H_2Ph.CO.ON_2H_4Ph$ is formed by the action of CO_2 on phenyl-hydrazine and water. It is deliquescent, and sl. sol. water and ether (Fischer, *A.* 190, 124).

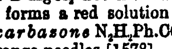
Methyl ether $NHPh.NH.CO_2Me$. [117°]. Short prisms (Heller, *A.* 263, 281).

Ethyl ether $NHPh.NH.CO_2Et$. [87°] (F.); [82°] (N.). Formed from phenyl-hydrazine and $ClCO_2Et$ (E. Fischer, *B.* 22, 1936), or $AcC(CO_2Et)_3$ (Nef, *A.* 266, 107). Needles. Ac_2O forms $C_6H_5.N_2HAc.CO_2Et$ [103°] (H.).

PHENYL-*semi*-CARBAZIDE $C_7H_9N_3O$ *i.e.* $NHPh.NH.CO.NH_2$. [172°]. Formed from potassium cyanate and phenyl-hydrazine hydrochloride (E. Fischer, *A.* 190, 113; Freund, *B.* 21, 2463). Formed also by heating phenyl-hydrazine hydrochloride (1 mol.) with urea (2 mols.) at 160° for 4 hours (Pinner, *B.* 20, 2358; 21, 2329) and by heating di-phenyl-carbazide with urea (Skinner a. Ruhemann, *C. J.* 53, 550; *B.* 20, 3378). Prisms, v. sol. hot water. Yields di-oxy-phenyl-triazole [263°] on heating with urea. By heating at 160° it is converted into di-phenyl-urazine $C_{14}H_{12}N_4O_2$ [264°] and other products. $COCl_2$ forms $C_8H_7N_3O_2$ [167°].

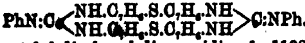
Benzoyl derivative $NPhBz.NH.CO.NH_2$. [203°]. Formed from benzoyl-phenyl-hydrazine cyanate (Michaelis a. Schmidt, *A.* 252, 317).

Di-phenyl-*semi*-carbazide $C_6H_5NH.CO.N_2HPh$. [173°]. Formed from phenyl-hydrazine by combination with phenyl cyanate; and also by heating phenyl-hydrazine with phenyl-urea (Kühn, *B.* 17, 2884; Skinner, *C. J.* 53, 552). Needles or plates (from alcohol or benzene), sl. sol. water. $COCl_2$ in benzene forms $C_{14}H_{11}N_3O_2$ [173°] (Freund, *B.* 21, 2465).

Di-phenyl-carbazide $CO(N_2H_2Ph)_2$. [151°] (S. a. K.); [164°] (E. Fischer, *B.* 22, 1930). Formed by heating phenyl-hydrazine (2 mols.) with carbamic ether (1 mol.) (Skinner a. Ruhemann, *C. J.* 53, 550; *B.* 20, 3372). Formed also from phenyl-hydrazine and $COCl_2$ (Heller, *A.* 263, 277). Crystalline. Forms with $HgCl_2$ a crystalline compound $B'HgCl_2$ not melted at 136°. Alcoholic potash forms a red solution containing *di-phenyl-carbazone* $N_2H_2Ph.CO.N:NPh$ crystallising in orange needles [157°]. Benzene and $CSCl_2$ form  $CS\left\langle\begin{matrix}NPh.N\\O\text{———}\end{matrix}\right\rangle C.N:NPh$ [176°] (Freund a. Kuh, *B.* 23, 2833).

PHENYL-CARBIMIDE *v. Phenyl isocyanate*, vol. ii. p. 315.

DI-PHENYL-DI-CARBIMIDO-TETRA-*p*-AMIDO-TETRA-TOLYL-DI-*o*-SULPHIDE


$PhN:C\left\langle\begin{matrix}NH.C_7H_6.S.C_7H_6.NH\\NH.C_7H_6.S.C_7H_6.NH\end{matrix}\right\rangle C:NPh$. *Di-thio-p-tolyl-di-phenyl-di-guanidine.* [c. 119°]. Formed by heating di-thiocarbonyl-tetra-amido-tetra-tolyl-di-sulphide with aniline and HgO (Truhlar, *B.* 20, 674). Amorphous; v. sol. alcohol.

DI-PHENYL-CARBINOL $C_{13}H_{12}O$ *i.e.* $Ph_2CH(OH)$. *Benzhydrol.* Mol. w. 184. [68°]. (298°). S. ·05 at 20°. *Initial velocity of etherification* 22 (Menschutkin, *J. R.* 1882, 162). Formed by reducing benzophenone with sodium-amalgam (Linnemann, *A.* 133, 6; Beckmann, *B.* 22, 915); or by heating benzophenone with zinc and alcoholic KOH (Zagumenny, *A.* 184, 174). Slender silky needles, v. e. sol. alcohol and ether. Converted into benzophenone by oxidation with chromic acid. Bromine forms a dibromo-benzhydrol [163°]. Zn and HOAc form benzpinacone. Zn and HCl in acetic acid solution reduce it to tetra-phenyl-ethane. Distillation partly resolves benzhydrol into water and benzhydrolic ether. P_2S_5 forms $C_{26}H_{22}(SH)_2$ [151°] and oily $Ph_2CH(SH)$ (Engler, *B.* 11, 922).

Ethyl derivative $C_{13}H_{11}OEt$. (288°). S.G. ^{20} 1·03. From benzhydrol, alcohol, and H_2SO_4, or from Ph_2CHBr and alcoholic KOH (Friedel a. Balsohn, *Bl.* [2] 33, 339). Liquid.

Isoamyl derivative $C_{13}H_{11}OC_5H_{11}$. (310°).

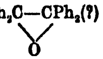
Chloride Ph_2CHCl. [14°]. From benzhydrol and HCl (Engler a. Bethge, *B.* 7, 1128).

Bromide Ph_2CHBr. [45°]. From di-phenyl-methane and bromine at 150° (F. a. B.). Water at 150° decomposes it into benzhydrol and benzhydrolic ether. Conc. NH_3Aq forms mono- and di-benzhydryl-amine (Friedel a. Balsohn, *Bl.* [2] 33, 587).

Acetyl derivative $Ph_2CH.OAc$. [42°]. (302°). S.G. ^{22} 1·49. Prisms, v. sol. alcohol, acetic acid, and ether (Vincent, *Bl.* [2] 35, 804).

Benzoyl derivative $Ph_2CH.OBz$. [89°]. Non-volatile. Trimetric, $a:b:c = 1 : ·477 : ·668$.

Succinyl derivative $(Ph_2CH.O)_2:C_2O_2:C_2H_4$. [142°]. Gives, on distillation, succinic acid and benzhydrolene $C_{13}H_{10}$ [210°].

Anhydride $C_{26}H_{20}O$ *i.e.*  $\underset{\diagdown\;\diagup\atop O}{Ph_2C{-}CPh_2}$(?) [111°]. (315°) at 745 mm. From benzhydrol by long boiling with water or by treatment with PCl_3, BzCl, or diluted H_2SO_4. Monoclinic crystals (from benzene). Reduced by zinc and HCl in HOAc to tetra-phenyl-methane (Zagumenny, *J. R.* 12, 431). Zincke a. Thörner (*B.* 11, 1398) obtained this anhydride by heating benzpinacone, $C_{26}H_{22}O_2$, and consequently assume the formula $C_{26}H_{20}O$.

References.—DI-AMIDO-, DI-BROMO-, and OXY-DI-PHENYL-CARBINOL.

Tri-phenyl-carbinol $C_{19}H_{16}O$ *i.e.* $CPh_3.OH$. Mol. w. 260. [159°]. (above 360°).

Formation.—1. By boiling tri-phenyl-methane with chromic acid mixture (Hemilian, *B.* 7, 1203).—2. From CPh_3Br and water.—3. By the action of water on CPh_3Cl got from $AlCl_3$, benzene, and CCl_4, or $CCl_3.COCl$ (Friede a. Crafts, *A. Ch.* [6] 1, 499; Hentschel, *J. pr.* [2] 36, 311).—4. By heating its dicarboxylic acid with baryta (Hemilian, *B.* 19, 3073).

Properties.—Six-sided plates, v. sol. alcohol.

Acetyl derivative $CPh_3.OAc$. [99°]. Prisms (Allen a. Kölliker, *A.* 227, 116).

Methyl ether $CPh_3.OMe$. [82°]. Laminæ.

Ethyl ether $CPh_3.OEt$. [79°] (F. a. C.); [83°] (A. a. K.).

Chloride v. CHLORO-TRI-PHENYL-METHANE.

DI-PHENYL-CARBINOL CARBOXYLIC ACID v. OXY-BENZYL-BENZOIC ACID.

Di-phenyl-carbinol dicarboxylic acid $CH(OH)(C_6H_4.CO_2H)_2$. Formed by heating benzil di-*o*-carboxylic (diphthalylic) acid with KOHAq (50 p.c.) at 180° for 5 minutes (Graebe a. Juillard, *A.* 242, 238). The acid splits up at the moment of liberation into water and anhydride.—BaA''aq.

Anhydride $C_{15}H_{10}O_4$. [203°]. S. ·022 at 23°. Formed as above, and also by reducing benzophenone di-*o*-carboxylic acid. Monoclinic crystals (from alcohol). On heating, it yields a white sublimate [172°] reconverted by treatment with NaOHAq and HCl into the original anhydride. Phenyl-hydrazine gives $C_{21}H_{16}N_2O_3$. H_2SO_4 and HNO_3 give $C_{15}H_8(NO_2)_2O_4$ [c. 275°], which forms EtA′ [148°].—$Ba(C_{15}H_9O_5)_2$ 2½aq.—CuA'_2 3aq.—AgA′.—$C_{15}H_9MeA'$. [155°].—EtA′. [100°].—$C_{15}H_9O_3(NH_2)$. [160°]. Needles.

Isomeride v. OXY-BENZYL-ISOPHTHALIC ACID.

Di-phenyl-carbinol tri-carboxylic acid $C(OH)(CO_2H)(C_6H_4.CO_2H)_2$.

Anhydride $C_{16}H_{10}O_6$. [170°]. Formed by heating benzil di-*o*-carboxylic acid with NaOHAq (4 p.c.) at 112° for 3 minutes (G. a. J.). Minute crystals, sl. sol. cold water. Gives off CO_2 on heating, yielding the anhydride of di-phenyl-carbinol dicarboxylic acid.

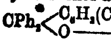
Ethers of the anhydride Me_2A''. [148°].—Et_2A''. [108°]. Prisms, v. sol. alcohol.

Tri-phenyl-carbinol *o*-carboxylic acid *$CPh_2(OH).C_6H_4.CO_2H$. The Na salt is formed by heating di-phenyl-phthalide with NaOHAq, but the acid splits up on liberation into water and its anhydride, di-phenyl-phthalide (Baeyer, *A.* 202, 50).

Tri-phenyl-carbinol *m*-carboxylic acid. [162°]. Formed by oxidation of di-phenyl-*m*-tolyl-methane with CrO_3 and HOAc (Hemilian, *B.* 16, 2369). Trimetric plates.

Tri-phenyl-carbinol *p*-carboxylic acid (?). [187°]. Formed by oxidation of $CHPh_2.C_6H_4.CHO$ (Oppenheim, *B.* 19, 2028) or of di-phenyl-tolyl-methane (Hemilian, *B.* 7, 1210). Needles.—$BaA'_2$7aq. Needles, v. sl. sol. cold water.

Tri-phenyl-carbinol dicarboxylic acid. *Anhydride*



$CPh_2{<}{\begin{matrix}C_6H_3(CO_2H)\\O\text{———}CO\end{matrix}}{>}$.

Di-phenyl-phthalide carboxylic acid. [246°]. Formed by oxidation of di-phenyl-*y*-xylyl-methane, di-phenyl-tolyl-methane *o*-carboxylic acid, di-phenyl-tolyl-carbinol *m*-carboxylic acid, or di-phenyl-methyl-phthalide (Hemilian, *B.* 16, 2372). Crystals, v. sol. alcohol and HOAc. Yields benzophenone and terephthalic acid on fusion with potash. Zinc-dust and NaOHAq reduce it to tri-phenyl-methane dicarboxylic acid.

Tri-phenyl-carbinol dicarboxylic acid $C_{21}H_{16}O_5$ *i.e.* $CPh_2(OH).C_6H_3(CO_2H)_2$ [1:3:4]. [180°]. Formed by oxidation of di-phenyl-xylyl-methane with $K_2Cr_2O_7$ and H_2SO_4Aq (Hemilian, *B.* 19, 3072). Needles (from water), v. e. sol. alcohol. On fusion it yields an amorphous anhydride $C_{21}H_{14}O_4$. On fusion with $Ba(OH)_2$ it forms tri-phenyl-carbinol.—Ag_2A'' : pp.

Tri-phenyl-carbinol dicarboxylic acid $CPh_2(OH).C_6H_3(CO_2H)_2$ [1:2:4]. *Anhydride* $C_{21}H_{14}O_4$. *Di-phenyl-phthalide carboxylic acid.* [228°]. Formed by oxidation of the corresponding di-phenyl-xylyl-methane (H.). Tables (containing EtOH).—CaA'_2 3aq.—AgA′: needles.

DI-PHENYL-CARBINYLAMINE $C_{13}H_{13}N$ *i.e.* $CHPh_2.NH_2$. *Benzhydrylamine. Exo-amido-di-phenyl-methane.* (289°). Formed, together with tetra-phenyl-di-carbinyl-amine, by leaving benzhydryl bromide, $CHPh_2Br$, with conc. NH_3Aq for 48 hours (Friedel a. Balsohn, *Bl.* [2] 33, 587). Got also by reducing benzophenone-oxim in alcoholic solution by sodium-amalgam and acetic acid (Goldschmidt, *B.* 19, 3233).

Properties.—Alkaline liquid, absorbing CO_2 from the air.

Salts.—B′HCl: [270°]; long needles, sl. sol. cold water.—$B'_2H_2PtCl_6$ 2aq : lancet-like needles (L. a. B.); $B'H_2PtCl_6$aq (G.).—*$B'_2H_2CO_3$. [91°].

Formyl derivative $Ph_2CH.NH.CHO$. [132°]. (360°). Formed, almost quantitatively, by heating benzophenone with ammonium formate at 200°–220° (Leuchart a. Bach, *B.* 19, 2129).

Urea $Ph_2CH.NH.CO.NH_2$. [143°] (L. a. B.).

Tetra-phenyl-di-carbinyl-amine $(Ph_2CH)_2NH$. [136°]. Prepared as above, crystallises from alcohol in slender needles, not affected by MeI or AcCl at 100° (F. a. B.).

Tri-phenyl-carbinyl-amine $CPh_3.NH_2$. [103°]. Formed by passing dry NH_3 through a solution of CPh_3Br in benzene (Hemilian a. Silberstein, *Bl.* [2] 43, 118; *B.* 17, 741; *cf.* Nauen, *B.* 17, 442). Needles, sl. sol. cold alcohol. Yields B′HCl, $B'_2H_2PtCl_6$ 7½aq, CPh_3NHMe [73°], CPh_3NMe_2 [97°], CPh_3NHPh [145°], CPh_3NHCH_2Ph [110°], and the acetyl derivative $CPh_3.NHAc$ [208°]. Forms a crystalline oxalate [253°] (Elbs, *B.* 17, 701), and the compounds $C_{19}H_{17}NBr_2$, $B'I_2$, and B'_2I_7.

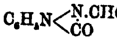
PHENYL-CARBINYL CHLORIDE v. CHLORO-TRI-PHENYL-METHANE.

TRI-PHENYL-CARBINYL-MALONIC ETHER $CPh_3.CH(CO_2Et)_2$. [133·5°]. Got from sodium malonic ether and CPh_3Br (Henderson, *B.* 20, 1014). Needles (from alcohol).

TRI-PHENYL-CARBINYL SULPHOCYANIDE $CPh_3.NCS$. [137°]. Formed from CPh_3Br and ammonium sulphocyanide (Elbs, *B.* 17, 700).

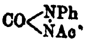
TRI-PHENYL-CARBINYL-TOLUIDINE $CPh_3.NHC_7H_7$. The *o* [142°] and *p* [177°] compounds are formed from CPh_3Br and *o* and *p* toluidine respectively (Elbs, *B.* 17, 706). The *p*-compound yields a crystalline nitrosamine [145°–148°].

PHENYL-CARBIZINE. *Formyl derivative*



$C_6H_4N{<}{\begin{matrix}N.CHO\\CO\end{matrix}}$. [72°]. (256°). Formed by the action of $COCl_2$ in benzene on the phenyl-hydrazide of formic aldehyde (Freund, *B.* 21, 1240, 2458). Needles (from CS_2), v. sol. alcohol and ether. Decomposed by boiling Na_2CO_3Aq into CO_2, and the phenyl-hydrazide of formic aldehyde.

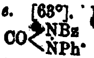
Acetyl derivative



$CO{<}{\begin{matrix}NPh\\NAc\end{matrix}}$. [94°]. (280°). Formed in like manner from acetic aldehyde. Monoclinic prisms; $a:b:c = 1·210:1:1·557$; $\beta = 73°$ 23′.

Propionyl derivative. [63°]. Needles.

Benzoyl derivative



$CO{<}{\begin{matrix}NBz\\NPh\end{matrix}}$. [114°]. Needles (from alcohol) or plates (from HOAc).

PHENYL CARBONATES.

Phenyl-carbonic acid *$C_6H_5O.CO_2H$.

Sodium salt $PhO.CO_2Na$. Prepared by treating dry sodium phenylate in the cold for a month with CO_2 until it has taken up the calculated quantity of the gas. The product is a very hygroscopic powder.

Reactions.—1. With *water* it gives off half its CO_2 in gaseous form: $2PhO.CO_2Na + H_2O = PhONa + PhOH + NaHCO_3 + CO_2$.—2. At 120° it splits up into CO_2 and PhONa.—3. Heated rapidly to 180°-200° it gives off smaller quantities of CO_2 together with phenol, the residue being sodium salicylate.—4. In a sealed tube at 120°-130° for several hours it changes completely to sodium salicylate: $C_6H_5O.CO_2Na = C_6H_4(OH)CO_2Na$ (R. Schmilt, *J. pr.* [2] 31, 408).

Di-phenyl carbonate $C_{13}H_{10}O_3$ *i.e.* $CO(OPh)_2$. [78°] (Kempf, *J. pr.* [2] 1, 404; Hentschel, *J. pr.* [2] 27, 41; 36, 315); [88°] (Richter, *J. pr.* [2] 27, 41). (303°). Formed by passing $COCl_2$ into an aqueous solution of NaOPh, or into phenol containing $AlCl_3$. Formed also from $ClCO_2CCl_3$, phenol, and $AlCl_3$. Needles (from alcohol). Alcoholic potash forms phenol and K_2CO_3. NaSEt gives NaSPh and $(EtS)_2CO$ (Seiffert, *J. pr.* [2] 31, 464).

References.—DI-BROMO- and NITRO- PHENYL CARBONATE.

DIPHENYL *o*-CARBOXYLIC ACID $C_{13}H_{10}O_2$ *i.e.* $C_6H_5.C_6H_4.CO_2H$ [1:2]. *Phenyl-benzoic acid.* Mol. w. 198. [111°]. Formed by potash-fusion from diphenylene ketone (Fittig a. Ostermaier, *B.* 5, 933; *A.* 166, 374; Schmitz, *A.* 193, 115). Formed also, together with diphenylene ketone oxide, by distilling sodium salicylate with triphenyl phosphate (R. Richter, *J. pr.* [2] 28, 305). Small needles (from hot alcohol), m. sol. hot water.—KA′aq.—BaA′$_2$aq.—CaA′$_2$2aq.—AgA′.

Ethyl ether EtA′. (300°-305°).

Tetrahydride $C_6H_5.C_6H_{10}.CO_2H$. *Phenyl-hexamethylene carboxylic acid.* [105°]. Formed by heating the corresponding dicarboxylic acid, and by the hydrolysis of phenylhexamethylenyl methyl ketone carboxylic ether (Kipping a. W. H. Perkin, jun., *C. J.* 57, 319). Rosettes of crystals (from ligroïn).—AgA′: amorphous pp.

Diphenyl *m*-carboxylic acid $C_6H_5.C_6H_4.CO_2H$. [161°]. Formed by oxidation by chromic acid and HOAc from [1:3] $C_6H_4Ph_2$, from C_6H_4PhMe, and from $C_6H_4Ph.CH_2Br$ (Schmidt a. Schultz, *A.* 203, 132; Adam, *A. Ch.* [6] 15, 243). It is also a product of the fusion of benzoic acid with potash (Barth a. Schreder, *M.* 3, 808). Leaflets (from alcohol), sl. sol. water. Yields isophthalic acid on oxidation.—NaA′$_2$ 2aq.—CaA′$_2$ 3aq.—BaA′$_2$ 3½aq: needles.—BaA′$_2$ 4½aq.

Ethyl ether EtA′. (above 360°). Oil.

Diphenyl *p*-carboxylic acid $C_6H_5.C_6H_4.CO_2H$. [219°]. Formed by saponification of its nitrile, which is got by heating potassium diphenyl sulphonate with KCy in a current of dry CO_2 (Doebner, *A.* 172, 109). Formed also by oxidation of [1:4] $C_6H_4Ph_2$ or [1:4] C_6H_4PhMe (Schultz, *A.* 174, 213; Carnelley, *C. J.* 37, 713). It is also a product of the fusion of benzoic acid with potash. Tufts of needles (from alcohol), v. sl. sol. hot water. May be sublimed. Yields terephthalic acid on oxidation.—BaA′$_2$.—CaA′$_2$.

Ethyl ether EtA′. [46°]. Prisms.

Nitrile $C_{12}H_9.CN$. [85°]. Crystals.

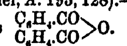
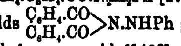
Anilide $C_{12}H_9.CO.NHPh$. [224°]. Got by heating $C_{12}H_9.C(NOH).C_6H_5$ with HOAc, Ac_2O, and dry HCl at 100° (Koller, *M.* 12, 503).

Diphenyl di-*o*-carboxylic acid $C_{14}H_{10}O_4$ *i.e.* [2:1]$CO_2H.C_6H_4.C_6H_4.CO_2H$[1:2]. *Diphenic acid.* Mol. w. 242. [228°]. Formed by the oxidation of phenanthraquinone or phenanthrene (Fittig a. Ostermayer, *A.* 166, 361; Schmitz, *A.* 193, 116). It is also produced when phenanthraquinone is boiled with conc. alcoholic potash (Anschütz a. Schultz, *A.* 196, 50; 203, 97). Plates or prisms, m. sol. hot water. May be sublimed. By exhaustive chlorination with $SbCl_5$ it yields perchloro-diphenyl, together with a small quantity of perchloro-benzene (Merz a. Weith, *B.* 16, 2872). Distillation over with red-hot CaO yields diphenylene ketone; distillation with $Ca(OH)_2$ gives diphenyl.

Salts.—BaA″4aq: v. sol. water.—CaA″ 2½aq.—MgA″4aq.—Ag$_2$A″: bulky white pp.

Methyl ethers Me$_2$A″. [73·5°].—MeHA″. [110°]. Plates, m. sol. water. Got by boiling the anhydride with MeOH.

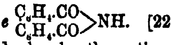
Ethyl ethers Et$_2$A″. [42°]. Crystals, insol. Aq (Hummel, *A.* 193, 128).—EtHA″. [88°].

Anhydride  $\left.\begin{matrix}C_6H_4.CO\\C_6H_4.CO\end{matrix}\right>O$. [213°].
Formed by boiling the acid with AcCl or Ac_2O (Anschütz, *B.* 10, 1884; 13, 1302: Graebe, *B.* 20, 848; *A.* 247, 261). Needles, insol. water, sol. alcohol. Decomposed by heat into CO_2 and diphenylene ketone. H_2SO_4 at 100° forms diphenylene ketone carboxylic acid [217°]. Phenyl-hydrazine forms the crystalline compound $CO_2H.C_6H_4.C_6H_4.CO.N_2H_2Ph$ [174° cor.] which at 250° yields  $\left.\begin{matrix}C_6H_4.CO\\C_6H_4.CO\end{matrix}\right>N.NHPh$ [150°]. Benzene and $AlCl_3$ form an acid [148°].

Chloride $C_{12}H_8(COCl)_2$. [98°]. Formed from the anhydride and PCl_5. Yields di-oxy-phenanthrene on reduction.

Amide $C_{12}H_8(CO.NH_2)_2$. [212°]. Formed by warming the imide with conc. NH_3Aq.

Amic acid $C_{12}H_8(CO_2H)(CONH_2)$. [193°]. Got by boiling the anhydride with NH_3Aq. Plates (from alcohol). Converted by heat into the imide.

Imide  $\left.\begin{matrix}C_6H_4.CO\\C_6H_4.CO\end{matrix}\right>NH$. [220°]. Formed as above, and also by the action of conc. HClAq on the mono-oxim of phenanthraquinone (Wegerhoff, *A.* 252, 18). Needles (from alcohol), sl. sol. hot water. Yields an acetyl derivative [92°], and forms $C_{14}H_8O_2(NNa)$, $C_{14}H_8O_2(NAg)$, and $C_{14}H_8O_2(NMe)$.

Diphenyl *om*-dicarboxylic acid [2:1] $CO_2H.C_6H_4.C_6H_4.CO_2H$ [1:3]. *Isodiphenic acid.* [216°]. Formed by fusing diphenylene ketone carboxylic acid with potash (Fittig a. Lieppmann, *B.* 12, 163; *A.* 193, 155; 200, 9). Needles (from hot water). Yields diphenylene ketone on heating with lime. Gives isophthalic acid on oxidation with CrO_3.—BaA″ 6aq. Crystalline.—CaA″ 2aq.—Ag$_2$A″: pp., sl. sol. hot water.

Methyl ether Me$_2$A″. [69·5°].

Ethyl ether Et$_2$A″. Thick oil.

Diphenyl *op*-di-carboxylic acid [2:1] $CO_2H.C_6H_4.C_6H_4.CO_2H$ [1:4]. [252°]. Formed by saponification of its nitrile [158°] which is got by Sandmeyer's reaction from *op*-di-amido-diphenyl (Reuland, *B.* 22, 3018).

Diphenyl di-*m*-carboxylic acid. [above 340°]. Formed by the action of nitrous acid on di-*p*-amido-diphenyl dicarboxylic acid (Griess, *B.* 21, 982). Small needles, almost insol. cold water.—BaA″ 3½aq: crystalline aggregates.

Diphenyl di-*p*-carboxylic acid [4:1] $CO_2H.C_6H_4.C_6H_4.CO_2H$ [1:4]. Formed by saponification of its nitrile, and also by oxidation of *p*-ditolyl (Doebner, *B.* 9, 129, 272; *A.* 172, 109). Amorphous powder, nearly insol. most solvents.—CaA″: insoluble pp.—BaA″.—Ag_2A'': white pp.

Ethyl ether Et_2A''. [112°]. Prisms.

Nitrile $C_{12}H_8(CN)_2$. [234°]. Formed by heating potassium diphenyl disulphonate with KCy. Needles (from alcohol).

Diphenyl dicarboxylic acid $C_6H_5.C_6H_3(CO_2H)_2$ [1:3:5]. [c. 310°]. Formed by heating benzoic aldehyde with $CH_3.CO.CO_2H$ and baryta-water (Doebner, *B.* 23, 2381; 24, 1750). Crystals, v. sl. sol. cold HOAc. Yields diphenyl on distillation with lime.—BaA″ 4½aq: needles.—CaA″.—CuA″.

Diphenyl tricarboxylic acid $C_{15}H_{10}O_6$ *i.e.* $CO_2H.C_6H_4.C_6H_3(CO_2H)_2$. Formed by fusing diphenylene ketone dicarboxylic acid with KOH (Bamberger a. Hooker, *B.* 18, 1035; *A.* 229, 160). White crystalline powder, v. sol. alcohol and ether, sl. sol. hot water.—$Pb_3A'''_2$: insoluble crystalline pp.—Ag_3A''', white pp.

References.—Amido-, Bromo-, Iodo-, Nitro-, and Oxy- diphenic and diphenyl carboxylic acids.

PHENYL-CETYL-AMINE *v.* Cetyl-aniline.

PHENYL-CHELIDAMIC ACID *v.* Chelidonic acid.

PHENYL-CHLORO-ACETIC ACID *v.* Chloro-phenyl-acetic acid.

PHENYL CHLORO-BENZYL KETONE $C_6H_5.CO.CHCl.C_6H_5$. [65°]. (Curtius, *J. pr.* [2] 44, 547). Formed by reducing phenyl dichloro-benzyl ketone with iron and acetic acid (Lachovitch, *B.* 17, 1163). V. sol. alcohol.

Phenyl di-chloro-benzyl ketone $C_6H_5.CO.CCl_2.C_6H_5$. [71°]. (Zinin, *A.* 119, 177); [61°] (L.). Formed from benzil and PCl_5. Prisms (from ether). Reduced by zinc and HCl to phenyl benzyl ketone.

PHENYL CHLORO-BENZYL SULPHONE $C_6H_5.CO.CHCl.C_6H_5$. Formed by heating benzylidene chloride with $C_6H_5.SO_2Na$ and alcohol at 150° (Otto, *J. pr.* [2] 40, 517). Needles (from HOAc), sl. sol. hot alcohol.

PHENYL-CHLORO-ETHANE *v.* Chloro-ethyl-benzene.

PHENYL CHLORO-ETHYL OXIDE *v.* *Chloro-ethyl derivative* of Phenol.

PHENYL CHLORO-ETHYL SULPHONE $C_6H_5.SO_2.CH_2.CH_2Cl$. [56°]. Formed by the action of PCl_5 or HCl on phenyl oxy-ethyl sulphone (Otto, *J. pr.* [2] 30, 197). Six-sided tablets (from benzene), sl. sol. water.

Reactions.—1. Boiling with alcohol and Ag_2O converts it into $C_6H_5.SO_2.C_2H_4OH$.—2. By heating with $C_6H_5SO_2Na$ in alcoholic solution it is converted into $(C_6H_5.SO_2)_2C_2H_4$.—3. *Sodium-amalgam* reduces it, in alcoholic solution, to benzene sulphinic acid.—4. Alcoholic NaOEt forms $C_6H_5.SO_2.C_2H_4OEt$.—5. Converted by heating in sealed tubes with dry Ag_2O and benzene into $(C_6H_5.SO_2.C_2H_4)_2O$.—6. *Ammonia* forms $(C_6H_5.SO_2.C_2H_4)_2NH$.—7. Alcoholic KHS produces $(C_6H_5.SO_2.C_2H_4)_2S$. [124°].

Phenyl chloro-ethyl sulphone $C_6H_5.SO_2.CHCl.CH_3$. [52°]. Formed by heating aqueous $CH_3.CCl_2.CO_2Na$ (1 mol.) with sodium benzene sulphinate (2 mols.) at 100° (Otto, *J. pr.* [2] 40, 532). Crystals (from alcohol).

PHENYL-CHLORO-IMESATIN *v.* Isatin.

PHENYL CHLORO-METHENYL DI-ETHYL TRI-SULPHONE $CCl(SO_2Ph)(SO_2Et)_2$. [130°]. Got by chlorinating $CH(SO_2Ph)(SO_2Et)_2$ (Laves, *B.* 25, 363). Plates, sl. sol. hot water.

TRI-PHENYL CHLORO-METHENYL TRI-SULPHONE $CCl(SO_2Ph)_3$. [260°]. Got by chlorinating $CH(SO_2Ph)_3$ (Laves, *B.* 25, 350).

PHENYL CHLORO-METHYL KETONE *v.* ω-Chloro-acetophenone.

PHENYL CHLORO-METHYL SULPHONE $C_6H_5.SO_2.CH_2Cl$. [53°]. Formed by boiling an aqueous solution of $C_6H_5SO_2Na$ (2 mols.) with $CHCl_2.CO_2Na$ (1 mol.), the yield being nearly the theoretical quantity (Otto, *J. pr.* [2] 40, 527; *B.* 21, 656). Formed also from $C_6H_5.SO_2Na$ and CH_2Cl_2.

Phenyl di-chloro-methyl sulphone $C_6H_5.SO_2.CHCl_2$. [59°]. Formed by treatment of $C_6H_5.SO_2.CH_2.CO_2H$ with Cl in diffused daylight (Otto, *J. pr.* [2] 40, 511). Monoclinic prismatic tables, v. sol. hot alcohol.

PHENYL-CHLORO-NAPHTHYL-AMINE. *Benzoyl derivative* $C_6H_5NBz.C_{10}H_6Cl$. [152°]. Formed from $NPhBz.C_{10}H_7$ and PCl_5 (Claus a. Richter, *B.* 17, 1590). Needles, sol. alcohol.

PHENYL-CHLORO-NITRO-PHENYL-HYDRAZINE $C_6H_5.N_2H_2.C_6H_3Cl(NO_2)$ [1:4:6]. [140°]. Formed from phenyl-hydrazine and $C_6H_3Cl(NO_2)_2$ in the cold (Willgerodt, *J. pr.* [2] 37, 355). Red prisms (from alcohol and ether).

PHENYL TRI-CHLORO-OXY-PROPYL KETONE $C_6H_5.COCH_2.CH(OH).CCl_3$. [6[illegible]°] and [77°]. Got from acetophenone, chloral, and HOAc (Koenigs, *B.* 25, 795). V. sl. sol. water. Converted by H_2SO_4 into $C_6H_5.CO.CH:CH.CCl_3$ [102°].

PHENYL CHLORO-PHENYL HYDRAZINE $C_6H_5.N_2H_2.C_6H_4Cl$ [1:4]. [90°]. Formed by reducing $C_6H_5.N_2.C_6H_4Cl$ with alcoholic ammonium sulphide (Heumann a. Mentha, *B.* 19, 1688).

PHENYL CHLORO-PHENYL KETONE *v.* Chloro-benzophenone.

PHENYL-CHLORO-PROPIONIC ACID *v.* Chloro-phenyl-propionic acid.

PHENYL ω-CHLORO-*p*-TOLYL KETONE $C_6H_5.CO.C_6H_4.CH_2Cl$. *Benzoylbenzyl chloride.* [98°]. Formed by chlorination of phenyl *p*-tolyl ketone at 110° (Thörner, *A.* 189, 89). Silky needles (from dilute alcohol). May be sublimed. On further chlorination at 135° it yields phenyl dichlorotolyl ketone or benzoyl benzylidene chloride $C_6H_5.CO.C_6H_4.CHCl_2$ [95°] and, at 155°, phenyl tri-chloro-tolyl ketone or benzoyl-benzotrichloride $C_6H_5.CO.C_6H_4.CCl_3$ [111°], which is converted by PCl_5 into $C_6H_5.CCl_2.C_6H_4.CCl_3$ [80°] crystallising in thin plates.

PHENYL-CHRYSYL-THIO-UREA $C_6H_5NH.CS.NH.C_{18}H_{11}$. [186°]. Formed from phenyl-thiocarbimide and chrysylamine and from chrysyl-thiocarbimide and aniline in benzene solution (Abegg, *B.* 24, 957). Crystals.

PHENYL-CINCHONIC ACID *v.* Phenyl quinoline carboxylic acid.

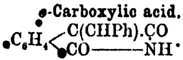
PHENYL-CINCHONIDINE $C_{19}H_{21}PhN_2O$. Formed in two modifications (an oil, sol. ether, and an amorphous powder, insol. ether) by heating cinchonidine with aniline (Claus a. Bätcke, *B.* 18, 2194). Both give $B''H_2PtCl_6$ 2aq.

PHENYL-CINNAMIC ACID $C_{15}H_{12}O_2$ *i.e.* $C_6H_5.CH:CPh.CO_2H$. [170°]. Formed by saponifying the nitrile or heating sodium phenyl-acetate with benzoic aldehyde and Ac_2O at 150° (Oglialoro, *G.* 9, 429). Needles, sol. alcohol and ether, v. sl. sol. cold water. Reduced by sodium-amalgam to *αβ*-di-phenyl-propionic acid.—BaA'_2 4aq: micaceous plates.

Methyl ether MeA'. [78°] (Cabella, *G.* 14, 114). Needles (from dilute alcohol).

Nitrile $C_6H_5CH:CPh.CN$. *Phenyl-styryl cyanide.* [87°]. (360° cor.). Formed by the action of benzyl cyanide on benzoic aldehyde or benzylidene chloride in presence of NaOEt or solid NaOH (Rossolymo, *B.* 22, 1235; Meyer, *A.* 250, 124; Janssen, *A.* 250, 129; Neure, *A.* 250, 155; Frost, *A.* 250, 157). White plates (from alcohol). Yields $CHPhBr.CPhBr.CN$ [130°] and $CHPhCl.CPhCl.CN$. [168°].

o-Carboxylic acid. *Imide*


$C_6H_4{<}\begin{matrix}C(CHPh).CO\\ CO\text{———}NH\end{matrix}$. [174°]. Formed by heating the imide of carboxy-phenyl-acetic acid (vol. i. p. 706) with benzoic aldehyde (Gabriel, *B.* 20, 1205). Needles.

References.—NITRO- and OXY- PHENYL-CINNAMIC ACID.

PHENYL-CINNAMYL-HYDRAZINE $CHPh:CH.CH_2.NPh.NH_2$. [54°]. Formed from sodium phenyl-hydrazine and cinnamyl bromide (Michaelis, *B.* 22, 2233). Crystals.

PHENYL-CINNAMYL KETONE *v.* PHENYL STYRYL KETONE.

PHENYL-*p*-COUMARIC ACID [1:4] $C_6H_4(OH).CH:CH.CO_2H$. [219°]. Formed by heating *p*-oxy-benzoic aldehyde with Ac_2O and sodium phenyl-acetate and boiling the resulting acetyl derivative with baryta-water (Oglialoro, *G.* 13, 173).—AgA': nearly insol. water.

Acetyl derivative. [170°].

Methyl ether MeA'. [170°].

Ethyl ether EtA'. [152°].

Methyl derivative. [189°]. Vol. iii. p. 738.

PHENYL-COUMARIN $C_{15}H_{10}O_2$. [140°]. Formed, together with $C_6H_4(OAc).CH:CPh.CO_2H$, by heating salicylic aldehyde with sodium phenyl-acetate and Ac_2O for 8 hours at 150° (Oglialoro, *G.* 9, 428). Prisms, sol. ether.

Mono-sulphonic acid $C_{15}H_9O_2(SO_3H)$ 2½aq. [263]. White needles (Curatolo, *G.* 14, 257). —BaA'_2.—PbA'_2 4aq: needles, m. sol. hot water.

Di-sulphonic acid $C_{15}H_8O_2(SO_3H)_2$ 6aq. [89°]. Deliquescent crystals.—BaA'_2 4aq: white prisms.—PbA'_2 5aq: needles, v. sol. water.

PHENYL-CROTONIC ACID $C_{10}H_{10}O_2$ *i.e.* $C_6H_5.CH:CMe.CO_2H$. *Phenyl-methacrylic acid. (α)-Methyl-cinnamic acid.* [82°]. Formed by heating benzoic aldehyde with propionic anhydride and sodium propionate (Perkin, *C. J.* 31, 391; 32, 661). Formed also by heating benzoic aldehyde with Ac_2O and sodium methyl-malonate; and by heating benzoic aldehyde with sodium propionate and HOAc or Ac_2O (Stuart, *C. J.* 43, 404; Slocum, *A.* 227, 57). Obtained also by oxidation of the corresponding aldehyde (Miller a. Kinkelin, *B.* 19, 526). It is also a product of the action of Na on benzyl propionate (Conrad a. Hodgkinson, *A.* 193, 314).

Transparent plates (from alcohol), sl. sol. hot water. When prepared by Perkin's method it appears to be accompanied by an isomeride [74°] crystallising in needles, which is converted into the acid [82°] by frequent recrystallisation (Raikoff, *B.* 20, 3396). Yields methrohol (*q.v.*) when heated with dilute H_2SO_4. Bromine forms $CHPhBr.CMeBr.CO_2H$ [137°] (Körner, *B.* 21, 276).

Salts.—BaA'_2 aq: very minute plates.—BaA'_2 4aq: small white crystals, got by slow cooling.—AgA'. S. ·374. Needles.

Methyl ether MeA'. [39°]. (254°).

Amide [128°] (Edeleano, *B.* 20, 619).

Phenyl-isocrotonic acid $C_6H_5.CH:CH.CH_2.CO_2H$. [86°] (J.); [88°] (B. a. D.). (302°). Formed by heating benzoic aldehyde with succinic anhydride and sodium succinate (Perkin), the yield being 2 p.c. (Jayne, *A.* 216, 100). Formed also by heating phenyl-trimethylene tricarboxylic acid $C_3H_2Ph(CO_2H)_3$ in a current of CO_2 at 190° (Buchner a. Dessauer, *B.* 25, 1155). Prepared by heating benzoic aldehyde with sodium succinate and Ac_2O at 125°, and separated from phenyl-paraconic acid by solution in CS_2. Long thin needles (from water) or prisms (from CS_2). When heated with H_2SO_4 (4 pts.) and water (4 pts.) it changes to the isomeric phenyl-butyrolactone and an acid [179°] (Erdmann, *A.* 227, 257). Yields *γ*-phenyl-*n*-butyric acid [49°] on reduction. Boiling NaOHAq converts it into the isomeric $C_6H_5.CH_2.CH:CH.CO_2H$ [65°]. Split up by long boiling into water and (*α*)-naphthol. Alkaline $KMnO_4$ at 0° forms di-oxy-phenyl-butyric lactone (Fittig a. Obermüller, *A.* 268, 44).—BaA'_2 3aq.—CaA'_2 3aq.—AgA': bulky pp.

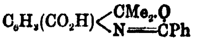
α-Phenyl-crotonic acid $CH_3.CH:CPh.CO_2H$. *Methylatropic acid.* [135°]. Formed by heating sodium phenyl-acetate with paraldehyde and Ac_2O (Oglialoro, *G.* 15, 514). Minute prisms (from water), sol. alcohol and ether.—AgA': m. sol. hot water.

Phenyl-crotonic acid $C_6H_5.CH:C(CH_2Ph).CO_2H$. [158°]. Formed from sodium phenyl-propionate, benzoic aldehyde, and Ac_2O at 160° (Oglialoro, *G.* 20, 162). Needles (from alcohol).

Reference.—OXY-PHENYL-CROTONIC ACID.

PHENYL-CROTONIC ALDEHYDE *v.* PHENYL-METHACRYLIC ALDEHYDE.

PHENYL-CUMAZONIC ACID.

$C_{17}H_{15}NO_3$ *i.e.*

$C_6H_3(CO_2H){<}\begin{matrix}CMe_2.O\\ N{=\!=\!=}CPh\end{matrix}$ (?). [220°]. Formed by heating (3,4,1)-amido-oxypropyl-benzoic acid with BzCl at 100°-120° (Widmann, *B.* 16, 2585). White crystals. Sol. alcohol, insol. water.—$HA'H_2SO_4$ 2aq: thin plates.

PHENYL-CUMINYL-AMINE $C_{16}H_{19}N$ *i.e.* $C_6H_5.NH.CH_2.C_6H_4Pr$. [41°]. Formed by reducing $C_6H_5.N:CH.C_6H_4Pr$ (Uebel, *A.* 245, 289). Plates or prisms. Yields a nitrosamine $C_{16}H_{18}(NO)N$ [94°].—B'HCl: white crystals.

PHENYL-CUMINYL-THIO-UREA $C_6H_4Pr.CH_2.NH.CS.NHPh$. [100°-106°]. Formed from cuminylamine and phenyl-thio-carbimide (Goldschmidt a. Gessner, *B.* 20, 2416).

PHENYL-CUMINYL-UREA $C_{17}H_{20}N_2O$ *i.e.* $C_6H_5NH.CO.NHC_{10}H_{13}$. [144°]. Formed from cuminyl cyanate and aniline (Raab, *B.* 8, 1151) and from phenyl cyanate and cuminylamine (Goldschmidt, *B.* 20, 2415). Small needles.

PHENYL-DI-CUMYL-GUANIDINE $NPh:C(NH.C_6H_4(C_3H_7)[1:4])_2$. Formed from di-cumyl-thio-urea and aniline (Francksen, *B.* 17, 1226). Resin.

PHENYL ψ-CUMYL KETONE $C_{16}H_{16}O$ *i.e.* $C_6H_5.CO.C_6H_2Me_3$ [1:2:4:5]. (329°). From BzCl, ψ-cumene, CS_2, and $AlCl_3$ (Elbs, *J. pr.* [2] 35, 491; *cf.* Claus, *B.* 19, 2881); the yield is 65 p.c. of the calculated.

Reactions.—1. Boiling produces small quantities of needles [180°], probably (*B.* 2,3)- di methyl-anthraquinone.—2. Conc. or fuming H_2SO_4 at 100° forms benzoic acid and ψ-cumene sulphonic acid $C_6H_2Me_3(SO_3H)$ [1:2:4:5].—3. Fuming HNO_3 mixed with $H_2S_2O_7$ gives two isomeric tri-nitro- derivatives; one [185°] is v. sl. sol. alcohol, the other [155°] is m. sol. alcohol.—4. Dilute nitric acid forms benzoyl-trimellitic acid, $C_6H_5.CO.C_6H_2(CO_2H)_3$ and $C_6H_5.CO.C_6H_2Me(CO_2H)_2$.

Phenyl cumyl ketone $C_6H_5.CO.C_6H_4Pr$. (343°) at 738 mm. Formed from cuminyl chloride, benzene, and $AlCl_3$ (Smith). Yields two oxims [106°] and [132°], the latter of which forms an acetyl derivative [90°].

Phenyl *n*-cumyl ketone. $C_6H_5.CO.C_6H_4Pr$. (345° at 716 mm.). Formed from *n*-cumene, BzCl, and $AlCl_3$ (Smith, *B.* 24, 4033). Prisms. Yields two oxims [130°] and [104°], which yield acetyl derivatives, melting at 116 and 66°.

PHENYL-ψ-CUMYL-METHANE CARBOXYLIC ACID [1:2:4] $C_6H_2Me_3.CH_2.C_6H_4.CO_2H$ [1:2] [186°]. Got by reducing $C_6H_2Me.CO.C_6H_4.CO_2H$ with Zn and NH_3Aq (Gresly, *A.* 234, 238).

DI-PHENYL-ψ-CUMYL-METAPYRAZOLE TETRAHYDRIDE $C_{24}H_{26}N_2$ *i.e.*

$C_9H_{11}.CH\left\langle\begin{matrix}NPh\\NPh\end{matrix}\right\rangle C_2H_4$. [125°]. Formed from *p*-cuminic aldehyde and di-phenyl-ethylene-diamine at 100° (Moos, *B.* 20, 733). Silky needles.

PHENYL-ψ-CUMYL-UREA $C_{16}H_{18}N_2O$ *i.e.* $NHPh.CO.NHC_6H_2Me_3$ [211°]. Formed from ψ-cumidine and phenyl cyanate (Goldschmidt a. Bardach, *B.* 25, 1361). White needles.

PHENYL-CYANAMIDE *v.* vol. ii. p. 316.

Di-phenyl-cyanamide $C_{13}H_{10}N_2$ *i.e.* $C(NPh)_2$. *Carbodiphenylimide.* Mol. w. 194. (331° cor.). Formed by warming a solution of *s*-di-phenyl-thio-urea in benzene with HgO (Weith, *B.* 7, 10, 1303; 9, 810). Syrup, drying up to a vitreous mass. Changes spontaneously into an opaque polymeride [170°] resembling porcelain.

Reactions.—1. Boiling *dilute alcohol* converts it into *s*-di-phenyl-urea.—2. *Aniline* yields (α)-tri-phenyl-guanidine.—3. H_2S passed into its solution in benzene forms $CS(NHPh)_2$.—4. *s-Di-phenyl-thio-urea* at 150° forms phenyl-thiocarbimide and (α)-tri-phenyl-guanidine.—5. *Di-phenyl-urea* at 150° acts in like manner, forming phenyl cyanate and tri-phenyl-guanidine.—6. *Phenyl-hydrazine* at 120° forms the compound $C_6H_5N_2:C(NHPh)_2$ [204°] which gives the salts B'HCl, $B'_2H_2PtCl_6$, and $B'H_2SO_4$, and is converted, by heating with phenyl-hydrazine at 185°, into $C_{25}H_{22}N_6$ [200°], which gives the salts $B'_2H_4Cl_4$ and $B'_22H_2PtCl_6$. The compound $PhN_2:C(NHPh)_2$ is converted by heating with phenyl-thiocarbimide at 190° into $C_{26}H_{22}N_6S$ [175°], and by heating with di-*p*-tolyl-cyanamide into $C_{34}H_{28}N_6$ [128°], which gives the salts $B'_2H_4Cl_4$ and $B'_22H_2PtCl_6$ (Wessel, *B.* 21, 2272).—7. HCy passed into its solution in benzene forms $C_{14}H_{11}N_3$ crystallising from alcohol in prisms [137°]. A little of its solution in H_2SO_4 mixed with water is coloured deep blue by NaOH (Laubenheimer, *B.* 13, 2155).—8. *Tolylene-o-diamine* at 135° forms $C_{20}H_{20}N_4$ [161°] which yields $B'_2H_2Cl_2$ [174°] (Dahm a. Gasiorowski, *B.* 19, 3057).

Salt.—B'HCl. Needles (from benzene).

Tri-phenyl-di-cyan-di-amide $C_{20}H_{16}N_4$. Formed from NHPh.CS.NH.C(NPh).NHPh, alcohol, and HgO, and also by heating di-phenyl-guanidine at 175° (Rathke a. Oppenheim, *B.* 23, 1673). Yellow needles (containing EtOH) (from alcohol).—B'HCl. Needles, insol. water.—$B'_2H_2PtCl_6 2aq$.—$B'_2H_2SO_4 2aq$.

Reference.—OXY-PHENYL-CYANAMIDE.

PHENYL CYANATE *v.* vol. ii. p. 315.

PHENYL-CYANIC ACID *v.* CYANIC ACID.

PHENYL CYANIDE *v.* BENZONITRILE and PHENYL-CARBAMINE.

Di-phenyl dicyanide $C_{14}H_{10}N_2$ *i.e.*

$PhC\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle CPh$? [152°]. Formed from benzamidine and benzoic aldehyde (Pinner, *B.* 22, 1610; 23, 2925). Prisms. Changes at 260°–270° into cyaphenine.

PHENYL-CYANURIC ACID *v.* *Cyanuric acid* in the article on CYANIC ACID.

PHENYL-*p*-CYMYL-CARBINOL $C_6H_5.CH(OH).C_6H_3(CH_3)(C_3H_7)$ [1:2:5]. (327° uncor.). Formed by reduction of phenyl *p*-cymyl ketone (Claus a. Elbs, *B.* 18, 1798; *J. pr.* [2] 35, 497). Thick colourless oil.

PHENYL *p*-CYMYL KETONE $C_{17}H_{18}O$ *i.e.* $C_6H_5.CO.C_6H_3MePr$ [1:2:5]. (224° at 40 mm.); (340°) at 760 mm.

Formation.—1. From cymene by heating with benzoic acid and P_2O_5 (Kollarits a. Merz, *B.* 6, 546).—2. From cymene, BzCl, and zinc (Grucarevic a. Merz, *B.* 6, 546, 1246).—3. From cymene, BzCl, CS_2, and $AlCl_3$ (Elbs, *J. pr.* [2] 35, 494].

Properties.—Yellowish oil, v. sol. alcohol and ether, m. sol. HOAc. Very slightly volatile with steam.

Reactions.—1. *Bromine* and *iron powder* at 140° give benzoic acid and bromo-cymene, $C_6H_3BrMePr$ [1:2:5] [232°].—2. Conc. H_2SO_4 and KNO_3 give an amorphous dinitro-derivative.—4. Dilute HNO_3 gives benzoyl-terephthalic acid.—5. Concentrated H_2SO_4 at 100° gives benzoic acid and cymene sulphonic acid, $C_6H_3MePr(SO_3H)$ [1:4:2].

PHENYL-CYSTEÏNE $C_9H_{11}NSO_2$ *i.e.* $CH_3.C(SPh)(NH_2).CO_2H$. Formed by boiling phenyl-mercapturic acid with dilute H_2SO_4 (Baumann a. Preusse, *H.* 5, 337). Plates (from NH_3Aq) or six-sided tables (from water), v. sol. acids and alkalis, sl. sol. cold water. Yields phenyl mercaptan on boiling with NaOHAq.

Reference.—BROMO-PHENYL-CYSTEÏNE.

PHENYL-DECOIC ACID. *Nitrile* $C_6H_5.CH(C_8H_{17}).CN$. (328°). Formed from benzyl cyanide, octyl iodide, and NaOH (Rossolymo, *B.* 22, 1237). Yellow oil.

PHENYL-DURYL-CARBINOL [6:4:3:2:1] $C_6HMe_4.CH(OH).C_6H_5$. (above 360°). Formed by reduction of phenyl iso-duryl ketone

Essner a. Gossin, *Bl.* [2] 42, 172). Liquid. Yields an *acetyl derivative* boiling above 360° and a *benzoyl derivative* [75°].

DI-PHENYL DURYLENE DIKETONE $C_{24}H_{22}O_2$ *i.e.* $(C_6H_5.CO)_2C_6Me_4$. [270°]. (above 380°). Formed from durene, BzCl, and $AlCl_3$ Friedel a. Crafts, *A. Ch.* [6] 1, 512). Prisms.

PHENYL DURYL KETONE $C_{17}H_{18}O$ *i.e.* $C_6H_5.CO.C_6HMe_4$. [119°]. (343°) at 725 mm. Got from durene, BzCl, and $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 511). Acicular prisms, v. sol. warm alcohol. Reduced by HI and P to $C_{17}H_{20}$ 60·5°] (310° at 716 mm.). Br forms $C_{17}H_{15}Br_3O$ 225°] and other products.

Phenyl isoduryl ketone. [63°]. (300°). Formed by the action of BzCl and $AlCl_3$ on the isodurene derived from toluene (Essner a. Gossin, *Bl.* [2] 42, 170). Successive treatment with HCy and alcoholic potash gives the acid $C_6HMe_4.CPh(OH).CO_2H$, sol. water and alcohol.

PHENYLENE. The radicle C_6H_4.

PHENYLENE-ACETAMIDINE

$C_6H_4<{NH \atop N}\gg C.CH_3$. [170°] (H.); [175°] (L.).

Formed by boiling phenylene-*o*-diamine with HOAc, or by reducing $C_6H_4(NO_2)(NHAc)$ with tin and HCl (Ladenburg, *B.* 8, 677; Hübner, *A.* 209, 353). Needles.—$B'HCl$.—$B'_2H_2PtCl_6$ aq.—$B'HNO_3$.—$B'H_2SO_4$.

Phenylene-di-acetamidine $C_{10}H_{14}N_4$ *i.e.* [1:4] $C_6H_4(CH_2.C(NH).NH_2)_2$. [182°]. Formed by the action of alcoholic NH_3, followed by NaOHAq, upon the hydrochloride of phenylene-di-acetimido-ether (Glock, *B.* 21, 2660). Plates.

***o*-PHENYLENE-DI-ACETIC ACID** $C_{10}H_{10}O_4$ *i.e.* [1:2] $C_6H_4(CH_2.CO_2H)_2$. Mol. w. 194. [150°]. Formed by saponification of its nitrile by boiling with dilute H_2SO_4 (Baeyer a. Pape, *B.* 17, 447). Slender needles, v. sol. alcohol, m. sol. cold water.—Ag_2A'': insoluble pp.

Nitrile $C_6H_4(CH_2.CN)_2$. [60°]. Formed by the action of KCy on di-ω-bromo-*o*-xylene.

***m*-Phenylene-di-acetic acid** $C_6H_4(CH_2.CO_2H)_2$. [170°]. Formed by boiling its nitrile with alcoholic potash (Kipping, *C. J.* 53, 42; *B.* 21, 42). Needles, v. sol. water.—Ag_2A'': white pp.

Nitrile $C_6H_4(CH_2.CN)_2$. [29°]. (308° at 300 mm.). From [1:3] $C_6H_4(CH_2Br)_2$ and KCy.

***p*-Phenylene-di-acetic acid** $C_6H_4(CH_2.CO_2H)_2$. [241°]. Got from its nitrile (Biedermann, *B.* 5, 703; Klippert, *B.* 9, 1766; Kipping, *C. J.* 53, 44). Needles, m. sol. water.—CaA'' 2aq.—CaA'' 3aq.—BaA'' 2½ aq: needles, v. sol. water.—ZnA''.—CuA''.—Ag_2A'': white amorphous pp.

Ethers.—Me_2A''. [57°].—Et_2A''. [58°].

Chloride. Oil (Klippert).

Amide. [above 290°]. Plates and needles.

Nitrile $C_6H_4(CH_2.CN)_2$. [96°]. Formed by the action of KCy on $C_6H_4(CH_2Br)_2$ or $C_6H_4(CH_2Cl)_2$. Three-sided prisms (from ether). Alcoholic ammonium sulphide at 100° converts it into $C_6H_4(CH_2.CS.NH_2)_2$ [206°] which crystallises from HOAc.

Di-phenylene-acetic acid ${C_6H_4 \atop C_6H_4}>CH.CO_2H$. [222°]. Formed by heating $C_{12}H_8:C(OH).CO_2H$ with HI and P at 140° (Friedländer, *B.* 10, 536). Small crystals (from alcohol). Decomposed by heating with soda-lime into CO_2 and fluorene.—AgA': unstable pp.

Ethyl ether EtA'. [165°].

Reference.—OXY-DIPHENYLENE-ACETIC ACID.

***p*-PHENYLENE DI-ACETIMIDO-ETHER** $C_6H_4(CH_2.C(NH).OEt)_2$. The hydrochloride $B''2HCl$ [above 240°] formed by the action of alcohol and HCl on $C_6H_4(CH_2.CN)_2$, crystallises in needles (Glock, *B.* 21, 2660). It is insol. ether.

***o*-PHENYLENE-DI-ACRYLIC ACID** $C_6H_4(CH:CH.CO_2H)_2$. [above 300°]. Formed by boiling $C_6H_4(CH_2.CCl(CO_2Et)_2)_2$ with alcoholic potash (Perkin, *C. J.* 53, 14; *B.* 19, 435). Sl. sol. water, v. sl. sol. alcohol.—Ag_2A'': pp.

***p*-Phenylene di-acrylic acid** $C_6H_4(CH:CH.CO_2H)_2$. [310°]. Obtained by saponifying the mono-ethyl ether HEtA'' [200°] which is got by heating *p*-aldehydo-cinnamic ether with NaOAc and Ac_2O (Löw, *A.* 231, 377). Got also by boiling $C_6H_4(CH_2.CBr(CO_2Et)_2)_2$ with alcoholic potash (Kipping, *C. J.* 53, 41). Yields a tetrabromide crystallising in needles.—Ag_2A''.

PHENYLENE-DI-ALLYL-DI-THIO-DI-UREA $C_6H_4(NH.CS.NHC_3H_5)_2$. The *o*- [159°], *m*- [105°], and *p*- [200°] compounds are formed by heating the corresponding phenylene-diamines with alcohol and allyl-thiocarbimide (oil of mustard) at 100° (Lellmann a. Würthner, *A.* 228, 201). The *o*- and *p*- compounds decompose when heated. They are all sol. HOAc.

***o*-PHENYLENE-DI-AMIDO-DI-ACETIC ACID** [1:2] $C_6H_4(NH.CH_2.CO_2H)_2$. The ether Et_2A'' [135°] is got from *o*-phenylene diamine and $ClCO_2Et$ (Zimmermann a. Knyrim, *B.* 16, 515).

m*-Phenylene-di-amido-di-acetic acid** [1:3] $C_6H_4(NH.CH_2.CO_2H)_2$. The ***ethyl ether Et_2A'' [78°] is got by heating *m*-phenylene-diamine with $CH_2Cl.CO_2Et$ (Zimmermann *B.* 15, 518; 16, 514). It is converted by conc. HClAq into crystalline $H_2A''H_2Cl_2$, v. sol. water.

***p*-Phenylene-di-amido-di-acetic acid.** The ethyl ether Et_2A'' [83°] and the hydrochloride $H_2A''H_2Cl_2$ are formed in like manner from *p*-phenylene-diamine.

***o*-PHENYLENE-DIAMINE** [1:2] $C_6H_4(NH_2)_2$. Mol. w. 108. [104°]. (252°). Prepared by reducing *o*-nitro-aniline with tin and HCl (Zincke a. Sintenis, *B.* 6, 123; Vignon, *Bl.* [3] 2, 675; Sandmeyer, *B.* 19, 2654). Formed also by heating the corresponding di-amido-benzoic acids with baryta (Griess, *J. pr.* [2] 3, 143; Salkowski, *A.* 173, 58) and by the action of tin and HCl on bromo-*o*-nitro-aniline (Wurster, *A.* 171, 63; Hübner, *A.* 209, 360) and on *o*-di-nitro benzene (Zincke, *B.* 7, 1874). Plates (from water) or tables (from chloroform), v. e. sol. hot water, alcohol, and ether.

Reactions.—1. $FeCl_3$ added to a solution of the hydrochloride forms di-amido-phenazine hydrochloride, which crystallises in ruby-red needles $C_{12}H_{10}N_4HCl$ (Fischer, *B.* 22, 355).—2. *Pyrocatechin* at 200° forms phenazine $C_6H_4:N_2:C_6H_4$.—3. (β)-*Naphthoquinone* forms naphthophenazine $C_{10}H_6:N_2:C_6H_4$.—4. *Cyanogen* gas forms $C_8H_6N_4$ a yellow crystalline powder [c. 280°], sl. sol. water, forming $B'_2H_2PtCl_6$ 3aq and $B'_2H_2PtCl_6$ aq. By heating with HCl it is converted into $C_8H_7N_3O$ [280°] and di-oxy-quinoxaline (Bladin, *Bl.* [2] 42, 104; *B.* 18, 672).—5. The *sulphocyanide* is converted by heat into a mixture of phenylene-thio-urea and thio-urea (Lellmann, *A.* 221, 8).—6. KNO_2 added to a very dilute solution of the sulphate forms 'amidoazophenylene' $C_6H_4N_3$, [illegible] from benzene in pearly white needles [98·5°] (Ladenburg, B. 9, 219).—7. ICy forms $C_{12}H_{12}N_4$, which yields the salts $B''H_2Cl_2$, $B''HCl\,2\frac{1}{2}aq$, $B''2HNO_3\,2\frac{1}{2}aq$, and $B''H_2SO_4\,2\frac{1}{2}aq$, and the benzoyl derivative $C_{12}H_{11}BzN_4$, and is converted by nitrous acid into $C_{12}H_8N_6O_2$ (Hübner, *B.* 9, 778; 10, 1716).—8. The hydrochloride is converted by benzoic aldehyde into dibenzylidene-phenylene diamine $(C_6H_4(N{:}CHPh)_2$ [134°], yielding $B'_2H_2PtCl_6$, $B'HNO_3$, $B'H_2SO_4$, $B'MeI$, and $B'EtI$ [213°] (Ladenburg, *B.* 11, 1658).

Salts.—$B''2HCl$. Needles, v. sol. water.—$B''H_2PtCl_6$.—$B''_2H_2SO_4$.—$B''H_2SO_4\,1\frac{1}{2}aq$: plates.

Di-acetyl derivative $C_6H_4(NHAc)_2$. [186°]. Long silky needles, v. sol. hot water and alcohol (Bistrzycki, *B.* 23, 1878).

Benzoyl derivative $C_6H_4(NH_2)(NHBz)$. [140°]. Got by reducing $C_6H_4(NO_2)(NHBz)$ with ammonium sulphide (Mixter, *Am.* 6, 26). Minute crystals, sol. water. When the reduction is effected by tin and HCl the product is benzenyl-phenylene-diamine (*q. v.*).

Dibenzoyl derivative $C_6H_4(NHBz)_2$. [c. 300°]. Thin prisms (from HOAc) (Bistrzycki).

Di-p-toluyl derivative $C_6H_4(NH.CO.C_6H_4Me)_2$. [228°]. Got, together with tolenyl-benzamidine $C_6H_4{:}N_2H{:}C.C_6H_4Me$ [268°], by the action of *p*-toluyl chloride on *o*-phenylene-diamine dissolved in benzene (Hübner, *A.* 210, 328). Colourless needles, sl. sol. alcohol.

***m*-Phenylene-diamine** $C_6H_4(NH_2)_2$. [63°]. (277° i.V.). Prepared by reduction of *m*-di-nitro-benzene or *m*-nitro-aniline (Hofmann, *Pr.* 11, 518; 12, 639; Zincke, *B.* 5, 792). Formed also by heating *s*-di-amido-benzoic acid with baryta (Wurster, *B.* 7, 214; Hübner, *A.* 222, 86), and by the action of tin and HCl on (4,2,1)-di-nitro-benzoic acid (Wurster, *B.* 7, 149) and on (1,2,4)-bromo-di-nitro-benzene (Z.). Got also by heating resorcin (1 pt.) with ammoniacal $CaCl_2$ (4 pts. containing 35 p.c. NH_3) for eight hours at 275° (Seyewitz, *C. R.* 109, 814). Crystalline, m. sol. water, v. sol. alcohol and ether. Its solutions are alkaline in reaction. KNO_2 added to a solution of a salt of *m*-phenylene-diamine forms a brown pp. containing $C_6H_3(NH_2)_2.N_2.C_6H_4.NH_2$. A solution in dilute H_2SO_4 is coloured yellow by a trace of nitrous acid. Aldehyde added to an alcoholic solution of *m*-phenylene-diamine hydrochloride forms an orange-red colour, with a green fluorescence. From this liquid NH_3Aq ppts. di-methyl-phenanthroline tetrahydride $C_{14}H_{16}N_2$ (Girard a. Roques, *C. R.* 107, 1158; Schiff, *A.* 253, 328). Benzoic aldehyde in alcohol forms with the hydrochloride the base $CHPh(C_6H_4(NH_2)_2)_2$. The hydrochloride of *m*-phenylene-diamine gives a crimson colour when boiled with oxygenated water (Denigès); in presence of ammonia the liquid becomes blue, but is turned red by NaOHAq. Hydrogen peroxide gives a bluish-green tint (Cazeneuve, *Bl.* [3] 5, 855). PbO_2 and dilute HOAc give a brown colour (Lauth, *C. R.* 111, 975). Alkaline NaOBr gives a maroon-red pp. (Denigès, *C. R.* 107, 662). CS_2 in alcohol at 35° forms yellow monoclinic prisms of $C_6H_4<\substack{NH\\NH}>CS$ and several other bodies (Gucci, *G.* 17, 523, 2657). The sulphocyanide is converted by heat into $C_6H_4(NH.CS.NH_2)_2$ (Lellmann, *A.* 221, 8). *m*-Phenylene-diamine is somewhat less poisonous than the *p*- isomeride (Dubois a. Vignon, *C. R.* 107, 533).

Salts.—$B''HCl$. Needles, v. sol. water, sl. sol. conc. HClAq.—$B''2HCl$.—$B''H_2PtCl_6$: needles.—$B''H_2Sn_2Cl_8$ (Gerdemann, *Z.* [2] 1, 51).—$B''H_2SnCl_6$.—$B''H_2SO_4$.

Hydriodide: Mills, *C. J.* 17, 153.

Di-formyl derivative $C_6H_4(NH.CHO)_2$. [155°]. Small crystals (Tobias, *B.* 15, 2447).

Mono-acetyl derivative $C_6H_4(NH_2)(NHAc)$. Crystalline solid, v. sol. water (Wallach a. Schulze, *B.* 15, 3020).—$B'HCl$. [280°].

Di-acetyl derivative $C_6H_4(NHAc)_2$. [189°] (Kelbe, *B.* 16, 1200; *cf.* Barbaglia, *B.* 7, 1257).

Mono-benzoyl derivative $C_6H_4(NH_2)(NHBz)$. [125°] (Bell, *B.* 7, 498); [260°] (Hübner, *A.* 208, 298). Got by reducing $C_6H_4(NO_2).NHBz$.—$B''HCl$.—$B''H_2SO_4$. Needles.

Di-benzoyl derivative $C_6H_4(NHBz)_2$. [240°] (Ruhemann, *B.* 14, 2651; Hinsberg, *A.* 254, 255). White plates.

m-Amido-benzoyl derivative $C_6H_4(NH_2)(NH.CO.C_6H_4NH_2)$. [129°]. Needles (from dilute alcohol) (Hugh, *B.* 7, 1268).

o-Oxy-benzoyl derivative $C_6H_4(NH_2).NH.CO.C_6H_4.OH$. [143°]. Crystals (Bell, *C. J.* 28, 1201).

***p*-Phenylene-diamine** $C_6H_4(NH_2)_2$. [140°]. (267°).

Formation.—1. By reduction of *p*-nitro-aniline and of *p*-di-nitro-benzene (Hofmann, *Pr.* 11, 518; 12, 639; Zincke, *B.* 7, 871).—2. By reduction of $C_6H_5.N_2.C_6H_4NH_2$ (Martius a. Griess, *Z.* 1866, 136).—3. By distilling (5,2,1)-di-amido-benzoic acid (Griess, *B.* 5, 201).—4. In the preparation of induline by heating $C_6H_5.N_2.C_6H_4.NH_2$ with aniline hydrochloride (Witt; Fischer a. Hepp, *B.* 23, 839).

Preparation.—From acetanilide by nitration and reduction with tin and HCl.

Properties.—Plates (by sublimation) or monoclinic crystals (from water) changing in the solution to trimetric plates. M. sol. water, v. sol. alcohol and ether. Forms a hydrate $C_6H_8N_2\,2aq$ [80°]. With PbO_2 and aqueous HOAc it gives a bright bluish-green colour (Lauth, *C. R.* 111, 975). *p*-Phenylene-diamine is very poisonous (Vignon, *C. R.* 107, 533). A mere trace of a mixture of *m*- and *p*- phenylene-diamine gives on warming with HOAc and $K_2Cr_2O_7$ a blue colour, changing on boiling to red (Witt, *C. J.* 35, 356; Meldola, *C. J.* 51, 105).

Reactions.—1. *Oxidised* to quinone by H_2SO_4 and MnO_2. Quinone is also formed together with NH_3 by oxidation of the sulphate with $K_2Cr_2O_7$ (Meldola a. Evans, *C. J. Proc.* 5, 115).—2. When exposed to *air*, O, H_2O_2, or K_3FeCy_6 *p*-phenylene-diamine and its salts are oxidised to $C_6H_6N_2$ a feeble red base with green lustre [230°] yielding $C_6H_5AcN_2$ [294°] (Bandrowski, *M.* 10, 126).—3. *Chlorine* passed into a solution in HOAc forms tetra-chloro-quinone.—4. $FeCl_3$ added to a solution of the hydrochloride saturated with H_2S ppts. Lauth's violet, which is v. sol. pure water, but ppd. by salts (Lauth, *C. R.* 82, 1441).—5. Potassium nitrite added to a solution of the hydrochloride forms $C_6H_4(NH_2Cl)N_2Cl$, and in presence of a large excess of HCl it forms $C_6H_4(N_2Cl)_2$.—6. Mixed with *aniline* (2 mols.) and oxidised by $K_2Cr_2O_7$ it yields pheno-safranine.—7. The *sulphocyanide* is converted by heat into $C_6H_4(NH.CS.NH_2)_2$ (Lellmann, *A.* 221, 8).—8. *Bleaching-powder* solution added to a solution in HClAq ppts. yellowish-white quinone di-chloro-di-imide which detonates at 124° (Krause, *B.* 12, 47).—9. *Aceto-acetic ether* at 170° forms $C_{14}H_{16}N_2O_4$ [176°] which is probably $C_6H_4(NH.CO.CH_2.CO.CH_3)_2$ (Knorr, *B.* 17, 545; 19, 3303).

Salts.—$B''H_2Cl_2$. Triclinic tables, v. sol. water, almost insol. HClAq.—$B''H_2PtCl_6$.—$B''H_2Sn_2Cl_6$ (Hübner, *A.* 209, 366).—$B''H_2Br_2$.—$B''H_2S_2O_6$ (Bernthsen, *A.* 251, 62).—$B''H_2SO_4$. Micaceous plates, sl. sol. water (Vignon, *Bl.* [2] 50, 152).—$B''H_2C_2O_4$. S. ·15 at 15°.

Di-formyl derivative $C_6H_4(NH.CHO)_2$. [204°]. Amorphous mass (Wundt, *B.* 11, 828).

Mono-acetyl derivative $C_6H_4(NH_2)(NHAc)$. [161°]. Formed by reduction of $C_6H_4(NO_2).NHAc$ with iron and acetic acid (Nietzki, *B.* 17, 343). Needles, sl. sol. cold water.—$B'_2H_2PtCl_6$.

Di-acetyl derivative $C_6H_4(NHAc)_2$. [above 295°]. Formed by boiling the base with HOAc (Biedermann a. Ledoux, *B.* 7, 1531). Small octahedra, sol. HOAc.

Benzoyl derivative $C_6H_4(NH_2)(NHBz)$. [128°]. Formed by reducing benzoyl-*p*-nitro-aniline (Hübner, *A.* 208, 295). Plates, sl. sol. water.—B'HCl.—$B'_2H_2SO_4$. Needles.

Di-benzoyl derivative $C_6H_4(NHBz)_2$. [above 300°]. Formed from the base, BzCl, and NaOHAq (Hinsberg, *A.* 254, 254). Plates. Yields a nitro- product [251°].

o-Oxy-benzoyl derivative $C_6H_4(NH_2)(NH.CO.C_6H_4.OH)$. [158°]. Glittering needles (Bell).

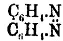
Hexahydride $C_6H_{10}(NH_2)_2$. *Di-amido-hexamethylene.* Formed by reducing the di-oxim of quinone tetrahydride in alcohol with Na (Baeyer a. Noyes, *B.* 22, 2172). Liquid, with faint ammoniacal odour, forming crystalline salts and an acetyl derivative melting above 310°.

References.—BROMO-, BROMO-NITRO-, CHLORO-, NITRO-, and OXY- PHENYLENE-DIAMINE.

PHENYLENE-DIAMINE SULPHONIC ACID *v.* DI-AMIDO-BENZENE SULPHONIC ACID.

PHENYLENE-DI-AMYL-DIAMINE [1:4] $C_6H_4(NH.C_5H_{11})_2$. [49°]. Colourless crystals (Baeyer a. Noyes, *B.* 22, 2173).

DIPHENYLENE-AZONE



$\begin{array}{l}C_6H_4.N\\C_6H_4.N\end{array}$ [156°].

Formed, together with $C_{12}H_8N_2O_2$ [240°] and $C_{12}H_8N_2O$ [152°] by boiling di-*o*-nitro-diphenyl with alcohol and zinc-dust (Täuber, *B.* 24, 3081, 3883). Greenish-yellow needles by sublimation, not volatile with steam. Almost insol. water, v. sol. alcohol, m. sol. ether, v. e. sol. HOAc. Reduced by tin and HCl to $C_{12}H_{10}N_2HCl$, which crystallises in white needles, rapidly re-oxidised by air to diphenylene-azone.

Salts.—B'HCl. Flat bronzed prisms.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$: yellow needles.—$B'H_2CrO_4$.—$B'C_6H_3N_3O_7$. [194°]. Brown needles.

PHENYLENE-BENZALDEHYDINE *v.* vol. i. p. 109.

PHENYLENE-BENZAMIDINE *v.* BENZENYL-PHENYLENE-DIAMINE.

PHENYLENE-DI-BENZIDENE-DIAMINE *v.* DI-BENZYLIDENE-PHENYLENE-DIAMINE.

PHENYLENE-BENZYL-*m*-DIAMINE $C_6H_4(NH_2).NHC_7H_7$. Formed by reducing benzyl-*m*-nitro-aniline (Meldola a. Coste, *C. J.* 55, 597). Oil.—$B''2HCl$: hexagonal tablets. $FeCl_3$ colours its solution red and gives a white pp. on heating.

Di-benzoyl derivative $C_6H_4(NHBz).NBz.C_7H_7$. [178°]. Sol. alcohol.

Phenylene-benzyl-*p*-diamine. [30°]. Got by reducing benzyl-*p*-nitro-aniline (Meldola a. Coste, *C. J.* 55, 590) or *p*-nitroso-benzyl-aniline (Boeddinghaus, *A.* 263, 302). Wax-like mass of crystals, turning red in air. When mixed with the *m*-isomeride it yields di-benzyl-amido-indamine on oxidation.—$B''2HCl$. White plates, v. sol. water. $FeCl_3$ colours its aqueous solution green, changing to red. After saturation with H_2S it gives a blue pp. with $FeCl_3$.

Di-acetyl derivative. [117°]. Prisms.

Di-benzoyl derivative. [124°]. Needles.

Phenylene-di-benzyl-diamine *v.* vol. i. p. 501.

Phenylene-tetra-benzyl-*m*-diamine $C_6H_4(N(C_7H_7)_2)_2$. [81°]. Formed by heating phenylene-*m*-diamine with NaOHAq and benzyl chloride. Amorphous powder, sol. HOAc.

Phenylene-tetra-benzyl-*p*-diamine. [149°]. White crystalline powder. HOAc and CrO_3 form a blue-violet colouring matter.

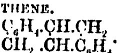
PHENYLENE - BENZYLIDENE - DI - METHYL-DIAMINE $C_{15}H_{16}N_2$ *i.e.* $C_6H_5.CH:N.C_6H_4.NMe_2$. [93°] (Calm, *B.* 17, 2940); [101°] (Köhler, *A.* 241, 361). Formed from phenylene-di-methyl-*p*-diamine and benzoic aldehyde.—$B''2HCl$.

PHENYLENE - BENZYL - DI - METHYL - DIAMINE $C_6H_5CH_2.NH.C_6H_4.NMe_2$. [48°]. Formed by reducing the preceding body in alcohol with sodium-amalgam (Köhler, *A.* 241, 361). Plates. Yields a nitrosamine [128°].

PHENYLENE-BLUE or *Lauth's violet* *v.* AMIDO-IMIDO-DI-PHENYL-SULPHIDE.

PHENYLENE - BROMO - ACETYLENE - KETONE *v.* BROMO-OXY-INDONAPHTHENE.

DI-PHENYLENE-BUTANE

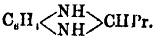


$\begin{array}{l}C_6H_4.CH.CH_2\\CH_2.CH.C_6H_4\end{array}$

Diphensuccindene. [100°]. Formed by heating (β)-di-phenyl-succinic anhydride with HI and P and 180° (Roser, *A.* 247, 156). White needles.

PHENYLENE-ISOBUTYL-*p*-DIAMINE $C_4H_9NH.C_6H_4.NH_2$. [39°]. Formed by reduction of *p*-nitroso-isobutyl-aniline (Wacker, *A.* 243, 299). Plates (from benzene-ligroïn).

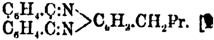
PHENYLENE - BUTYLIDENE - *o* - DIAMINE



$C_6H_4\!<\!\begin{array}{l}NH\\NH\end{array}\!>\!CHPr$. [233°]. Formed from phenylene-*o*-diamine and isobutyric aldehyde (Lassar-Cohn, *B.* 22, 2724). Needles (by sublimation).—B'HCl. [184°].—$B'_2H_2PtCl_6$.

The isomeric compound from phenylene-*m*-diamine melts at 216°, while that from phenylene-*p*-diamine is oily, and yields $B'_2H_2PtCl_6$.

DI - PHENYLENE - ISOBUTYL - QUINOXALINE



$\begin{array}{l}C_6H_4.C:N\\C_6H_4.C:N\end{array}\!>\!C_6H_3.CH_2Pr$. [147°]. Formed from phenanthraquinone in HOAc and isobutyl-phenylene-diamine in alcohol (Gelzer, *B.* 20, 3256). Yellowish needles.—B'HCl: needles.

***o*-PHENYLENE-DICARBAMIC ETHER** $C_6H_4(NH.CO_2Et)_2$. [88°]. Formed by heating o-phenylene-diamine with $ClCO_2Et$ (Snape, *C. J.* 49, 259). Needles (from alcohol).

***m*-Phenylene-dicarbamic ether.** [145°].

***p*-Phenylene-dicarbamic ether.** [193°]. Got *by heating p-phenylene dicyanate with alcohol* (Gattermann a. Wrampelmeyer, *B.* 18, 2605).

Di-phenylene-dicarbamic acid. *Ethyl ether* $CO_2Et.NH.C_6H_4.C_6H_4.NH.CO_2Et$. [230°]. Formed from benzidine and $ClCO_2Et$ or by boiling diphenylene dicyanate with alcohol (Snape, *C. J.* 49, 256; Schiff a. Vanni, *A.* 258, 369).

Di-phenyl ether. [c. 240°]. Made by heating diphenylene dicyanate with phenol at 140° (Snape). Tables, sl. sol. alcohol.

DI-PHENYLENE CARBINOL $C_{13}H_{10}O$ *i.e.*

$\substack{C_6H_4\\C_6H_4}{>}CH.OH$. *Fluorene alcohol.* [153°]. Formed by reducing diphenylene ketone with sodium-amalgam (Barbier, *A. Ch.* [5] 7, 504). Hexagonal plates (from benzene). Oxidised by CrO_3 to diphenylene ketone. Ac_2O at 100° forms an acetyl derivative [75°]. When heated above its melting-point, diphenylene carbinol yields $C_{26}H_{18}O$ [290°], a nearly colourless resin.

***o*-PHENYLENE CARBONATE** $C_6H_4CO_3$. [118°]. (225°–230°). Formed from sodium pyrocatechin and $ClCO_2Et$ (Wallach, *A.* 226, 84). Four-sided prisms (from alcohol-benzene).

***m*-Phenylene carbonate**

$C_6H_4{<}\substack{O\\O}{>}CO$. Formed by heating resorcin with cyanuric acid and $ZnCl_2$, and also by the action of $COCl_2$ on resorcin (Birnbaum, *B.* 14, 1753). Amorphous solid, sol. HOAc.

***m*-PHENYLENE DICARBONIC ETHER** $C_6H_4(O.CO_2Et)_2$. (298°–302°). Formed from sodium resorcin and $ClCO_2Et$ in ether (Wallach, *A.* 226, 84). The *p*-isomeride, [100°], (310°), is got in like manner from hydroquinone (Bender, *B.* 13, 697).

PHENYLENE-CHLORO-OXY-ACETYLENE KETONE *v.* Chloro-di-oxy-indonaphthene.

PHENYLENE-CINNAMYLIDENE-DI-METHYL-DI-AMINE $C_{17}H_{18}N_2$ *i.e.* $C_6H_5.CH:CH.CH:N.C_6H_4.NMe_2$. [141°]. Formed from cinnamic aldehyde and phenylene-di-methyl-*p*-diamine (Nuth, *B.* 18, 575). Needles.

PHENYLENE-CUMINYLIDENE-DI-METHYL-DIAMINE $C_{18}H_{22}N_2$ *i.e.* $C_3H_7.C_6H_4.CH:N.C_6H_4.NMe_2$. [100°]. Formed from cuminol and phenylene-di-methyl-diamine (Nuth, *B.* 18, 575; Uebel, *A.* 245, 299). Needles.

***m*-PHENYLENE DICYANATE** $C_6H_4(N:CO)_2$. [51°]. Got by distilling *m*-phenylene-dicarbamic ether (Bender, *Bn.* 3, 897). Crystals.

***p*-PHENYLENE DI-CYANATE** $C_6H_4(N:C:O)_2$. [91°]. (231° at 745 mm. i.V.). V.D. 5·79 (for 5·54). Prepared by passing a stream of carbonyl chloride $COCl_2$ through *p*-phenylene-diamine hydrochloride heated to 200°–250° (Gattermann a. Wrampelmeyer, *B.* 18, 2604). Colourless needles. Sublimable. Pungent vapour. Reacts like phenyl-cyanate, forming di-ureas with amines, and di-carbamic ethers with alcohols.

PHENYLENE DI-CYANIDE *v.* *Nitrile of* Phthalic acid.

PHENYLENE ETHYL-ACETAMIDINE

$C_6H_4{<}\substack{NEt\\N}{>}C.CH_3$. [180°]. Formed by the action of Ac_2O on phenylene-ethyl-*o*-diamine (Hempel, *J. pr.* [2] 39, 200; 41, 166). Plates.

PHENYLENE-ETHYL-*o*-DIAMINE $C_6H_4(NH_2)(NHEt)$. (249°). Formed by reducing *o*-nitro-ethylaniline with tin and HCl (Hempel, *J. pr.* [2] 39, 199; 41, 164). *Oil, turning red in air and light.*

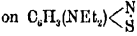
Acetyl derivative $C_6H_8N_2EtAc$. [104°].

Phenylene-ethyl-*m*-diamine $C_6H_4(NH_2)(NHEt)$. (276° uncor.). Oil, formed in like manner (Nölting a. Stricker, *B.* 19, 546). $B''H_2Cl_2$: white powder.

Phenylene-ethyl-*p*-diamine. (270°). Oil, sol. benzene (Nölting a. Collin, *B.* 17, 267; Schweizer, *B.* 19, 149; Fischer a. Hepp, *B.* 19, 2994; Bernthsen a. Goske, *B.* 20, 930).—$B''H_2SO_4$: needles or prisms.—$B''H_2Cl_2$. Plates, v. sol. water.—$B''H_2PtCl_6$.

Phenylene-di-ethyl-*m*-diamine $C_6H_4(NH_2)(NEt_2)$. (277°). Formed by reducing *m*-nitro-di-ethyl-aniline (N. a. S.; Groll, *B.* 19, 200). Oil.

Phenylene-di-ethyl-*p*-diamine. (261° uncor.). Formed by reducing nitroso-diethyl aniline or $C_6H_4(NEt_2).N_2.C_6H_4.NEt_2$ (Lippmann a. Fleissner, *B.* 16, 1424). Oil.—$B'H_2Cl_2PtCl_4$. Red crystals.—$B''ZnCl_2$ 2aq. Converted by treatment in aqueous solution with aluminium sulphate, $Na_2S_2O_3$, and $K_2Cr_2O_7$ into $NEt_2.C_6H_3(NH_2).S.SO_3H$ [229°], whence by diazo-



tisation $C_6H_3(NEt_2){<}\substack{N_2\\S}$ [107°] may be got (Bernthsen, *A.* 251, 1).

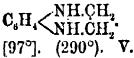
Phenylene-*s*-di-ethyl-*p*-diamine. *Nitrosamine* $C_6H_4(NEt.NO)_2$. [90°]. Formed from *p* phenylene-diamine by successive treatment with EtBr and HNO_2 (Nietzki, *B.* 16, 465). Yellowish plates (from benzene-ligroïn).

Phenylene-tetra-ethyl-*p*-diamine $C_6H_4(NEt_2)_2$. [52°]. (280° uncor.). Got by heating phenylene-di-ethyl-diamine or $N_2(C_6H_4.NEt_2)_2$ with EtI (Lippmann a. Fleissner, *B.* 16, 1427; *M.* 4, 301). Monoclinic plates (from dilute alcohol), $a:b:c = \cdot99:1:1\cdot833$; $\beta = 90°\ 30'$.—$B''H_2PtCl_6$.—$B''H_2Hg_4Cl_6$. Monoclinic prisms.—B''_2I_6: black prisms.—$B''2HI$.—$B''HI_3$.

PHENYLENE-ETHYL-BENZAMIDINE

$C_6H_4{<}\substack{NEt\\N}{>}CPh$. [81°]. Got by ethylation of phenylene-benzamidine (Howe, *Am.* 5, 421).—$B'HCl$ 3aq.—$B'_2H_2PtCl_6$.—$B'HNO_3$ aq [155°].—$B'EtOH$ [136°].—$B'EtI$ aq.—$B'EtCl$ 2aq.—$B'_2Et_2PtCl_6$. $B'EtHSO_4$ aq.

PHENYLENE-ETHYLENE-*o*-DIAMINE



$C_6H_4{<}\substack{NH.CH_2\\NH.CH_2}$. *Quinoxaline tetrahydride.* [97°]. (290°). V.D. 4·44 (calc. 4·64). Formed by heating pyrocatechin with ethylene-diamine hydrate at 200°–210° (Merz a. Ris, *B.* 20, 1191). Formed also by reducing quinoxaline with alcohol and Na. Plates (from water). $FeCl_3$ colours its dilute aqueous solutions blue or violet. Alkaline K_3FeCy_6 oxidises it to quinoxaline.—B''_23HCl. [above 150°]. Scales.—$B''_2H_2C_2O_4$. [184°].—$B''_32C_6H_3N_3O_7$. [above 120°]. Yellow crystalline pp., sl. sol. ether.

Acetyl derivative $C_6H_4:N_2Ac_2:C_2H_4$. [144°]. [350° uncor.). Granules, sl. sol. cold water.

Di-phenylene-ethylene-tetramine *v.* vol. ii. p. 491.

PHENYLENE-ETHYLENE-DISULPHONE $C_6H_4(SO_2)_2C_2H_4$. Formed by heating ethylene bromide with potassium benzene *m*-disulphinate

(Otto, *J. pr.* [2] 36, 450). White plates, m. sol. conc. HNO_3.

PHENYLENE DI-ETHYL DIKETONE $C_6H_4(CO.C_2H_5)_2$. [220°]. Formed from terephthalic chloride and $ZnEt_2$ in ether (Münchmeyer, *B.* 19, 1850). Needles (from ether).

PHENYLENE DI-ETHYL DISULPHONE $C_6H_4(SO_2Et)_2$. [142°]. Obtained by heating $C_6H_4(SO_2K)_2$ [1:4] with EtBr at 100° (Otto, *J. pr.* [2] 36, 449). Colourless plates.

PHENYLENE-FURFURALDEHYDINE *v.* vol. i. p. 109.

PHENYLENE-DIGLYCOLLIC ACID *v.* OXY-DIPHENYLENE-ACETIC ACID.

DIPHENYLENE-DIHYDRAZINE $C_{12}H_{14}N_4$ *i.e.* $N_2H_3.C_6H_4.C_6H_4.N_2H_3$. [167°]. Formed from benzidine hydrochloride by diazotisation and reduction by Na_2SO_3 or $SnCl_2$ (Arheidt, *A.* 239, 206). Small white plates, sol. hot water. Aqueous potassium cyanate forms the semicarbazide $C_{14}H_{16}N_6O_2$ [307°]. Nitrous acid forms a di-nitrosamine $C_{12}H_{12}N_4O_2$ [112°]. Pyruvic acid forms $C_{18}H_{14}N_4O_4$ [197°]. Acetone yields $C_{18}H_{22}N_4$ [198°], whence fusion with $ZnCl_2$ yields di-phenyl-di-methyl-indole $C_{18}H_{16}N_2$ [270°].

Reference.—DI-OXY-DI-PHENYLENE DIHYDRAZINE.

DIPHENYLENE-IMIDE *v.* CARBAZOLE.

DIPHENYLENE KETONE $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!CO$. [83°]. (above 300°).

Formation.—1. By distilling phenanthraquinone or diphenyl di-*o*-carboxylic acid with CaO (Fittig a. Ostermayer, *A.* 166, 373; Anschütz a. Schultz, *B.* 9, 1400).—2. By heating anthraquinone with lime (Anschütz, *B.* 11, 1213).—3. By dry distillation of the Ag salt of its dicarboxylic acid (Bamberger a. Hooker, *B.* 18, 1034; *A.* 229, 156).—4. By passing a mixture of phenol and CS_2 over hot copper (Carnelley a. Dunn, *C. J. Proc.* 4, 53; *B.* 21, 2005, who regard the product thus obtained as isomeride).

Properties.—Yellow needles or plates (from alcohol). Yields phenyl-benzoic acid by potash-fusion. Distillation over zinc-dust gives diphenylene-methane [113°] (Fittig, *B.* 6, 187). Forms a nitro- derivative [220°] and a di-nitro-derivative [290°] (Schultz, *A.* 203, 104). Alkaline $KMnO_4$ oxidises it to phthalic acid (Anschütz a. Japp, *B.* 11, 213). H_2SO_4 forms at 260° a disulphonic acid, whence CaA″ (Schmidt a. Schultz, *A.* 207, 345).

Oxim. [192°] (Spiegler, *M.* 5, 195).

References.—BROMO-, DI-CHLORO-, NITRO-, and OXY- DIPHENYLENE KETONE.

DIPHENYLENE KETONE CARBOXYLIC ACID [1:2] $C_6H_4\!<\!\overset{CO}{\underset{—}{}}\!>\!C_6H_3.CO_2H\left[\begin{smallmatrix}1\\2\end{smallmatrix}6\right]$. [192°]. Formed by oxidation of fluoranthene by chromic acid mixture (Fittig, *A.* 193, 149; 200, 6). Orange-red needles (from dilute alcohol).

Reactions.—1. *Potash-fusion* gives diphenyl *om*-dicarboxylic acid.—2. Yields diphenylene ketone on distillation.—3. Distillation with *zinc-dust* gives diphenylene-methane (fluorene).

Salts.—BaA'_2 4aq.—CaA'_2 2aq.—AgA′.

Diphenylene ketone carboxylic acid. [above 275°]. Formed by heating the dicarboxylic acid (Bamberger a. Hooker, *B.* 18, 1034; *A.* 229, 158). Pale yellow needles, sl. sol. alcohol. May be sublimed.—BaA'_2.—AgA′: yellow pp.

Diphenylene ketone carboxylic acid [1:2] $C_6H_4\!<\!\overset{CO}{\underset{—}{}}\!>\!C_6H_3.CO_2H\left[\begin{smallmatrix}1\\2\end{smallmatrix}3\right]$. [227° cor.].

Formation (Graebe, *B.* 13, 1303; *B.* 20 845; *A.* 247, 275).—1. From diphenyl di-*o*-carboxylic acid by heating with H_2SO_4 at 120° or with $POCl_3$ or $ZnCl_2$.—2. By heating diphenylene dicarboxylic acid with H_2SO_4 for 10 minutes at 150°.

Properties.—Yellow needles, v. sol. hot alcohol. Conc. H_2SO_4 forms a red solution.

Reactions.—1. *Potash-fusion* yields diphenyl di-*o*-carboxylic acid.—2. PCl_5 (1 mol.) forms $\begin{matrix}C_6H_4\\C_6H_3(COCl)\end{matrix}\!>\!CO$ [128°], which may be crystallised from ligroïn.—3. PCl_5 (2 pts.) at 160° yields $\begin{matrix}C_6H_4\\C_6H_3(COCl)\end{matrix}\!>\!CCl_2$ [95°], which yields fluorene carboxylic acid on reduction with zinc-dust and dilute acetic acid.—4. *Zinc-dust* and *ammonia* reduce it to $\begin{matrix}C_6H_4\\C_6H_3(CO_2H)\end{matrix}\!>\!CH(OH)$.—5. HI and P give fluorene.—6. *Phenol* and $SnCl_4$ at 120° give $\begin{matrix}C_6H_4\\C_6H_3(CO_2H)\end{matrix}\!>\!C(C_6H_4.OH)_2$ [165°], which yields AgA′ and $C_{26}H_{16}Ac_2O_4$ [c. 130°].—7. *Resorcin* gives rise, on heating, to $\begin{matrix}C_6H_4\\C_6H_3(CO_2H)\end{matrix}\!>\!C(C_6H_3(OH)_2)_2$, a yellowish-brown powder which exhibits green fluorescence in alkaline solutions.

Salts. — NH_4A' aq. — NaA′ 6aq: yellow needles, v. sol. hot water.—AgA′: yellow pp.

Methyl ether MeA′. [132°]. Needles.

Ethyl ether EtA′. [103°]. Needles.

Chloride $C_{14}H_7ClO_2$. [128°].

Amide $C_{14}H_7(NH_2)O_2$. [225°]. Silky yellow needles (containing ½HOEt). Formed from the chloride, and also by heating phenanthraquinone mono-oxim with H_2SO_4 at 100° (Wegerhoff, *B.* 21, 2357).

Oxim $C_{14}H_7(CO_2H)(C:NOH)$. [263°].

Phenyl-hydrazide $C_{14}H_7(CO_2H)(C:N_2HPh)$. [205°]. Brownish-yellow prisms, m. sol. alcohol.

Diphenylene ketone dicarboxylic acid $C_6H_4\!<\!\overset{CO}{\underset{—}{}}\!>\!C_6H_2(CO_2H)_2\left[\begin{smallmatrix}1\\2\end{smallmatrix}3:6\right]$. Formed by oxidation of retene-quinone and of oxyisopropyl-diphenylene-ketone carboxylic acid (Bamberger a. Hooker, *B.* 18, 1033; *A.* 229, 151). Yellow needles (from HOAc). Not melted at 270°, but loses CO_2 at a higher temperature. Yields diphenyl on heating with CaO. Potash-fusion forms diphenyl tricarboxylic acid.—BaA″.—Ag_2A'': yellow pp.

Methyl ether Me_2A''. [184°]. Yellow needles.

Ethyl ether EtA″. [115°]. Needles.

Oxim $C_{12}H_6(CO_2H)_2{:}C(NOH)$. Yellow pp., not melted at 280°.

DIPHENYLENE KETONE OXIDE $CO\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!O$. *Xanthone.* [174°]. (350°) at 730 mm. (Graebe, *A.* 254, 280). S. (alcohol) ·7 in the cold; 8·5 at 78°.

Formation.—1. Obtained by oxidation of $CH_2\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!O$ with CrO_3 and HOAc (Merz a.

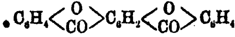
Weith, *B.* 14, 192).—2. By the dry distillation of salicylide; the yield being 35 p.c. of the theoretical (Perkin, *B.* 16, 339).—3. By distilling phenyl phosphate with sodium *m*- or *p*-oxy-benzoate (Richter).—4. By the action of $POCl_3$ on potassium-salicylate of ethyl.—5. By distilling neutral or basic sodium salicylate with P_2O_5.—6. In small quantities, when salicylic acid is distilled.—7. By strongly heating sodium *o*-chlorobenzoate.—8. From sodium *o*-phenyl-benzoate and $POCl_3$.—9. To the amount of 12 p.c. of the theoretical quantity, by the action of *o*-chlorobenzoyl chloride on basic sodium salicylate.—10. By the action of conc. H_2SO_4 on [1:2] $C_6H_4(OPh).CO_2H$ (Graebe, *B.* 21, 503).—11. By distilling phenyl salicylate (Seiffert, *J. pr.* [2] 31, 479).—12. By heating salicylic acid (1 mol.) with PCl_5 (1 mol.), then adding phenol and distilling (Klepl, *J. pr.* [2] 28, 217.—13. By distilling calcium *p*-oxy-benzoate (Goldschmidt, *M.* 4, 128).—14. A product of the electrolysis of a solution of phenol in KOHAq at 200° (Bamberger a. Berlé, *B.* 24, 3212).

Preparation.—1. Phenyl phosphate (20 g.) and sodic salicylate (20 g.) are distilled together; a violent action ensues; when it is over the residue is distilled over at 400°, best in a current of air. The crude product is shaken with solution of NaOH and distilled with steam. The residue is extracted with alcohol, from which, on cooling, the ketone crystallises (R. Richter, *J. pr.* [2] 28, 276).—2. By distilling salicylic acid with Ac_2O, the salicylide which is first formed splitting off CO_2 when the temperature rises (Perkin, *C. J.* 43, 35). In this process there is formed a by-product $C_{14}H_8O_3$ [192°] which is converted by boiling alcoholic potash into an acid $C_{14}H_8O_4$ [275°] (A. G. Perkin, *C. J.* 43, 187).

Properties.—Long white needles, grouped concentrically. M. sol. ether, alcohol and benzoline, more sol. benzene and chloroform, insol. water. The solution in conc. H_2SO_4 shows blue fluorescence (Graebe, *B.* 15, 1679). Does not react with hydroxylamine or phenyl-hydrazine (Spiegler, *B.* 17, 808).

Reactions.—1. Reduced by *zinc*-dust or by HI to $CH_2{<}\substack{C_6H_4\\C_6H_4}{>}O$ [100·5°] but no further.—2. *Potash-fusion* converts it into salicylic acid and phenol.—3. If the fusion be stopped when the mass is pasty (at about 200°), dissolved in water and ppd. by HCl, di-oxy-benzophenone is obtained, $CO(C_6H_4OH)_2$.—4. *Sodium-amalgam* reduces the di-phenylene-ketone oxide (in dilute alcoholic solution) to $C_{26}H_{18}O_3$ [200°]. This body crystallises from $CHCl_3$ in prisms. It is split up by chromic acid into di-phenylene-ketone oxide and diphenylene methane oxide, so that it is perhaps a molecular compound of these two bodies.—5. *Bromine* at 200° forms a di-bromo- derivative [212°].—6. Fuming H_2SO_4 gives a disulphonic acid which forms BaA″ aq, crystallising from hot water in needles (A. G. Perkin, *C. J.* 43, 192).

Isomeride $C_{13}H_8O_2$. [91°] (R.); [96°] (G.). A product of the action of $POCl_3$ on sodium salicylate (Richter, *J. pr.* [2] 28, 294). Formed also by heating the sulphate of *o*-diazobenzoic acid with phenol (Griess, *B.* 21, 981). Needles, v. e. sol. ether. Yields diphenyl on distillation with zinc-dust. Br gives $C_{13}H_7BrO_2$ [193°]. H_2SO_4 yields a disulphonic acid, which gives BaA″aq crystallising in needles.

Dixanthone  $C_6H_4{<}\substack{O\\CO}{>}C_6H_2{<}\substack{O\\CO}{>}C_6H_4$. [256°]. Occurs in the product of the action of salicylic acid on resorcin (Kostanecki a. Seidmann, *B.* 25, 1654). It crystallises from HOAc in groups of needles, and its solution in H_2SO_4 shows greenish fluorescence.

References. — Di-amido-, Nitro-, and Oxy-diphenylene ketone oxide.

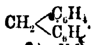
PHENYLENE MERCAPTAN *v.* Di-thio-resorcin and Di-thio-hydroquinone.

Diphenylene mercaptan $C_6H_4(SH).C_6H_4(SH)$. [176°]. Formed by diazotising benzidine, and treating the product with potassium xanthate and alcoholic potash successively (Leuckart, *J. pr.* [2] 41, 212; *cf.* Gabriel, *B.* 13, 390). White plates (from alcohol).

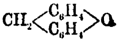
Di-methyl ether Me_2A''. [184°]. Plates.

Di-ethyl ether Et_2A''. [135°]. Plates.

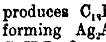
oo-**DIPHENYLENE-METHANE** *v.* Fluorene.

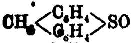
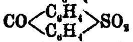
(γ) - Diphenylene - methane  $CH_2{<}\substack{C_6H_4\\C_6H_4}$. *Methylene-diphenyl.* [118°]. (295° uncor.). V.D. 84 (calc. 83). Occurs, together with the (δ)-isomeride, among the products of the passage of a mixture of benzene and toluene through a red-hot tube (Carnelley, *C. J.* 37, 708). Pearly plates (from alcohol), sl. sol. cold alcohol, v. sol. ether. Its alcoholic solution shows faint blue fluorescence. CrO_3 and HOAc oxidise it to $C_{13}H_8O_2$ [281° cor.]. Bromine in ether gives $C_{13}H_8Br_2$ [162°]. Picric acid forms a compound $C_{13}H_{10}C_6H_3N_3O_7$ crystallising in blood-red needles [81°].

(δ)-Diphenylene-methane $C_{13}H_{10}$. [205°]. (320°). V.D. 86·2 (calc. 83). Formed as above. Pearly plates (from alcohol). Oxidised by CrO_3 in HOAc to $C_{13}H_8O_2$ [288° cor.] which sublimes in white needles.

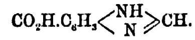
DIPHENYLENE-METHANE OXIDE  $CH_2{<}\substack{C_6H_4\\C_6H_4}{>}O$. [100°]. (315° cor.). Formed, to the amount of 2 p.c., in the preparation of Ph_2O by heating phenol with $AlCl_3$ (Merz a. Weith, *B.* 14, 191). Formed also from diphenylene ketone oxide by heating with fuming HIAq at 160° or by distilling with zinc-dust (R. Richter, *J. pr.* [2] 28, 280; Graebe, *A.* 254, 282); and by distilling euxanthone over heated zinc-dust (Wichelhaus a. Salzmann, *B.* 10, 1399; Graebe a. Ebrard, *B.* 15, 1678). White plates (from alcohol).

Reactions.—1. Oxidised by CrO_3 or dilute HNO_3 to diphenylene ketone oxide.—2. PCl_5 forms HCl and a product whence water at 0° produces $C_{13}H_9O.PO(OH)_2$ [255°-260°] an acid forming Ag_2A'' and $(NH_4)_2A''$.—3. Br forms $C_{13}H_4Br_6O$ and $C_{13}H_3Br_7O$ [136°].

DIPHENYLENE - METHANE SULPHIDE  $CH_2{<}\substack{C_6H_4\\C_6H_4}{>}S$. [128°]. (342°). Formed by reducing $CO{<}\substack{C_6H_4\\C_6H_4}{>}S$ with HI and P at 170°; and also by passing phenyltolyl sulphide through a red-hot tube (Graebe a. Schultess, *A.* 263, 12). Needles, sl. sol. cold alcohol, v. e. sol. $CHCl_3$.

DIPHENYLENE - METHANE SULPHONE  $CH_2{<}\substack{C_6H_4\\C_6H_4}{>}SO_2$. [170°]. Formed by heating  $CO{<}\substack{C_6H_4\\C_6H_4}{>}SO_2$ with HI and P at 170° (Graebe a. Schultess, *A.* 263, 15). Needles, v. sol. hot alcohol.

PHENYLENE-METHENYL-AMIDINE $C_6H_4{<}\substack{NH\\N}{\geqslant}CH$. [167°]. (above 360°). Formed by boiling phenylene-*o*-diamine with formic acid (Wundt, *B.* 11, 826; Fischer, *B.* 22, 645). Trimetric crystals (from alcohol).—B'HCl aq.—B'HAuCl$_4$. Yields on methylation $C_8H_8N_2$ [33°] (278° at 730 mm.).

Carboxylic acid  $CO_2H.C_6H_3{<}\substack{NH\\N}{\geqslant}CH$. Formed by reducing the formyl derivative of (2,1,4)-nitro-amido-benzoic acid (Zehra, *B.* 23, 3634). White needles, blackening without fusion when heated.—HA'HCl: white needles.

***m*-PHENYLENE - METHYL - DIAMINE** [1:3] $C_6H_4(NH_2).NHMe$. *Methyl-phenylene diamine. Amido-methyl-aniline* (265°-270° uncor.). Formed by reduction of *m*-nitro-methyl-aniline (Nölting a. Stricker, *B.* 19, 548). Oil. Gives a methyl-chrysoïdine with diazobenzene chloride.

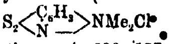
***p*-Phenylene-methyl-diamine** [1:4] $C_6H_4(NH_2)(NHMe)$. (258° uncor.). Formed by reduction of *p*-nitroso-methyl-aniline (Fischer, *B.* 19, 2992) or of $C_6H_4(NHMe).N_2.C_6H_4.SO_3H$ (Bernthsen a. Goske, *B.* 20, 929). Oil, v. sol. water. $FeCl_3$ gives a red colour, which on successive treatment with HCl and H_2S becomes blue (dimethylthionine).—$B'_2H_2SO_4$: white needles (from water).

***m*-Phenylene-di-methyl-diamine** [1:3] $C_6H_4(NH_2)(NMe_2)$. (269°) at 740 mm. S.G. ^{25} ·995 (Groll, *B.* 19, 200); (258°) (Staedel a. Bauer, *B.* 19, 1945). Formed by reduction of *m*-nitro-di-methyl-aniline. Oil. With nitrous acid it yields a colouring-matter closely resembling Bismarck brown. With diazobenzene chloride it yields a di-methyl-chrysoïdine which dies a somewhat redder shade than chrysoïdine. PbO_2 and aqueous HOAc gives a yellowish-brown colour (Lauth, *C. R.* 111, 975).—B'HCl.

Acetyl derivative $C_6H_4(NMe_2)(NHAc)$. [87°].

***p*-Phenylene-di-methyl-diamine** [1:4] $C_6H_4(NH_2)(NMe_2)$. [41°]. (257° i.V.). Prepared by reduction of nitroso-di-methyl aniline and of $(C_6H_4NMe_2)_2N_2O$ by tin and HCl (Schraube, *B.* 8, 616; Wurster, *B.* 12, 522; Weber, *B.* 10, 760). Prepared also by reduction of $C_6H_4(NMe_2).N_2.C_6H_4.SO_3H$ (E. Fischer, *B.* 16, 2255). Formed also together with di-chloro-*p*-phenylene-diamine and di-chloro-*p*-phenylene-di-methyl diamine by boiling nitroso-di-methyl-aniline with HCl (S.G. 1·2) (Möhlau, *B.* 19, 2010).

Properties.—Long white needles or short prisms, v. sol. water, alcohol, and ether. PbO_2 and aqueous HOAc give a magenta-red solution changing to violet-black (Lauth, *C. R.* 111, 975). Colours wood, and paper made from wood, crimson (Wurster, *B.* 20, 808).

Reactions.—1. Yields quinone on oxidation with MnO_2 and H_2SO_4.—2. *Bromine* in HOAc forms $C_8H_{11}N_2Br$, which crystallises from its red alcoholic solution in green scales [146°] (Wurster a. Sendtner, *B.* 12, 1803).—3. H_2S and an oxidising agent (*e.g.* $FeCl_3$) gives methylene-blue (*v.* vol. iii. p. 265). Methylene-red  $S_2{<}\substack{C_6H_3\\N\,—}{>}NMe_2Cl$ is a by-product (Bernthsen, *A.* 230, 137; 251, 1).—4. $Na_2S_2O_3$ and CrO_3 give $C_6H_3(NMe_2)(NH_2)S.SO_3H$, which yields methylene-blue on further oxidation.—5. *Aldehydes* and *ketones* form products of condensation, *e.g.* $C_6H_4(NMe_2).N{:}CHPh$ [93°] (Calm, *B.* 17, 2938), $C_6H_4(NMe_2).N{:}CH.C_6H_4OH$ [1:2] [134°], and $C_6H_4(NMe_2).N{:}CH.C_6H_4.OMe$ [1:4] [148°] (Nuth, *B.* 18, 574; Steinhart, *A.* 241, 343). Benzil and alcoholic KOH form $CPhBz{:}N.C_6H_4NMe_2$ [139°]; benzoyl-acetone forms in like manner $CH_2Bz.CMe{:}N.C_6H_4NMe_2$ [136°] (Vogtherr, *B.* 25, 635). Benzoïn gives $CHPh(OH).CPh{:}N.C_6H_4NMe_2$ [127°] on heating, while deoxybenzoïn forms $C_{22}H_{22}N_2$ [139°].—6. *Oxalic ether* forms, on heating, the ether $C_6H_4(NMe_2).NH.CO.CO_2Et$ [117°] which yields a corresponding acid [192°] and amide [259°] (Sendtner, *B.* 12, 530).

Salts.—B''2HCl. Very deliquescent plates.—$B''H_2SnCl_4$. Cubes.—$B''H_2PtCl_6$.

Acetyl derivative $C_6H_4(NMe_2)(NHAc)$. [130°]. (355°). Small leaflets or needles.

***p*-Phenylene-tri-methyl-diamine** [1:4] $C_6H_4(NMe_2)(NMeH)$. (265°). Obtained by reduction of its nitrosamine, which is formed by the action of nitrous acid on *p*-phenylene-tetra-methyl-diamine (Wurster a. Schobig, *B.* 12, 1809). Oil.

Acetyl derivative. [95°]. Prisms.

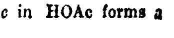
Nitrosamine $C_6H_4(NMe_2)(NMe.NO)$. [99°]. Leaflets or tables, sl. sol. cold water.

***m*-Phenylene-tetra-methyl-diamine** [1:3] $C_6H_4(NMe_2)_2$. [−2°]. (266° i.V.). S.G. ^{15} ·992. Prepared by heating phenylene-*m*-diamine with methyl alcohol and HCl at 190° (Wurster a. Morley, *B.* 12, 1814). Purified by distilling with Ac_2O (Romburgh, *R. T. C.* 7, 2). Oil, sl. sol. water. HOAc and nitric acid give $C_6H(NO_2)_3N_2Me_3NO$ [132°]. *s*-Tri-nitro-benzene forms $B''C_6H_3(NO_2)_3$ [121°]. *m*-Di-nitro-benzene gives $B''C_6H_4(NO_2)_2$ [58°] crystallising in needles. Bromine forms oily $C_{10}H_{14}Br_2N_2$. $NaNO_2$ and dilute HClAq give oily $C_6H_3(NO)(NMe_2)_2$, which forms a hydrochloride B'HCl, crystallising in dark-red needles (Witt, *B.* 18, 877).

Salts.—$B''H_2Cl_2$ 2aq: hygroscopic crystals.—$B''H_4FeCy_6$ aq. Pearly plates (Wurster a. Roser, *B.* 12, 1826).

Methyl iodide B''MeI. [192°]. Crystals, v. sol. water.—$B''MeHI_2$.

Di-methylo-di-iodide $B''Me_2I_2$. Plates, v. sol. water (Hofmann, *Pr.* 12, 639).

***p*-Phenylene-tetra-methyl-diamine** [1:4] $C_6H_4(NMe_2)_2$. [51°]. (260° i.V.). Prepared by heating *p*-phenylene-di-methyl-diamine with MeOH and HClAq at 200° (Wurster, *B.* 12, 526, 1803, 1827). White leaflets, sl. sol. cold water, v. sol. alcohol. Its aqueous solution becomes violet-blue on exposure to air or addition of oxidising agents. The blue substance appears only to exist as a salt, *e.g.*  $C_6H_4{<}\substack{NMe_2Cl\\NMe\,—}{>}CH_2$ (Wurster, *B.* 19, 3195; 20, 256; 21, 921). It becomes colourless on further oxidation.

Reactions.—1. *Bromine* in HOAc forms a blue colouring matter $C_{10}H_{14}N_2$, which forms blue solutions in water and alcohol.—2. K_3FeCy_6 added to a solution of the sulphate forms $C_{10}H_{14}N_2 2H_4FeCy_6$ crystallising in lustrous blue needles. — 3. Sodium nitrite and hydrochloric acid give $C_6H_4(NMe_2)(NMeNO)$ [98°] and *$C_6H_3(NO_2)(NMe_2).NMe.NO$ [87°].*

Salts.—B''2HCl; crystals.—B''H_2PtCl_6.—B''$2H_2SO_4$.—B''H_4FeCy_6: white needles.

Methylo-iodides B''MeI. [above 270°]. Leaflets (W.).—B''Me_2I_2. Plates (Hofmann).

Reference.—NITRO-PHENYLENE-DI-METHYL-DI-AMINE.

PHENYLENE - DI - METHYL - DI - AMINE SULPHONIC ACID $C_6H_3(NH_2)(NMe_2).SO_3H$. Got by reduction of *p*-nitro-di-methyl-amido-benzene sulphonic acid (Michler a. Walder, *B.* 14, 2176). Large rhombohedra, v. sol. water.—BaA'_2.—CaA'_2: plates.

***p*-PHENYLENE-DI-METHYL-DI-ETHYL-DIAMINE** $C_6H_4(NMe_2)(NEt_2)$. (264°). Formed from [1:4] $C_6H_4(NEt_2)(NH_2)$, MeOH, and HClAq at 200° (Lippmann a. Fleissner, *M.* 4, 791). Liquid. Coloured blue by oxidising agents.

Methylo-iodide B''2MeI. [218°]. Yields B''Me_2PtCl_6, B''Me_2AuCl_8, B''Me_2CdI_4, and B''$Me_2(C_6H_2N_3O_7)_2$ [235°].

***o*-PHENYLENE - METHYL - ETHYLENE - DIAMINE** $C_6H_4{<}\begin{matrix}NMe\\NH\end{matrix}{>}C_2H_4$. *v-Methyl-quinoxaline tetrahydride.* (274°). Formed by heating phenylene-ethylene-diamine with MeI at 110° (Ris, *B.* 21, 381). Liquid. Its aqueous solution is coloured blue by $FeCl_3$.

Methylo-iodide B'MeI. [above 200°]. Crystals.—$B'_2Me_2PtCl_6$. Yellow needles.

DIPHENYLENE - METHYL - FURFURANE $\begin{matrix}C_6H_4.C—CH\\C_6H_4.C.O.CMe\end{matrix}$. [124°]. Got by reducing $\begin{matrix}C_6H_4.C(OH).CH_2Ac\\C_6H_4.CO\end{matrix}$ (Japp a. Klingemann, *B.* 21, 2932).

PHENYLENE-DI-METHYL-DI-MALONIC ACIDS $C_6H_4(CH_2.CH(CO_2H)_2)_2$. The ethers of these acids are formed by the action of zinc-dust on the acids $C_6H_4(CH_2.CCl(CO_2Et)_2)_2$ which are formed from sodium chloro-malonic ether and ω-di-bromo-xylenes (Perkin a. Kipping, *C. J.* 53, 16; *B.* 19, 437; 21, 36). The *o*- and *m*- ethers are oily, the *p*- ether is crystalline [51°]. The ethers form deliquescent sodium derivatives $Na_2C_{22}H_{28}O_8$, and the *o*- compound of this formula is converted by iodine into the tetrahydride of naphthalene tetracarboxylic ether. The *m*- acid is a liquid v. sol. water, the *p*- acid is crystalline [195°]. The *p*- acid forms Ag_4A'', and when heated splits up into CO_2 and $C_6H_4(CH_2.CH_2.CO_2H)_2$ [223°].

PHENYLENE - METHYL - METHENYL - AMIDINE $C_6H_4{<}\begin{matrix}NMe\\N\end{matrix}{\gg}CH$. [33°]. (278°) at 780 mm. Formed from phenylene-methenyl-amidine, MeI, and MeOH at 100° (O. Fischer, *B.* 22, 644). Prisms.—B'$HAuCl_4$. Needles.

DIPHENYLENE-METHYL-PYRAZINE $\begin{matrix}C_6H_4.C.N:CMe\\C_6H_4.C.N:CH\end{matrix}$. [128°]. Formed from phenanthraquinone and propylene-diamine (Strache, *B.* 21, 2362). White needles.—$B'_2H_2PtCl_6$.

***v-p*-DIPHENYLENE-TETRA-METHYL-DI-PYRROLE** $C_{24}H_{24}N_2$ *i.e.* $\begin{matrix}CH:CMe\\CH:CMe\end{matrix}{>}N.C_6H_4.C_6H_4.N{<}\begin{matrix}CMe:CH\\CMe:CH\end{matrix}$. [150°]. Got by heating an alcoholic solution of acetonyl-acetone (2 mols.) and benzidine (1 mol.) (Paal a. Schneider, *B.* 19, 3158). Colourless tables. *Sol. alcohol, ether, benzene, and ligroïn.*

DIPHENYLENE-METHYL-QUINOXALINE $C_{21}H_{14}N_2$ *i.e.* $C_6H_3Me{<}\begin{matrix}N:C.C_6H_4\\N:C.C_6H_4\end{matrix}$. [213°]. Formed from (1,3,4)-tolylene-diamine and phenanthraquinone in HOAc (Hinsberg, *B.* 17, 323). Yellow hair-like crystals, v. sol. benzene.

DIPHENYLENE - NAPHTHOQUINOXALINE $C_{10}H_6{<}\begin{matrix}N:C.C_6H_4\\N:C.C_6H_4\end{matrix}$. [273°]. Formed by boiling an alcoholic solution of (1,2)-naphthylene-diamine with phenanthraquinone in HOAc (Lawson, *B.* 18, 2426). Small yellow crystals.

The **sulphonic acid**, got by mixing a hot aqueous solution of naphthylene-*o*-diamine sulphonic acid with phenanthraquinone dissolved in $NaHSO_3Aq$ with addition of NaOAc, forms a yellow crystalline Na salt, sol. hot water, but ppd. by alkalis (Witt, *B.* 19, 1719, 2791). When fused with KOH it yields the insoluble eurhodol $C_{12}H_8{<}\begin{matrix}N\\N\end{matrix}{>}C_{10}H_5(OH)\left[\begin{matrix}1&4\\2&\end{matrix}\right]$, which forms a scarlet hydrochloride.

***m* - PHENYLENE - DI - (β) - NAPHTHYL - DIAMINE** $C_6H_4(NHC_{10}H_7)_2$. [126°]. Formed by heating *m*-phenylene-diamine with (β)-naphthol (Ruhemann, *B.* 14, 2654). Felted needles, sol. alcohol and ether.

***p*-Phenylene-di-(β)-naphthyl-diamine** $C_6H_4(NHC_{10}H_7)_2$. [235°]. (over 400° *in vacuo*). Formed by heating *p*-phenylene-diamine with (β)-naphthol at 200° (Ruell, *B.* 22, 1080). White plates, almost insol. boiling alcohol, v. sol. nitro-benzene. KNO_2 added to its solution in conc. H_2SO_4 gives a greenish-violet colour, changing to blue.—$B'2C_6H_3N_3O_7$. [c. 217°].

Acetyl derivative $C_6H_4(NAc.C_{10}H_7)_2$. [210°]. Plates (from benzene).

Benzoyl derivative $C_{26}H_{18}Bz_2N_2$. [220°].

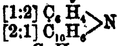
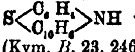
Reference.—NITRO-PHENYLENE-NAPHTHYL-DI-AMINE.

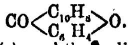
PHENYLENE - NAPHTHYLENE - AMINE $C_{16}H_{11}N$ *i.e.* $\begin{matrix}[1:2]\ C_6H_4\\ [2:3]\ C_{10}H_6\end{matrix}{>}NH$. *Phenyl-naphthyl-carbazole.* [330°]. (454°) (Schweizer, *A.* 264, 195). S. (alcohol) ·25 at 78°; S. (toluene) ·5 at 111° (Bechi, *B.* 12, 1978). Occurs in crude anthracene, from which it may be got from the residues after sublimation of the anthracene (Graebe a. Knecht, *B.* 12, 341, 2242; *A.* 202, 1). Formed by passing phenyl-(β)-naphthyl-amine through a red-hot tube. Colourless plates, v. sl. sol. HOAc. Its solutions show blue fluorescence. Oxidation by $K_2Cr_2O_7$ and H_2SO_4 forms the quinone $\begin{matrix}C_6H_4—\\C_{10}H_4O_2\end{matrix}{>}NH$ [307°] which crystallises from HOAc in reddish-yellow needles, and is accompanied by $\begin{matrix}C_6H_4—\\C_{10}H_4O_2\end{matrix}{>}O$ which crystallises from benzene in red prisms.

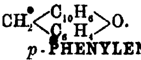
Acetyl derivative $C_{18}H_{13}NO$. [121°].

Nitrosamine $C_{16}H_{10}N_2O$. [210°].

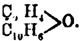
Tetrahydride $C_{16}H_{15}N$. Formed by reduction with HIAq and P at 210°. Syrup.—B'HI. Long needles.

Phenylene-naphthylene-amine

$\begin{matrix}[1{:}2]\,C_6H_4\\ [2{:}1]\,C_{10}H_6\end{matrix}\!\!>NH$. [225°]. Formed by heating

$S\!\!<\!\!\begin{matrix}C_6H_4\\ C_{10}H_6\end{matrix}\!\!>NH$ with reduced copper at 240° (Kym, *B.* 23, 2465). Greenish-yellow plates, sl. sol. cold benzene, v. sol. hot alcohol.

PHENYLENE - NAPHTHYLENE - KETONE OXIDE

$CO\!\!<\!\!\begin{matrix}C_{10}H_5\\ C_6H_4\end{matrix}\!\!>O$. [155°]. Formed by boiling (*a*)-naphthyl salicylate (Graebe a. Feer, *B.* 19, 2612). Formed also by heating (*a*)-naphthol with salicylic acid and HOAc; and by distilling (1,2)-(*a*)-naphthol carboxylic acid with salicylic acid (Kostanecki, *B.* 25, 1643). Crystals, sl. sol. cold alcohol. Its solution in H_2SO_4 shows green fluorescence. Converted by potash-fusion into *o*-(*a*)-di-oxy-phenyl-naphthyl-ketone (Phomina, *A.* 257, 92).

Isomeride. [140°]. Formed in like manner from (*β*)-naphthyl salicylate; and by heating (2,1)-(*β*)-naphthol carboxylic acid with salicylic acid. Needles. Reduced by zinc-dust to

$CH_2\!\!<\!\!\begin{matrix}C_{10}H_6\\ C_6H_4\end{matrix}\!\!>O$. [80°].

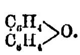
p-**PHENYLENE-DI-(β)-NAPHTHYL-DI-METHYL-DIAMINE** $C_6H_4(NMe.C_{10}H_7)_2$. [180°]. Formed from $C_6H_4(NHC_{10}H_7)_2$, MeI, and MeOH at 140° (Rueff, *B.* 22, 1080). Plates.

PHENYLENE - NAPHTHYLENE OXIDE

$\begin{matrix}C_6H_4\\ C_{10}H_6\end{matrix}\!\!>O$. [178°]. Formed by distilling a mixture of phenol and (*a*)-naphthol with PbO (Arx, *B.* 13, 1726; *A.* 209, 141). Yellow needles, sl. sol. alcohol. H_2SO_4 forms a tetrasulphonic acid which gives $Ba_2C_{16}H_6S_4O_{13}$ 4aq. CrO_3 and HOAc form $C_{16}H_8O_3$ [140°].—$C_{16}H_{10}O2C_6H_3N_3O_7$. [165°].

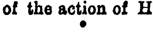
Isomeride $C_{16}H_{10}O$. [296°] (A.); [300°] (G. a. K.). Formed in like manner from (*β*)-naphthol (A.). Got also by distilling the compound $C_{16}H_8O_3$ (from phenylene-naphthylene-amine) with zinc-dust (Graebe a. Knecht, *A.* 202, 15). Plates, v. sol. toluene.

References.—DI-BROMO-, DI-CHLORO-, and DI-NITRO- PHENYLENE-NAPHTHYLENE OXIDE.

PHENYLENE OXIDE C_6H_4O? [103°]. A product of the distillation of *o*-oxy-benzoyl-*o*-oxy-benzoic acid (Märker, *A.* 124, 249). Silky needles (from alcohol). HNO_3 yields the nitro-compound $C_6H_3(NO_2)O$ [150°].

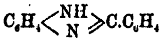
Diphenylene oxide $C_{12}H_8O$ *i.e.*

$\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\!\!>O$. [87°]. (283°) (Galewsky, *A.* 264, 188).

Formation.—1. By distilling Ph_3PO_4 over lime, MgO, or PbO (Lesimple, *A.* 138, 375; Hoffmeister, *Z.* [2] 7, 24; *A.* 159, 211; Kreysler, *B.* 18, 1720).—2. By distilling phenol (2 pts.) with PbO (3 pts.) (Behr a. Dorp, *B.* 7, 398; Graebe, *A.* 174, 190).—3. By distilling $Ca(OPh)_2$ (Niederhäusern, *B.* 15, 1120).—4. By the action of red-hot lime on di-phenylene-ketone oxide.—5. One of the products of the action of HCl on mucic acid at 150°.

Properties.—White plates (from alcohol). Converted by AcCl into

$\begin{matrix}CH_3.CO.C_6H_3\\ C_6H_4\end{matrix}\!\!>O$ [81°], which yields an oxim [146°] and a phenyl-hydrazide [133°]. H_2SO_4 forms a deliquescent disulphonic acid, which yields $BaC_{12}H_6S_2O_7$ aq.

Picric acid compound $C_{12}H_8OC_6H_3N_3O_7$. [24°]. Yellow crystals (Goldschmiedt a. Schmidt, *M.* 2, 14).

References.—AMIDO-, BROMO-, TETRA-CHLORO-, DI-IODO, DINITRO- PHENYLENE OXIDES.

o-**PHENYLENE - OXY - BENZAMIDINE**

$C_6H_4\!\!<\!\!\begin{matrix}NH\\ N\end{matrix}\!\!\gg C.C_6H_4.OH$. [223°]. Formed by reducing salicyl-*o*-nitro-aniline with tin and HCl (Mensching, *A.* 210, 345). Needles.—B'HCl aq.—$B'_2H_2SO_4$ 4aq. Needles, sl. sol. Aq.

o-**PHENYLENE-PHENYL-DIAMINE.** The *sulphonic acid* which gives the barium salt BaA'_2 2aq may be got from its anilide [1:2:4] $C_6H_3(NHPh)(NH_2).SO_2NHPh$ [157°] which is got by reduction of $C_6H_3(NHPh)(NO_2).SO_2NHPh$, and yields B'HCl [182°] (Fischer, *B.* 24, 3794).

p-**Phenylene-phenyl-diamine** $C_6H_4(NHPh).NH_2$. *Amido-diphenylamine.* [67°] and [75°]. (354°).

Formation.—1. By reduction of nitro-diphenylamine (Nietzki a. Witt, *B.* 12, 1401). 2. From *p*-nitroso-diphenylamine by boiling with alcoholic potash, by reduction with tin and HCl (Ikuta, *A.* 243, 279), or by treatment with phenyl-hydrazine in ether (O. Fischer, *B.* 21, 2615).—3. Together with azophenine, by heating *p*-nitroso-diphenylamine with aniline and aniline hydrochloride (O. Fischer a. Hepp, *B.* 20, 2480). 4. By reducing $C_6H_4(NHPh)N_2C_6H_4SO_3Na$ (Hess a. Bernthsen, *B.* 18, 692).

Properties.—Plates or needles, sl. sol. water, v. sol. alcohol. Melts at 75° after crystallisation from ligroïn. $FeCl_3$ added to a solution of its salts gives a red colour, turned green by excess. Yields quinone on oxidation.

Salt.—$B'_2H_2SO_4$. Plates.

Nitrosamine $C_{18}H_{14}N_4O_2$. [c. 130°].

Acetyl derivative $C_{14}H_{14}N_2O$. [158°].

Benzoyl derivative (Lellmann, *B.* 15, 826).

Sulphonic acid. [1:4:2] $C_6H_3(NHPh)(NH_2).SO_3H$. Formed by reducing $C_6H_3(NHPh)(NO_2).SO_3H$ (Fischer, *B.* 24, 3800). Yields BaA'_2 aq and an anilide [171°], which gives B'HCl [215°].

m-**Phenylene-di-phenyl-diamine** $C_6H_4(NHPh)_2$. [95°]. Formed by heating resorcin (2 mols.) with aniline (8 mols.), $CaCl_2$ (8 mols.) and $ZnCl_2$ (1 mol.) for 35 hours at 210° (Calm, *B.* 16, 2792). Flat needles, v. sol. ether. Oxidising agents give a green colour passing to bluish violet. Amyl nitrite and alcohol HCl form the *p*-nitroso- derivative $C_{18}H_{15}N_3O$, crystallising in brown-red prisms and yielding B''2HCl (Fischer a. Hepp, *A.* 255, 145). B''2HCl: needles decomposed by water.

Acetyl derivative $C_6H_4(NPhAc)_2$. [163°].

Benzoyl derivative $C_6H_4(NPhBz)_2$. [184°].

Nitrosamine $C_6H_4(NPh.NO)_2$. [102°]. Yellow needles, forming a violet solution in H_2SO_4.

p-**Phenylene-di-phenyl-diamine** $C_6H_4(NHPh)_2$. [132°] (Bandrowski, *M.* 8, 475); [141°] (Limpricht, *B.* 22, 2910); [145°] (O. Fischer, *B.* 21, 2615); [152°] (Calm, *B.* 16, 2803). Formed by heating hydroquinone (5 pts.) with aniline (17 pts.), $CaCl_2$ (20 g.), and $ZnCl_2$ (5 g.) for 18 hours at 210°. Formed also by the action of phenyl-hydrazine on nitroso-diphenyl-

amine in alcohol, and from the hydrochloride of amido-salicylic acid and aniline. Plates, v. sol. hot benzene. HNO_3 added to its solution in H_2SO_4 gives a blue liquid, changing to red.—B″2HCl: needles, decomposed by water.

Acetyl derivative $C_6H_4(NPhAc)_2$. [192°].

Benzoyl derivative $C_6H_4(NPhBz)_2$. [219°].

Nitrosamine $C_{18}H_{14}N_4O_2$. [c. 120°].

Phenylene-di-phenyl-diamine $C_6H_4(NH_2).NPh_2$. Formed by reducing nitro-tri-phenyl-amine (Herz, *B.* 23, 2537). Crystalline.—B′HCl: silvery needles.

Acetyl derivative $C_6H_4(NHAc).NPh_2$. [197°].

o-**PHENYLENE-PHENYL-GUANIDINE** $C_6H_4<\genfrac{}{}{0pt}{}{NH}{NH}>C:NPh$. [190°]. (440°-450°).

Formed by heating phenylene *o*-diamine with di-phenyl-cyanamide at 215° (Keller, *B.* 24, 2499). White needles (from benzene) or prisms (from alcohol). Phenyl-cyanate forms the compound $NPh<\genfrac{}{}{0pt}{}{CO}{CO}>N_2(CNPh)C_6H_4$. [266°]. — B′HCl.—$B'_2H_2PtCl_6$.—$B'H_2SO_4$: long needles.

Mono-acetyl derivative. [160°].

Di-benzoyl derivative. [171°]. Needles.

PHENYLENE-DI-PHENYL-DIHYDRAZINE. *Hexahydride* $C_6H_{10}(NH.NHPh)_2$ [148°]. Formed by reducing the di-phenyl-di-hydrazide of quinone with sodium and alcohol (Baeyer a. Noyes, *B.* 22, 2175). Crystalline, sl. sol. alcohol.—$B'H_2C_2O_4$ aq.

m-**PHENYLENE DI-PHENYL DIKETONE** $C_6H_4(CO.C_6H_5)_2$. *Isophthalophenone.* [95°] (M.); [100°] (A.). (above 360°). Formed from isophthalyl chloride, benzene, and $AlCl_3$ (Ador, *Bl.* [2] 33, 56; *B.* 13, 320; Münchmeyer, *B.* 19, 1848). Plates (from alcohol). Yields a mono-oxim [201°] (Nölting a. Kohn, *B.* 19, 146), a dioxim [70°–75°], and two di-nitro- derivatives [260°] and [c. 100°].

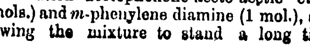
p-**Phenylene diphenyl diketone** $C_6H_4(CO.C_6H_5)_2$. [160°]. Formed from terephthalic chloride, benzene, and $AlCl_3$ (M.). Yields a dioxim [235°].

Diphenylene di-phenyl diketone $C_{12}H_8(CO.C_6H_5)_2$. [218°]. Got from diphenyl, BzCl, and $AlCl_3$ (Wolf, *B.* 14, 2031). Crystals.

DIPHENYLENE-PHENYL-METHANE $C_{19}H_{14}$ *i.e.* $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CHPh$. [145·5°]. Formed by the action of P_2O_5 or $AlCl_3$ on a mixture of benzene and diphenylene-carbinol; and also by heating CPh_3Cl at 200° (Hemilian, *B.* 11, 202, 837; *Bl.* [2] 34, 325). Formed also in small quantity in the distillation of calcium benzoate or phthalate (Kekulé, *B.* 5, 910; Miller, *B.* 12, 1489). Needles, sl. sol. ether. Yields *o*-benzoyl-benzoic acid on oxidation.

Reference.—DI-BROMO-DI-PHENYLENE-PHENYL-METHANE.

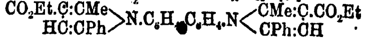
v-*m*-**PHENYLENE-DI-PHENYL-DI-METHYL-DI-PYRROLE DI-CARBOXYLIC-ETHER** $C_{34}H_{[illegible]}O_4N_2$ *i.e.*



$$\genfrac{}{}{0pt}{}{CO_2Et.C:CMe}{HC:CPh}>N.C_6H_4.N<\genfrac{}{}{0pt}{}{CMe:C.CO_2Et}{CPh:CH}$$

[185°]. Obtained by mixing together in acetic acid solution acetophenone-aceto-acetic ether (2 mols.) and *m*-phenylene diamine (1 mol.), and allowing the mixture to stand a long time (Paal a. Schneider, *B.* 19, 3161). Slender white needles. V. sol. ordinary solvents, except Aq.

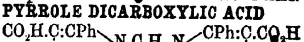
v-*p*-**Diphenylene-di-phenyl-di-methyl-di-pyrrole di-carboxylic-ether** $C_{40}H_{36}O_4N_2$ *i.e.*



$$\genfrac{}{}{0pt}{}{CO_2Et.C:CMe}{HC:CPh}>N.C_6H_4.C_6H_4.N<\genfrac{}{}{0pt}{}{CMe:C.CO_2Et}{CPh:CH}$$

[179]. Obtained by mixing together in acetic acid solution acetophenone-aceto-acetic ether (2 mols.) and benzidine (1 mol.), and allowing the mixture to stand for a long time (P. a. S.). Hair-like needles. Sol. alcohol and acetic acid, v. sol. ether, chloroform, and petroleum-spirit.

p-**PHENYLENE-TETRA-PHENYL-DI-PYRROLE DICARBOXYLIC ACID**



$$\genfrac{}{}{0pt}{}{CO_2H.C:CPh}{HC:CPh}>N.C_6H_4.N<\genfrac{}{}{0pt}{}{CPh:C.CO_2H}{CPh:CH}$$

[above 300°]. Formed by saponification of its ether [250°] which is got from phenacyl-benzoyl-acetic ether and phenylene-*p*-diamine (Paal a. Braikoff, *B.* 22, 3095). Small grains.

m-**PHENYLENE DI-PHENYL SULPHONE** $C_6H_4(SO_2Ph)_2$. [191°]. Formed by heating benzene with P_2O_5 and benzene *m*-disulphonic acid or di-phenyl sulphone *m*-sulphonic acid (Otto, *B.* 19, 2421; 20, 185). Minute needles (from HOAc). Alcoholic potash at 170° forms $O(C_6H_4.SO_2Ph)_2$ [70°] and $C_6H_5.SO_2K$.

Di-phenylene di-phenyl trisulphone $SO_2(C_6H_4.SO_2C_6H_5)_2$. [193°]. Formed from $SO_2(C_6H_4.SO_3H)_2$, benzene, and P_2O_5 at 200° (Otto a. Rössing, *B.* 19, 3127).

PHENYLENE-DI-PHENYL-DI-THIO-DI-UREA $C_6H_4(NH.CS.NHPh)_2$. Formed from phenylene-diamine and phenyl thiocarbimide in alcohol (Lellman a. Würthner, *A.* 221, 28; 228, 200). The *o*- and *p*- compounds are decomposed by heat into di-phenyl-thio-urea and phenylene-thio-urea; the *m*- compound melts at 161°, and the *o*- isomeride at about 290°. They are insol. ether.

m-**PHENYLENE-DI-PHENYL-UREA** $C_6H_4(NH.CO.NHPh)_2$. Formed from *m*-phenylene-diamine and phenyl cyanate (Kühn, *B.* 18, 1478). Amorphous.

PHENYLENE-PROPENYL-DIAMINE $C_6H_4<\genfrac{}{}{0pt}{}{NH}{N}>CEt$. [169°]. (above 360°). Got by boiling *o*-phenylene-diamine with propionic acid (Wundt, *B.* 11, 829), and by reducing propionyl-*o*-nitro-aniline with tin and HOAc (Smith, *Am.* 6, 172). Plates (from water).—B′HCl.—$B'HgCl_2$.—$B'_2H_2PtCl_6$ 2aq.—$B'_2H_2Cr_2O_7$.

PHENYLENE-DI-PROPIONIC ACIDS $C_6H_4(CH_2.CH_2.CO_2H)_2$. Formed by heating $C_6H_4(CH_2.CH(CO_2H)_2)_2$ (Perkin a. Kipping, *C. J.* 53, 8, 32; *B.* 21, 27, 40). The *o*- acid [162°] forms Ag_2A''. The *m*- acid [147°] forms Me_2A'' [51°] and Et_2A'' (250° at 60 mm.). The *p*- acid [224°] forms Ag_2A'' and Me_2A'' [115°].

p-**PHENYLENE-PROPYL-DIAMINE** $C_6H_4(NH_2)(NHPr)$. (281°). Got by reducing *p*-nitroso-propyl-aniline with $SnCl_2$ (Wacker, *A.* 243, 294). Plates.—B″2HCl. Plates, v. e. sol. Aq.

o-**PHENYLENE-PROPYLENE-DIAMINE** $C_6H_4<\genfrac{}{}{0pt}{}{NH}{NH}>C_3H_6$. [72°]. (285°). Formed by heating pyrocatechin with propylene-diamine at 200° (Ris, *B.* 21, 382). Plates (from ligroïn).—$B'_2$3HCl.—$B'_2 2C_6H_3N_3O_7$. Thin needles.

DIPHENYLENE-PYRAZINE. *Dihydride* $C_{16}H_{12}N_2$ *i.e.* $\genfrac{}{}{0pt}{}{C_6H_4.C.N.CH_2}{C_6H_4.C.N.CH_2}$. Formed from phenanthraquinone and ethylene-diamine (Mason, *B.* 19, 112; 20, 267).—$B'_2H_2PCl_6$.

(*a*)-**PHENYLENE-PYRIDYL-KETONE** $C_6H_4<\genfrac{}{}{0pt}{}{CO.C.CH:CH}{——C-N:CH}$. [141°]. Formed by distilling the dicarboxylic acid $C_7H_4O<\genfrac{}{}{0pt}{}{C.C(CO_2H):CH}{C.N\ :\ C(CO_2H)}>$ [284°], which is formed by oxidising (*a*)-styryl-(*β*)-naphthoquinoline carboxylic acid (Doebner a. Peters, *B.* 23, 1241). Yields a *picric acid compound* [197°]. The dicarboxylic acid yields Ag_2A''.

(*β*)-**Phenylene-pyridyl-ketone** $C_6H_4<\genfrac{}{}{0pt}{}{CO.C.N\ :CH}{——C.CH:CH}$. [129°]. Formed in like manner from the corresponding dicarboxylic acid [264°] which is got by oxidising (*a*)-styryl-(*a*)-naphthoquinoline carboxylic acid with $KMnO_4$. Needles. Yields $B'_2H_2PtCl_6$ 2aq. The dicarboxylic acid forms Ag_2A'' as a pp.

PHENYLENE-QUINOLYLENE KETONE OXIDE $C_{16}H_9NO_2$ *i.e.* $O<\genfrac{}{}{0pt}{}{C_6H_4}{C_9H_5N}>CO$. *Phenoquinoxanthone.* [188°]. Formed by distilling *p*-oxy-quinoline with salicylic acid. Needles (from alcohol).—B'HCl: needles.

DIPHENYLENE-QUINOXALINE $C_{20}H_{12}N_2$ *i.e.* $\genfrac{}{}{0pt}{}{C_6H_4.C.N}{C_6H_4.C.N}>C_6H_4$. [217°]. Got from phenylene-*o*-diamine and phenanthraquinone (Hinsberg, *A.* 237, 340). V. sl. sol. alcohol.

DIPHENYLENE-STYRYL-OXAZOLE $\genfrac{}{}{0pt}{}{C_6H_4.C.O}{C_6H_4.C.N}>C.CH:CHPh$. [172°]. Formed from phenanthraquinone, cinnamic aldehyde, and alcoholic NH_3 at 100° (Wadsworth, *C. J.* 57, 11). Yellow needles.

p-**PHENYLENE DISULPHIDE** $C_6H_4S_2$. Formed by oxidising dithiohydroquinone with an alkaline ferricyanide solution (Leuckart, *J. pr.* [2] 41, 206). Chars without melting at 300°, insol. ordinary solvents. Is reduced by fusing with potash to dithiohydroquinone.

Diphenylene sulphide $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>S$. [97°]. (333° i.V.). Formed by passing Ph_2S through a red-hot tube (Stenhouse, *A.* 156, 332; Graebe, *A.* 174, 185). Needles, m. sol. alcohol. Yields on oxidation the sulphone $C_{12}H_8SO_2$ [230°].

Diphenylene-disulphide $C_6H_4<\genfrac{}{}{0pt}{}{S}{S}>C_6H_4$ [154°]. (366°). A product of the distillation of sodium benzene sulphonate (Stenhouse, *Pr.* 17, 62; *A.* 149, 252). Formed also by heating phenol with P_2S_5 (Graebe, *A.* 174, 185; 179, 178), by heating benzene with S and $AlCl_3$ at 80° (Friedel a. Crafts, *A. Ch.* [6] 1, 530; 14, 439), and by heating $C_6H_4<\genfrac{}{}{0pt}{}{N}{S}>N$ (Jacobson a. Elley, *B.* 22, 910). Prisms (from CS_2). Conc. H_2SO_4 forms a purple solution. CrO_3 in HOAc gives the sulphone $C_{12}H_8S_2O_4$ [325°] and the sulphoxide $C_{12}H_8S_2O_2$ [241°], sl. sol. cold benzene. Br forms $C_{12}H_8S_2Br_4$ crystallising from CS_2 in small black prisms.

m-**PHENYLENE SULPHOCYANIDE** $C_6H_4(SCN)_2$. [54°]. Formed by heating the lead salt of di-thio-resorcin with ICy and alcohol at 100° (Gabriel, *B.* 10, 184). Needles, v. e. sol. hot alcohol. Yields a nitro-compound $C_6H_3(NO_2)(SCN)_2$ [150°].

DIPHENYLENE SULPHONE *v.* DIPHENYLENE SULPHIDE.

DI-PHENYLENE SULPHONE KETONE $C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{CO}>C_6H_4$. [185°]. Formed by heating benzophenone with fuming H_2SO_4 (Beckmann, *B.* 6, 1112; 8, 992), and by oxidising $C_6H_4<\genfrac{}{}{0pt}{}{S}{CO}>C_6H_4$ (Graebe a. Schultess, *A.* 263, 10). Yellowish needles, v. sol. alcohol.

PHENYLENE DITHIOCARBAMIC ETHERS $C_6H_4(NH.CO.SEt)_2$. Formed by boiling from phenylene-thiocarbimide with alcohol (Billeter a. Steiner, *B.* 20, 230). The *m*-compound [116°] and the *p*-compound [197°] are crystalline and yield Ag_2A'' as white pps.

PHENYLENE-DI-THIO-CARBIMIDE $C_6H_4(NCS)_2$. Formed from phenylene-diamine and $CSCl_2$ (Billeter a. Steiner, *B.* 20, 231). The *o*-compound [5?°], *m*-compound [53°] (250°), and *p*-compound [130°] all crystallise in needles.

m-**PHENYLENE-DI-THIO-DIGLYCOLLIC ACID** $C_6H_4(SCH_2.CO_2H)_2$. [127°]. Formed from di-thio-resorcin and $ClCH_2CO_2H$ (Gabriel *B.* 12, 1639). Microcrystalline powder.

Diphenylene-di-thio-di-glycollic acid $C_{12}H_8(S.CH_2.CO_2H)_2$. [252°]. Formed from $C_{12}H_8(SH)_2$, NaOHAq, and chloro-acetic acid (Gabriel, *B.* 13, 390).

o-**PHENYLENE-THIO-UREA** $C_6H_4<\genfrac{}{}{0pt}{}{NH}{NH}>CS$. [298°]. Formed by heating *o*-phenylene-diamine hydrochloride with ammonium sulphocyanide and water at 180 (Lellmann, *B.* 15, 2146; *A.* 221, 9). Formed also from *o*-phenylene-diamine and $CSCl_2$ (Billeter a. Steiner, *B.* 20, 231). Plates (from dilute alcohol, sl. sol. water). The crystalline *m*-isomeride is got by heating *m*-phenylene-diamine with CS_2 and some alcohol at 150° (Gucci *G.* 17, 524). The *p*-isomeride melts at 271°.

Phenylene-di-thio-di-ureas $C_6H_4(NH.CS.NH_2)_2$. *m*- [215°]. *p*- [220°] Formed by heating phenylene-diamine hydrochloride with ammonium sulphocyanide (Lellmann, *A.* 221, 11; *B.* 15, 2840). The *p*-compound is also formed from *p*-phenylene dithiocarbimide and alcoholic NH_3 (Billeter a. Steiner, *B.* 20, 230).

Diphenylene-thio-urea $\genfrac{}{}{0pt}{}{C_6H_4.NH}{C_6H_4.NH}>CS$. [238°]. Formed by heating di-*op*-amido-diphenyl with alcohol and CS_2 (Reuland, *C. J.* 58, 167; *B.* 22, 3014).

o-**PHENYLENE-TOLENYL-AMIDINE** $C_6H_4Me.C\genfrac{}{}{0pt}{}{\leqslant NH}{\leqslant N}>C_6H_4$. [268°]. Formed from *o*-phenylene-diamine and *p*-toluic chloride, and also by reduction of *p*-toluyl-*o*-nitro-aniline (Hübner, *A.* 210, 328; *cf.* Brückner, *A.* 205, 115). Prisms (from alcohol).—B'HCl.—$B'_2H_2PtCl_6$.—$B'HNO_3$.—$B'_2H_2SO_4$: slender needles.

PHENYLENE-DI-*p*-TOLYL-*m*-DIAMINE $C_{20}H_{20}N_2$ *i.e.* $C_6H_4(NH.C_6H_4Me)_2$. [187°]. Formed by heating resorcin with *p*-toluidine, $ZnCl_2$, and $CaCl_2$ (Hatschek a. Zega, *J. pr.* [2] 33, 218). Needles. Yields a di-nitrosamine $C_{20}H_{18}N_4O_2$ [c. 150°], a di-acetyl derivative

$C_{20}H_{18}Ac_2N_2$ [176°], and a di-benzoyl derivative $C_{20}H_{18}Bz_2N_2$ [152°].—B″2HCl; crystalline powder, decomposed by water.

Phenylene-di-*o*-tolyl-*p*-diamine [135°]. (420°). Formed by heating hydroquinone with *o*-toluidine and $CaCl_2$ at 290° (Philip, *J. pr.* [2] 34, 65). Plates (from HOAc). Yields a di-nitrosamine [140°]. Yields $C_{20}H_{18}Bz_2N_2$ [235°] and $C_{20}H_{18}Ac_2N_2$ [189°].—B″2HCl: needles.

Phenylene-di-*p*-tolyl-*p*-diamine. [182°]. Formed by heating hydroquinone or phenyl-*p*-amido-phenol with *p*-toluidine and $ZnCl_2$ at 220° (H. a. Z.); Calm, *B.* 16, 2810). Plates. Yields a di-nitrosamine [152°], a di-acetyl derivative [173°], and a di-benzoyl derivative [222°].—B″2HCl.

PHENYLENE-TOLYLENE-KETONE OXIDE $C_6H_4{<}\substack{CO\\O}{>}C_6H_3Me$. *Methyl-xanthone.* [105°]. Formed by boiling *p*-tolyl salicylate (Graebe a. Feer, *B.* 19, 2612; *cf.* Seifert, *J. pr.* [2] 31, 478).

Isomeride $C_6H_4{<}\substack{O\\CO}{>}C_6H_3Me\left[\substack{3\\4}\,1\right]$. [176°]. Made by heating $C_6H_3Me(OH)CO_2Ph$ [49°] (Weber, *B.* 25, 1745). Crystals (from alcohol).

***o*-PHENYLENE-*p*-TOLYL-GUANIDINE** $C_6H_4{<}\substack{NH\\NH}{>}C{:}N.C_6H_4Me$. [209°]. Formed by heating *o*-phenylene-diamine with di-*p*-tolyl-cyanamide at 210° (Keller, *B.* 24, 2509). Tables. Yields a mono-acetyl derivative [152°], a di-benzoyl derivative [191°], and a nitrosamine $C_{14}H_{12}(NO)N_3$ [150°-160°]. Phenyl cyanate forms $C_6H_5N{<}\substack{CO\\CO}{>}N_2(C_6H_4){:}C{:}NC_6H_4Me$ [254°] crystallising from benzene in small needles. Di-*p*-tolyl-cyanamide at 210° forms the compound $(NHC_7H_7)_2C{:}N_2(C_6H_4){:}C{:}N.C_6H_4Me$ [188°].

Salts.—$B'HCl$.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$.

DIPHENYLENE-TOLYL-METHANE $C_{20}H_{16}$ *i.e.* $\substack{C_6H_4\\C_6H_4}{>}CH.C_6H_4Me$. [128°]. Formed by the action of P_2O_5 on a mixture of diphenylene-carbinol and toluene, or of $AlCl_3$ on diphenylene-carbinyl chloride dissolved in toluene (Hemilian, *B.* 11, 208; *Bl.* [2] 34, 325). Silky needles.

PHENYLENE-DI-*p*-TOLYL-DI-METHYL-*m*-DIAMINE $C_6H_4(NMe.C_6H_4Me)_2$. (c. 400°). Got by heating phenylene-di-*p*-tolyl-*m*-diamine with MeI and KOH at 150° (Hatschek a. Zega, *J. pr.* [2] 33, 223). Liquid smelling like geraniums.

The isomeric **phenylene-di-*o*-tolyl-di-methyl-*p*-diamine** (385°-390°) and **phenylene-di-*p*-tolyl-di-methyl-diamine** [153°] may be prepared in like manner (Philip, *J. pr.* [2] 34, 57; H. a. Z.).

***o*-PHENYLENE-UREA** $C_6H_4{<}\substack{NH\\NH}{>}CO$. [308°]. Formed by heating *o*-amido-phenyl-carbamic ether at 90° (Rudolph, *B.* 12, 1296), by heating *o*-amido-di-phenyl-urea (Lellmann a. Würthner, *A.* 228, 220), by heating its ethyl derivative with HCl (Sandmeyer, *B.* 19, 2654), and by the action of $COCl_2$ in toluene on a solution of *o*-phenylene-diamine hydrochloride at 100° (Hartmann, *B.* 23, 1046). Leaflets, sl. sol. water.—B′HCl. Decomposed by water.

Ethyl derivative $C_6H_4{<}\substack{NH\\N}{>}C.OEt$. [160°]. Formed from *o*-phenylene-diamine and $NH{:}C(OEt)_2$. Plates.

***m*-Phenylene-urea.** [above 300°]. Formed by similar methods (Michler a. Zimmermann, *B.* 14, 2177; L. a. W.). Insoluble powder.

***p*-Phenylene-urea.** [above 320°]. Got by heating *p*-amido-di-phenyl-urea (L. a. W.).

Isomeride. [130°]. Got by boiling an alcoholic solution of oxy-phenyl-thio-urea with HgO (Bendix, *B.* 11, 2264). Tables, sol. water.

Phenylene-di-ureas $C_6H_4(NH.CO.NH_2)_2$. *o-* [290°]. *m-* [above 300°]. Formed from phenylene-diamine hydrochloride and potassium cyanate in cold aqueous solutions (Warder, *B.* 8, 1180; Lellmann, *A.* 221, 13; *B.* 16, 592).

The *p-* compound can be heated to carbonisation without melting.

References.—AMIDO- and NITRO- PHENYLENE-UREA.

PHENYL-ENNOIC ACID.

Nitrile $C_6H_5.CH(C_7H_{15}).CN$. (327°). Formed from $CH_2Ph.CN$, heptyl iodide, and NaOH (Rossolymo, *B.* 22, 1237). Yellow oil.

DI-PHENYL-ENNYL TRICYANIDE $C_9H_{19}C_3N_3Ph_2$. [c. 38°]. (c. 293° at 15 mm.). Formed from decoic chloride, benzonitrile, and $AlCl_3$ (Krafft a. Koenig, *B.* 23, 2384).

PHENYL-ENNYL-THIO-UREA $C_{16}H_{26}N_2S$ *i.e.* $NHPh.CS.NHC_9H_{19}$. [60°]. Formed from ennyl-thiocarbimide and aniline (Freund a. Schönfeld, *B.* 24, 3359). Tables, v. sol. alcohol and ligroïn.

PHENYL-ENNYL-UREA $C_{16}H_{26}N_2O$ *i.e.* $NHPh.CO.NHC_9H_{19}$. [63°]. Formed from phenyl cyanate and aniline in alcohol (Freund a. Schönfeld, *B.* 24, 3358). Long prisms.

***s*-DI-PHENYL-ETHANE** $C_{14}H_{14}$ *i.e.* $CH_2Ph.CH_2Ph$. *Dibenzyl.* Mol. w. 182. [53°]. (277°). S.V.S. 174·2 (Schiff, *A.* 223, 261). H.F. - 31,200. H.C.v. 1,828,300. H.C.p. 1,830,200 (Berthelot a. Vieille, *Bl.* [2] 47, 866).

Formation.—1. By the action of Na on benzyl chloride (Cannizzaro a. Rossi, *A.* 121, 250; Fittig, *A.* 137, 257).—2. From ethylene chloride, benzene, and $AlCl_3$ (Silva, *C. R.* 89, 606; *A. Ph. S.* 18, 345).—3. From CHBr:CHBr, benzene, and $AlCl_3$ (Anschütz, *A.* 235, 155).—4. From acetylene, benzene, and $AlCl_3$ (Varet a. Vienne, *Bl.* [2] 47, 919).—5. By heating benzyl chloride with copper powder (Onufrovitch, *B.* 17, 833).—6. A product of the action of Na on *o*-bromo-benzyl-bromide (Jackson a. White, *Am.* 2, 390).—7. By adding sodium (70 g.) to an alcoholic solution of phenyl-cinnamonitrile (Freund a. Remse, *B.* 23, 2859).

Properties.—Long colourless needles, sol. alcohol, ether, and CS_2.

Reactions.—1. Yields toluene and di-phenyl-ethylene when passed through a *red-hot tube* (Otto, *Z.* [2] 6, 22; *A.* 154, 176; Barbier, *C. R.* 78, 1769).—2. Chlorine passed into fused *s*-di-phenyl-ethane forms first CHPh:CHPh and then $C_6H_4Cl.CH{:}CH.C_6H_4Cl$ (Kade, *J. pr.* [2] 19, 466). In presence of I, chlorine forms *p*-di-chloro-di-phenyl-ethane in the cold. Exhaustive *chlorination* yields C_2Cl_6 and C_6Cl_6 (Merz a. Weith, *B.* 16, 2877).—3. H_2SO_4 forms a disulphonic acid $C_{14}H_{12}(SO_3H)_2$ 5aq, which yields K_2A'' 2aq, BaA'' ½aq, and PbA'' aq (Kade, *B.* 6, 953). A tetra-sulphonic acid, $C_{14}H_{10}(SO_3H)_4$ 3aq, is also formed.

***u*-Di-phenyl-ethane** $CH_3.CHPh_2$. (270°) (O.); (286°) (H.).

Formation.—1. From $CCl_3.CHPh_2$, alcohol, and Na (Goldschmiedt, *B.* 6, 1501).—2. From $CH_2Ph.CH_2Br$, benzene, and zinc-dust (Radziszewski, *B.* 7, 140).—3. From paraldehyde, benzene, and H_2SO_4 (Baeyer, *B.* 7, 1190).—4. Together with ethyl-benzene and di-methyl-anthracene dihydride by heating ethylidene chloride with benzene and $AlCl_3$ (Silva, *Bl.* [2] 41, 448; Anschütz, *B.* 17, 165).—5. By distilling its dicarboxylic acid (Haiss, *B.* 15, 1481).

Properties.— Oil, with blue fluorescence. Solidifies in a freezing mixture. Yields benzophenone on oxidation. Fuming HNO_3 added to its solution in HOAc forms benzophenone, $CPh_2(OH).CH_2.O.NO_2$ [107°], di-phenyl-vinyl nitrite [87°], and a body [148°] which yields di-phenyl-acetonitrile on reduction (Anschütz a. Romig, *A.* 233, 329).

Tri-phenyl-ethane $CH_2Ph.CHPh_2$. (above 360°). Formed from $CH_2Cl.CHCl.OEt$, benzene, and $AlCl_3$ (Waas, *B.* 15, 1128). Liquid, with violet fluorescence. Insol. cold alcohol.

s-Tetra-phenyl-ethane $C_{26}H_{22}$ *i.e.* $CHPh_2.CHPh_2$. Mol. w. 334. [210°]. S. (benzene) 14 at 80°. S. (95 p.c. alcohol) ·8 on boiling.

Formation.—1. By distilling benzoyl- and succinyl- di-phenyl-carbinol and by distilling di-phenyl-carbinol with succinic acid (Linnemann, *A.* 133, 24).—2. By distilling benzophenone with zinc-dust (Staedel, *B.* 6, 1401).—3. By reducing benzpinacone $CPh_2(OH).CPh_2(OH)$ with HI and P (Graebe, *B.* 8, 1055).—4. From di-phenyl-carbinol, glacial HOAc, conc. HClAq, and zinc (Zagumenny, *A.* 184, 176; *Bl.* [2] 34, 329).—5. By reducing (β)-benzpinacolin $CPh_3.CO.C_6H_5$ with HI and P (Zincke a. Thörner, *B.* 11, 67).—6. By boiling $(CHPh_2)_2S_2$ with alcohol and copper powder (Engler, *B.* 11, 926).—7. By reducing $CPh_2:CPh_2$ (Friedel a. Balsohn, *Bl.* [2] 33, 338).—8. From $CHPh_2Cl$ and Na (Engler). 9. By the action of benzene and $AlCl_3$ on $CBr_3.CH_2Br$, on $CHBr_2.CHBr_2$, on $CPhHBr.CHBr_2$, on $CPhBr_2.CPhBr_2$, and on CHPhBr.CHPhBr, the yield in the last case being excellent (Anschütz, *A.* 235, 196).—10. By distilling CPh_2HCl (Anschütz, *A.* 235, 220).

Properties.—Needles (by sublimation), sl. sol. alcohol. Crystallises from benzene with C_6H_6. Yields a crystalline tetra-nitro- derivative, a crystalline tetra-sulphonic acid, which gives Ba_2A^{iv} and $C_{26}H_{18}(OH)_4$ [248°].

u-Tetra-phenyl-ethane $CPh_3.CH_2Ph$. [140°]. Formed from CPh_3K and benzyl chloride (Hanriot, *C. R.* 108, 1119).

References.—Amido-, Bromo-, Bromo-amido-, Di-bromo-di-nitro-, Chloro-, Penta-chloro-di-nitro-, Nitro-, and Oxy-, Phenyl-ethanes.

PHENYL-ETHANE DICARBOXYLIC ACID *v.* Carboxy-phenyl-propionic acid and Phenyl-succinic acid.

Phenyl-ethane tricarboxylic acid $CHPh(CO_2H).CH(CO_2H)_2$. [171°]. Got by saponifying its ether, which is made by the action of α-chloro- or α-bromo- phenyl-acetic ether on sodium malonic ether (Spiegel, *A.* 219, 31; Alexander, *A.* 258, 71). Small tablets, v. sol. hot water. Decomposed on fusion into CO_2 and phenyl-succinic acid. **Salts.**—$Ca_3A'''_2$ 10aq.—$Ca_3A'''_2$ 5aq: ppd. from aqueous solution by alcohol.—Ag_3A''': crystalline pp.

Ethyl ether Et_3A'''. [46°]. (202° at 10 mm.). Needles (from dilute alcohol).

Di-phenyl-ethane o-carboxylic acid $C_{15}H_{14}O_2$ *i.e.* $C_6H_5.CH_2.CH_2.C_6H_4.CO_2H$. [131°]. Formed by the action of HI and P at 200° on iso-benzylidene-phthalide, and on deoxybenzoïn carboxylic acid (Gabriel, *B.* 11, 1019; 18, 2446). Tablets (from dilute alcohol).—AgA': pp.

Isomerides *v.* Di-phenyl-propionic acid.

Di-phenyl-ethane di-o-carboxylic acid $C_{16}H_{14}O_4$ *i.e.* $CO_2H.C_6H_4.CH_2.CH_2.C_6H_4.CO_2H$. [186°] (H.); [229°] (D.).

Formation.—1. By heating diphthalyl with HI and P (Graebe, *B.* 8, 1055).—2. By the action of HI and phosphorus on the acid $CO<\begin{matrix}C_6H_4\\O\end{matrix}>CH.CH_2.C_6H_4.CO_2H$ (Wislicenus, *B.* 17, 2181; Hasselbach, *A.* 243, 254), and on diphthalylic acid (Dobreff, *A.* 239, 66).

Properties.—Small needles, v. sol. alcohol and dilute HOAc. $KMnO_4$ in alkaline solution forms diphthalylic acid [263°]. Distillation over soda-lime forms *s*-di-phenyl-ethylene.

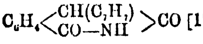
Salts.—$(NH_4)_2A''$ (dried at 100°).—CaA' (at 100°).—BaA''.—$Cu_2A''O$.—$Pb_2A''O$.—$Zn_2A''O$.—AgHA''.

Methyl ether Me_2A''. [101°].

Ethyl ether Et_2A''. [71°]. Converted by alcoholic NH_3 into the amic ether $C_2H_4(C_6H_4.CO_2Et)(C_6H_4.CONH_2)$ [c. 67°].

Di-phenyl-ethane dicarboxylic acid $C_6H_5.CH_2.CH(CO_2H).C_6H_4.CO_2H$ [1:2]. [154°]. (above 300°). Formed by heating the nitrile with conc. HCl at 220° (Eichelbaum, *B.* 21, 2682). Small prisms, sol. alcohol, insol. ether.

Nitrile $C_6H_5.CH_2.CH(CN).C_6H_4.CN$. [110°]. (above 300°). Formed from benzyl chloride and [1:2] $C_6H_4(CN).CH_2.CN$. Plates, insol. water, alkalis, and acids.

Amide. [221°]. Formed by the action of conc. H_2SO_4 on the nitrile. Converted by conc. HCl (S.G. 1·19) at 100° into the imide  $C_6H_4<\begin{matrix}CH(C_7H_7)\\CO-NH\end{matrix}>CO$ [176°] (above 300°).

Di-phenyl-ethane di-carboxylic acid $CH_3.CH(C_6H_4.CO_2H)_2$. [275°]. Got by heating the tri-carboxylic acid (Haïss, *B.* 15, 1481). Long needles. May be sublimed.—CaA''.

Isomeride *v.* Di-phenyl-succinic acid.

Di-phenyl-ethane tri-carboxylic acid $CO_2H.CMe(C_6H_4.CO_2H)_2$. [255°]. Formed by oxidation of di-α-tolyl-propionic acid with $KMnO_4$ (Haïss, *B.* 15, 1479). Sol. alcohol and ether.—Ag_2HA'''.—Ag_3A'''.

Di-phenyl-ethane tri-carboxylic acid $C_{17}H_{14}O_6$ *i.e.* $CHPh(CO_2H).CPh(CO_2H)_2$.

Amide $CHPh(CO_2H).CPh(CO_2H).CONH_2$. [190°]. Got from $CHPh(CO_2Et).CPh(CN).CO_2Et$ [105°] which is got by heating α-chloro-phenyl-acetic ether with alcoholic KCy on a water-bath (Poppe, *B.* 23, 114).

Mono-nitrile $CO_2H.CHPh.CPh(CN).CO_2H$. The ethers Me_2A'' [101°] and Et_2A'' (*v. supra*) are got from α-chloro-phenyl-acetic acid and KCy in MeOH or EtOH. Conc. H_2SO_4 converts Et_2A'' into $CO_2Et.CHPh.CPh(CO_2Et).CONH_2$ [157°] crystallising in aggregates of needles.

References.—Nitro- and Oxy- Di-phenyl-ethane carboxylic acid.

PHENYL-ETHENYL-AMIDINE *v.* PHENYL-ACETAMIDINE.

PHENYL - ETHENYL - AMIDO - PHENYL - MERCAPTAN $C_{14}H_{11}NS$ *i.e.* $C_6H_4<^{N}_{S}>C.CH_2Ph$. Formed by heating phenyl-acetic chloride with *o*-amido-phenyl mercaptan (Hofmann, *B.* 13, 1234). Oil, sol. alcohol and ether. On fusion with potash it yields phenyl-acetic acid and amido-phenyl mercaptan.—B'HCl.—$B'_2H_2PtCl_6$ 5aq: needles.

PHENYL-ETHENYL-AMIDOXIM $C_8H_{10}N_2O$ *i.e.* $C_6H_5.CH_2.C(NOH).NH_2$. *Phenyl-acetamidoxim.* [67°]. Got by heating phenyl-acetonitrile with a solution of hydroxylamine in dilute alcohol (Knudson, *B.* 18, 1068, 2482). Thin prisms, v. sol. water. Converted by phenyl cyanate into $C_6H_5.CH_2.C(NH.CO.NHPh):NOH$ [123°].—B'HCl. [155°]. White prisms.

Acetyl derivative. [124°]. Plates.

Benzoyl derivative $C_7H_7.C(NOBz).NH_2$. [144°]. Prisms, v. sol. alcohol.

Ethyl ether $C_7H_7.C(NOEt).NH_2$. [58°]. Converted by potassium cyanate into $CH_2Ph.C(NOEt).NH.CO.NHPh$ [148°].

Benzyl ether. [55°]. Prisms.

Phenyl-ethenyl-amidoxim $CH_3.C(NOH).NHPh$. [121°]. Formed by heating thioacetic anilide with hydroxylamine solution at 100° (Müller, *B.* 22, 2408; *cf.* Nordmann, *B.* 17, 2746). Satiny plates, v. sol. alcohol. $FeCl_3$ gives a violet colour, changing to olive green and, on heating, to red.—B'HCl: needles.—$B'_2H_2PtCl_6$: yellow needles.

Benzoyl derivative $C_2H_3(NOBz).NHPh$. [110°]. White needles (from dilute alcohol).

PHENYL-ETHENYL-AZOXIM *v.* AZOXIMS.

PHENYL-ETHENYL - DI-ETHYL - TRI - SULPHONE $CH_3.C(SO_2Et)_2(SO_2Ph)$. [109°]. Got by oxidation of $CH_3.C(SPh)(SO_2Et)_2$ (Laves, *B.* 25, 364). Needles, v. sol. alcohol.

TRI-PHENYL ETHENYL TRISULPHONE $CH_3.C(SO_2Ph)_3$. [182°]. Formed by the action of alcoholic NaOH, and MeI on $CH(SO_2Ph)_3$. Got also by oxidation of $CH_3.C(SPh)_3$ by $KMnO_4$ (Laves, *B.* 25, 352). Needles, v. sol. $CHCl_3$.

DI-PHENYL-ETHENYL-DI-UREA NHPh.CO.N:CMe.NH.CO.NHPh. [169°]. Formed by adding aqueous NaOH (2 mols.) to an aqueous solution of acetamidine hydrochloride (2 mols.) shaken with phenyl cyanate (1 mol.) (Pinner, *B.* 23, 2923). Needles, m. sol. alcohol. Converted by boiling dilute (50 p.c.) acetic acid into acetyl-phenyl-urea [183°].

PHENYL ETHER *v.* DI-PHENYL OXIDE.

α-PHENYL-ETHYL ALCOHOL $C_8H_{10}O$ *i.e.* $CH_3.CHPh.OH$. Mol. w. 122. (203°). S.G. 1·013. Formed from $CH_3.CHBr.C_6H_5$ by successive treatment with AgOAc and NaOH (Radziszewski, *B.* 7, 141; Berthelot, *Z.* 1868, 589). Got also by reducing acetophenone with sodium-amalgam (Emmerling a. Engler, *B.* 6, 1005). Yields an acetyl derivative C_8H_9OAc (217°–220°) which yields styrene on treatment with alcoholic potash.

Ethyl ether C_8H_9OEt. (186°). S.G. ^{22} ·931. Formed from $CH_3.CHBr.C_6H_5$ and alcoholic NH_3 at 100° (Thorpe, *Z.* 1871, 131).

β-Phenyl - ethyl alcohol $CH_2Ph.CH_2OH$. *Benzyl-carbinol.* (212°). S.G. ^{21} 1·034. Formed by reducing phenyl-acetic aldehyde with sodium-amalgam (Radziszewski, *B.* 9, 373). Oil. Ac_2O at 150° converts it into an acetyl derivative C_8H_9OAc, (224°), S.G. 1·029.

PHENYL-ETHYL-ALLOPHANIC ETHER $C_{12}H_{16}N_2O_3$ *i.e.* $C_8H_9.NH.CO.NH.CO_2Et$. [106°]. Formed from phenyl-ethyl-urea and $ClCO_2Et$ (Neubert, *B.* 19, 1825). Needles (from water).

PHENYL-ETHYL-ALLYL-GUANIDINE $C_{12}H_{17}N_3$ *i.e.* $CN_3H_2PhEt(C_3H_5)$. Formed by boiling ethyl-allyl-thio-urea with NHPh.HgCl and alcohol (Forster, *A.* 175, 41).—$B'HgCl_2$ aq.

PHENYL-ETHYL-ALLYL-THIO-UREA $NH(C_3H_5).CS.NPhEt$. [c. 26°]. Formed from allyl-thiocarbimide and ethyl-aniline (Gebhardt, *B.* 17, 3037). Colourless very soluble crystals.

PHENYL - ETHYL - ω - AMIDO - ACETOPHENONE $C_{16}H_{17}NO$ *i.e.* $C_6H_5.CO.CH_2.NPhEt$. [95°]. Formed from ω-bromo-acetophenone and diethyl-aniline (Weller, *B.* 16, 26). Needles.

PHENYL ETHYLAMIDO - ETHYL SULPHONE $C_6H_5.SO_2.C_2H_4.NHEt$. Formed from $C_2H_4(SO_2C_6H_5)_2$ and ethylamine at 85° (Otto, *J. pr.* [2] 30, 337).—B'HCl. [130°]. Needles.

PHENYL - ETHYL - AMIDO - (α) - NAPHTHOQUINONE $C_{10}H_5(NPhEt)O_2$. [155°]. Formed by heating (α)-naphthoquinone (2 pts.) with ethyl-aniline (3 pts.) and HOAc (5 pts.) (Elsbach, *B.* 15, 1810). Violet needles (from alcohol).—B'HCl. [c. 230°]. Yellow needles, decomposed by water.

Phenyl - ethyl - amido - (β) - naphthoquinone. [165°]. Formed by heating (β)-naphthoquinone with ethyl-aniline and alcohol (Elsbach, *B.* 15, 691). Dark-red needles (from ether). Decomposed by boiling HClAq into ethyl-aniline and oxy-naphthoquinone.

PHENYL-ETHYL-AMIDO-PHENOL. *Ethyl ether* $C_{16}H_{19}NO$ *i.e.* $NPhEt.C_6H_4.OEt$. (319°). Formed by heating phenyl-*p*-amido-phenol with alcoholic potash and EtI (Philip a. Calm, *B.* 17, 2434). Oil.

α-PHENYL-ETHYL-AMINE $C_8H_{11}N$ *i.e.* $CH_3.CHPh.NH_2$. (187·5° i.V.). S. 4·166 at 20°. Formed by reducing the phenyl-hydrazide or the oxim of acetophenone in alcoholic solution with HOAc and sodium-amalgam (Tafel, *B.* 19, 1929; 22, 1856; Kraft, *B.* 23, 2783). Formed also from acetophenone and sodium formate (Leuckart a. Janssen, *B.* 22, 1413). Liquid, miscible with alcohol and ether.—B'HCl. [158°].—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$. [170°].—$B'_2H_2C_2O_4$. [238°]. Prisms, almost insol. alcohol.—$B'H_2C_2O_4$. Plates, m. sol. boiling alcohol.

Isomerides:— AMIDO-PHENYL-ETHANE and ETHYL-ANILINE.

Di-phenyl-ethyl-amine $C_{14}H_{15}N$ *i.e.* NPh_2Et. *Ethyl diphenylamine.* (296°) (Girard, *Bl.* [2] 23, 3); (286°) (Lippmann a. Fleissner, *M.* 4, 797). Got by heating diphenylamine with alcohol and HClAq. Oil.

Di-phenyl-ethyl-amine $CHPh_2.CH_2NH_2$. Formed by reducing di-phenyl-acetonitrile in alcohol with Na (Freund a. Immerwahr, *B.* 23, 2845). Oil.—B'HCl. [255°]. V. sol. water.

Di-phenyl-ethyl-amine $CH_2Ph.CHPh.NH_2$. (310°) at 737 mm. Formed by heating deoxybenzoïn (1 pt.) with ammonium formate (2 pts.) at 225° (Leuckhart a. Janssen, *B.* 22, 1409). Liquid, sl. sol. water. Potassium cyanate forms $C_2H_3Ph_2.NH.CO.NH_2$ [99°]. Phenylthiocarbimide forms the corresponding $C_2H_3Ph_2NH.CS$ NHPh

[170°]; while phenyl cyanate gives the compound $C_2H_3Ph_2.NH.CO.NHPh$ [129].—B'HCl.—$B'_2H_2PtCl_6$.—$B'HNO_3$: needles.—$B'H_2SO_4$.

Acetyl derivative. [148°]. Needles.

Benzoyl derivative. [178°]. Needles.

Di-phenyl-di-ethyl-amine $NH(CH_2.CH_2Ph)_2$. (336° at 603 mm.). Formed, together with $NH_2.CH_2.CH_2Ph$ and $N(CH_2.CH_2Ph)_3$ by the action of zinc and HClAq on phenyl-acetonitrile (Spica, *G.* 9, 567). Formed also by distilling $CH_2Ph.CH_2.NH_3Cl$ (Fileti a. Piccini, *G.* 9, 294). Liquid, sl. sol. water.—B'HCl. [270°]. Pearly scales.—$B'_2H_2PtCl_6$, m. sol. water.

Tri-phenyl-ethyl-amine $CPh_3.CH_2.NH_2$. [116°]. Formed by reducing $CPh_3.CN$ with zinc and HClAq (Elbs, *B.* 17, 700).—B'HCl. [247°].

Tri-phenyl-tri-ethyl-amine $N(CH_2.CH_2Ph)_3$. A product of the action of zinc and HCl on phenyl-acetonitrile (Spica, *G.* 9, 567). Oil.—B'HCl. [138°]. Needles, sl. sol. water.

PHENYL-ETHYL-ARSINE *v.* vol. i. p. 321.

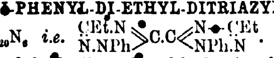
PHENYL-ETHYL-TRIAZOLE CARBOXYLIC ACID $\begin{matrix}N.NPh\\CEt:N\end{matrix}\!\!>C.CO_2H$. [145°]. Got by saponifying its nitrile (Bladin, *B.* 18, 1548; 25, 175). Melts at 123° when crystallised from water or alcohol, but at 145° when crystallised from benzene.—B'HCl: plates.—CuA'_2 3½aq.—AgA': crystalline pp.

Methyl ether MeA'. [41°].

Ethyl ether EtA'. Oil.

Nitrile $C_{11}H_{10}N_4$. [38°]. Formed by the action of propionic anhydride on phenyl-hydrazine dicyanide. Converted by alcoholic NH_3 and H_2S into $C_2N_3PhEt.CS.NH_2$ [150°] which crystallises in yellow prisms.

Amide $C_2N_3PhEt.CO.NH_2$. [152·5°]. Formed from the nitrile, alcoholic potash, and H_2O_2. Small prisms, sl. sol. water.

DI-PHENYL-DI-ETHYL-DITRIAZYL $C_{20}H_{20}N_6$ *i.e.*  $\begin{matrix}CEt.N\\N.NPh\end{matrix}\!\!>C.C<\!\!\begin{matrix}N\cdot CEt\\NPh.N\end{matrix}$. [187°]. Formed by boiling phenyl-hydrazine dicyanide with propionic anhydride (Bladin, *B.* 22, 3115). Groups of prisms.—B''2HCl: minute prisms, decomposed by water.

PHENYL-ETHYL-CARBAMIC CHLORIDE NPhEt.COCl. [c. 52°]. Formed from ethyl-aniline and CO_2 (Michler, *B.* 9, 396). Needles.

PHENYL-ETHYL-SEMICARBAZIDE $C_9H_{13}N_3O$ *i.e.* NHPh.CO.NH.NHEt. [112°]. Formed from ethyl-hydrazine and phenyl cyanate (E. Fischer, *A.* 199, 295). Thin plates, m. sol. hot water. Yields a crystalline nitrosamine.

Phenyl-ethyl-semicarbazide NHEt.CO.NH.NHPh. [151°]. Formed from phenyl-hydrazine and ethyl cyanate (Fischer, *A.* 190, 109). Monoclinic tables (from dilute alcohol) $a:b:c = \cdot827:1:1\cdot146$; $\beta = 61°$. Gives a bluish-black pp. with cold Fehling's solution, and Cu_2O on warming. Its nitrosamine crystallises from acetone in yellow needles [86·5°].

PHENYL ETHYL CARBONATE $C_9H_{10}O_3$ *i.e.* $C_6H_5O.CO.OEt$. (*c.* 234°) (P.). S.G. $\frac{0}{4}$ 1·1134 (P.). Formed from KOPh and $ClCO_2Et$ (Fatianoff, *Z.* 1864, 77). Formed also by the action of $AlCl_3$ on a mixture of phenol and $ClCO_2Et$ (Pawlewski, *B.* 17, 1205). Liquid. By long heating at 300° it is split up into Ph_2CO_3 and Et_2CO_3 (Bender, *B.* 19, 2268).

Reference.—NITRO-PHENYL ETHYL CARBONATE.

PHENYL-ETHYL-CYANAMIDE. Formed by boiling phenyl-ethyl-thio-urea in benzene with PbO (Weith, *B.* 8, 1530). Vitreous mass.

DI-PHENYL-ETHYL-TRICYANIDE $C_3N_3Ph_2Et$. V.D. 129. [67°]. (234° at 15 mm.). Formed by the action of $AlCl_3$ on a mixture of benzonitrile and propionyl chloride at 70° (Krafft a. von Hausen, *B.* 22, 806).—$B''H_2PtCl_6$.

PHENYL-ETHYLENE *v.* STYRENE.

s-Di-phenyl-ethylene $C_{14}H_{12}$, *i.e.* CHPh:CHPh. *Stilbene.* Mol. w. 180. [124°]. (307° i.V.). H.C.v. 1,775,600. H.C.p. 1,777,300 (from diamond) (Berthelot a. Vieille, *A. Ch.* [10] 4, 50); 1,773,331 (Ossipoff, *Z. P. C.* 2, 646).

Formation.—1. By the dry distillation of benzyl, or benzylidene, sulphide (Laurent, *B. J.* 25, 616; Maercker, *A.* 136, 91; Anschütz, *A.* 235, 206).—2. By distilling benzoic aldehyde with Na (Williams, *Z.* 1867, 432).—3. By heating benzoic aldehyde with phenyl-acetic acid and NaOAc at 250°; the yield being 55 p.c. (Michael, *Am.* 1, 313).—4. From *s*-di-phenyl-ethane and Cl (Kade, *J. pr.* [2] 19, 465).—5. By heating benzylidene chloride with Na or with alcohol and zinc-dust (Limpricht, *A.* 139, 318; Lippmann, *J.* 1877, 405).—6. By passing *s*-di-phenyl-ethane through a red-hot tube (Otto a. Dreher, *A.* 154, 177).—7. By heating benzoïn with zinc-dust (Limpricht, *A.* 155, 80).—8. By passing toluene over heated PbO (Behr a. Dorp, *B.* 6, 754).—9. By heating di-phenyl-acetylene with HI and P at 175° (Barbier, *J.* 1874, 421).—10. By distilling lead phenyl-acetate with sulphur (Radziszewski, *B.* 6, 390).—11. Together with benzonitrile by the action of zinc-dust and HCl on $C_6H_5.CSNH_2$ (Bamberger, *B.* 21, 55).—12. By heating di-phenyl-fumarate or di-phenyl-cinnamate (Anschütz, *B.* 18, 1945).—13. By heating CHPhBr.CHPhBr with alcoholic KSH in a sealed tube at 100° (Auwers, *B.* 24, 1779). 14. By heating thio-benzoic aldehyde at 190° (Baumann a. Klett, *B.* 24, 3308).

Properties.—Monoclinic plates, v. sol. ether, sl. sol. cold alcohol. Combines with N_2O_4 forming $C_2H_2Ph_2N_2O_4$ [c. 300°] crystallising in needles, sl. sol. hot alcohol (Gabriel, *B.* 18, 2438). Picryl chloride forms a combination $C_{14}H_{12}C_6H_2(NO_2)_3Cl$ [71°] (Liebermann, *B.* 8, 378).

Reactions.—1. Yields phenanthrene and toluene when passed through a *red-hot tube* (Graebe, *B.* 6, 126).—2. Reduced by HIAq at 150° to *s*-di-phenyl-ethane (Limpricht a. Schwanert, *A.* 145, 333).—3. *Bromine* added to an ethereal solution forms a product containing $C_{14}H_8Br_2O_2$ [121°] which gives rise to $C_{14}H_8Br_4O_2$ [150°] and $C_{14}H_5Br_5O_2$ [206°] and when dissolved in alcohol and reduced by sodium-amalgam yields $C_{14}H_{10}O_2$, crystallising from alcohol in flat plates [172°], whence PCl_5 forms $C_{14}H_9ClO_2$ [58°], $C_{14}H_7Cl_3O_2$ [87°], and $C_{14}H_5Cl_5O_2$ [190°] (Limpricht a. Schwanert, *A.* 153, 121).—4. Fuming HNO_3 added to an ethereal solution forms $C_{14}H_{11}N_3O_2$ [220°], which is converted by boiling alcohol into $C_{28}H_{22}N_2O_4$ [57°-73°] (Lorenz, *B.* 7, 1097; 8, 1050).

u-Di-phenyl-ethylene $CH_2:CPh_2$. (277°); (162° at 15 mm.). Formed by boiling $CHPh_2.CH_2Cl$ with alcoholic potash (Hepp, *B.* 7, 1409). Formed also by the action of benzene and $AlCl_3$ on

CH_2:CBr_2 and on CHBr:CBr_2 (Demole, *B.* 12, 2245; Anschütz, *A.* 235, 154. Liquid. Oxidised by CrO_3 to benzophenone. Combines with Br, forming $CPh_2Br.CH_2Br$, which readily gives off HBr, and forms bromo-di-phenyl-ethylene [40°] (c. 170° at 11 mm.).

Isomeride. [190°]. A product of the action of alcoholic potash on *exo*-chloro-di-phenyl-ethane (Hepp, *B.* 7, 1412). Small plates (from ether), v. sl. sol. alcohol.

Tetra-phenyl-ethylene $C_{26}H_{20}$ *i.e.* C_2Ph_4. Mol. w. 332. [221°]. (193° at 30 mm.).

Formation.—1. By heating CPh_2Cl_2 with finely-divided silver (Behr, *B.* 3, 751; 5, 277).—2. By heating benzophenone with zinc-dust (Staedel, *B.* 6, 178; *A.* 194, 307).—3. By strongly heating chloro-di-phenyl-ethane (Engler a. Bethge, *A.* 174, 194).—4. From CPh_2Br, by repeated distillation (Friedel a. Balsohn, *Bl.* [2] 33, 337).—5. A by-product in the preparation of tri-phenyl-methane from benzene, chloroform, and $AlCl_3$ (Schwarz, *B.* 14, 1526).

Preparation.—1. By adding Br to di-phenyl-methane and warming the resulting $CHPh_2Br$; the yield is 80 p.c. (Boissieu, *Bl.* [2] 49, 681).—2. By heating di-phenyl-methane (20 g.) with sulphur (8 g.) for 9 hours to 250°, and finally for one hour to 290°, exhausting with ether, and recrystallising the residue from benzene; the yield is 75 p.c. (Ziegler, *B.* 21, 780).

Properties.—White needles, v. sol. hot benzene and CS_2, v. sl. sol. ether. Yields benzophenone (2 mols.) on oxidation (Anschütz, *A.* 235, 221). Yields a tetrasulphonic acid.

Isomeride $C_{13}H_{10}$? [244°]. Formed by heating (α)-benzpinacolin with soda-lime at 370° (Zincke a. Thörner, *B.* 11, 1397). Needles (from alcohol). Perhaps identical with the preceding.

References.—Di-amido-, Bromo-, Di-chloro-, Di-iodo-, Nitro-, Nitro-amido-, and Oxy- Phenyl-ethylene.

PHENYL-ETHYLENE-DIAMINE $C_8H_{12}N_2$ *i.e.* $C_6H_5NH.CH_2.CH_2.NH_2$. (262° uncor.). Formed by boiling phenyl-amido-ethyl-phthalimide (got from bromo-ethyl-phthalimide and aniline) with conc. HClAq (Gabriel, *B.* 22, 2224). Liquid, miscible with water, forming an alkaline solution. Absorbs CO_2 from the air, forming a crystalline carbonate.—B''2HCl: small greenish needles, acid in reaction.—B''HCl. Neutral to methyl-orange.—B''H_2Br_2.—**Picrate** [143°]. Flat yellow tables.

Di-acetyl derivative $C_8H_{10}Ac_2N_2$. [116°]. Crystals, v. e. sol. Aq (Newman, *B.* 24, 2193).

Di-benzoyl derivative. [143·5°]. Prisms.

Phenyl-di-ethylene-triamine $C_6H_5N(C_2H_4.NH_2)_2$. (above 300°). Formed by the action of boiling conc. HBr upon its di-phthalyl derivative $NPh(C_2H_4.N:C_8H_4O_2)_2$ [211°], which is a product of the action of aniline on bromo-ethyl-phthalimide at 100°–180° (G.). Thick ammoniacal liquid, miscible with water. Absorbs CO_2 from the air.—B''H_3Br_3.—**Picrate.** [202°]. Needles (from alcohol).

Di-phenyl-ethylene-diamine $C_{14}H_{16}N_2$ *i.e.* $C_2H_4(NHPh)_2$. [63°]. Prepared by heating ethylene bromide (1 mol.) with aniline (4 mols.); the yield being 80 p.c. of the theoretical (Morley, *B.* 12, 1794; *cf.* Hofmann, *Pr.* 10, 104; Gretillat, *M. S.* [3] 3, 383). Plates, v. sol. alcohol. Yields a di-nitrosamine $C_2H_4(NPh.NO)_2$ [157°]. Reacts with benzoic aldehyde forming the compound $C_2H_4(NPh)_2$:CHPh [137°], while cuminic, salicylic, anisic, isobutyric, and heptoic aldehydes yield corresponding compounds [125°], [116°], [164°], and [95°] respectively (Moos, *B.* 20, 732).—B''2HCl.—B''H_2PtCl_6.

Mono-acetyl derivative. [128°]. Got by heating the base with chloro-acetic acid and NaOAc at 170° (Bischoff a. Nastvogel, *B.* 22, 1783).

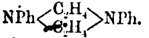
Di-acetyl derivative. [158°]. Crystals.

Di-phenyl-ethylene-diamine $C_{14}H_{16}N_2$ *i.e.* $CHPh(NH_2).CHPh(NH_2)$. [121°]. Formed, together with benzoic aldehyde, by the action of boiling HClAq on $C_{28}H_{24}N_2$, which is a product of the action of Na on amarine (Grossmann, *B.* 22, 2299). Formed also by the action of ammonia on the hydrocyanide of benzoic aldehyde (Limpricht a. Müller, *A.* 111, 142). Is perhaps identical with lophine. Plates (from hot water). Reacts with benzoic aldehyde forming CHPh:N.CHPh.CHPh.N:CHPh [164°], *m*-nitro-benzoic aldehyde forming $C_{28}H_{22}N_4O_2$ [161°], with salicylic aldehyde forming $C_{28}H_{24}N_2O_2$ [205°], and with cuminol forming a compound [168°].—B''2HCl. White needles (from hot water).—B''H_2PtCl_6: dark-yellow crystals.

Di-acetyl derivative. [above 350°].

Phthalyl derivative C_6H_4:C_2O_2:N_2H_2:$C_2H_2Ph_2$. [213°]. Minute crystals.

Di-phenyl-di-ethylene-diamine $C_{16}H_{18}N_2$ *i.e.*



$NPh\left<\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\right>NPh$. *Diphenylpiperazine. Di-phenylpyrazine hexahydride.* [163°]. (c. 300°). Prepared by heating ethylene bromide (1 pt.) with aniline (1 pt.) and NaOAc, and by the action of ethylene bromide on di-phenyl-ethylene-diamine at 120° (Morley, *B.* 12, 1795; Bischoff, *B.* 22, 1777; *cf.* Hofmann, *Pr.* 9, 277; 10, 104; Lellmann a. Schleich, *B.* 22, 1387; Bischoff, *B.* 22, 1778). Formed also by heating pyrazine hexahydride (1 pt.) with bromo-benzene (11 pts.) at 270° (Schmidt a. Wichmann, *B.* 24, 3239). Needles, sol. alcohol and ether. Its solutions are neutral to litmus. Yields a crystalline di-nitroso-derivative which may be reduced by tin and HCl to

$C_6H_3(NH_2)N\left<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\right>NC_6H_3NH_2$, which, when diazotised and combined with naphthyl-amine sulphonic acid, yields a colouring matter which dyes cotton.—B''2HCl.—B''H_2PtCl_6.

Methyl-iodide B'MeI. Crystalline. Yields $B'_2Me_2PtCl_6$.

Ethylo-iodide B'EtI. [100°]. Yields $B'_2Et_2PtCl_6$.

References.—Nitro- and Oxy- Di-phenyl-ethylene-diamine.

DI-PHENYL-ETHYLENE-DI-BENZYL-DI-AMINE $CHPh(NHCH_2Ph).CHPh(NHCH_2Ph)$. [153°]. Formed by reducing the compound CHPh(N:CHPh).CHPh(N:CHPh) [163°], which is itself got by reducing amarine with Na (Grossmann, *B.* 22, 2301). White needles.

DI-PHENYL-ETHYLENE-DICARBAMIC ACID $C_2H_4(NPh.CO_2H)_2$.

Ethyl ether Et_2A''. [88°]. Needles.

Chloride $C_2H_4(NPh.COCl)_2$. [183°]. Formed from di-phenyl-ethylene-diamine and $COCl_2$ (Hanssen, *B.* 20, 781). Prisms.

DI-PHENYL-ETHYLENE DI-*o*-CARBOXYLIC ACID $C_6H_4(CO_2H).CH:CH.C_6H_4.CO_2H$. [26[illegible]°]. Formed by heating for four hours at 215° $CO<\substack{C_6H_4\\O}>CH.CH_2.C_6H_4.CO_2H$ (2 pts.) with KCy (5 pts.) (Hasselbach, *A.* 243, 258). Small needles (from dilute HOAc). Changes on heating into the parent acid [196°]. Reduced by conc. HIAq to $C_2H_4(C_6H_4.CO_2H)_2$ [185°].—Ag_2A''. Flocculent pp.

Ethyl ether Et₂A''. [80°]. Needles.

Isomeride *v.* DI-PHENYL-MALEÏC ACID.

References.—NITRO- and OXY- DI-PHENYL-ETHYLENE CARBOXYLIC ACIDS.

DI-PHENYL-ETHYLENE-DI-ETHYL-DIAMINE $C_{18}H_{24}N_2$ *i.e.* $C_2H_4(NPhEt)_2$. [70°]. Formed from di-phenyl-ethylene-diamine and EtI (Hofmann, *Pr.* 10, 104).—$B''2HI$.—$B''H_2PtCl_6$: needles.

PHENYL-ETHYLENE-GLYCOL *v.* DI-OXY-ETHYL-BENZENE.

DI-PHENYL-ETHYLENE-DI-HYDRAZINE $C_{14}H_{18}N_4$ *i.e.* $C_2H_4(NPh.NH_2)_2$. [90°]. Formed from sodium phenyl-hydrazine and ethylene bromide in benzene (Burchard a. Michaelis, *B.* 21, 3202; *A.* 254, 116). Prisms or plates. Aldehyde forms $C_2H_4(NPh.N:CHMe)_2$ [82°]. Benzoic aldehyde forms an analogous body [193°]. Acetone and acetophenone form analogous compounds [72°] and [118°]. Phenyl-thiocarbimide forms $NH_2.NPh.C_2H_4.NPh.NH.CS.NHPh$ [164°] and $C_2H_4(NPh.NH.CS.NHPh)_2$ [194°]. Yields a crystalline nitroso- derivative [160°]. $SOCl_2$ forms $C_2H_4(NPh.N:SO)_2$ [123°] (Michaelis a. Ruhl, *A.* 170, 122).—$B''H_2Cl_2$. [212°]. Needles, sl. sol. HClAq.—$B''H_2SO_4$.—$B''2HNO_3$ [173°].—$B''H_2C_2O_4$ [183°].

Acetyl derivative $C_{14}H_{16}Ac_2N_2$. [222°].

Succinyl derivative $C_{14}H_{16}N_2:C_4H_4O_2$. [c. 126°].

Succinoxyl derivative $C_2H_4(NPh.NH.CO.C_2H_4.CO_2H)_2$. [203°].

Oxalyl derivative $C_{14}H_{16}N_2:C_2O_2$. [c. 183°].

Di-phenyl-di-ethylene-dihydrazine $(C_2H_4)_2(N_2HPh)_2$. [178°]. Got by heating phenyl-hydrazine with $C_2H_4Br_2$ and alcohol (Marckwald, *C. C.* 1888, 1410).

DI-PHENYL ETHYLENE DIKETONE $C_6H_5.CO.CH_2.CH_2.CO.C_6H_5$. *Diphenacyl. Succinophenone.* [134°] (A.); [140°] (C.); [142°-145°] (P.). *Formation.*—1. Together with the isomeric $\substack{CH_2.CO\\CH_2.CPh_2}>O$, by the action of succinyl chloride and $AlCl_3$ on benzene (Auger, *A. Ch.* [6] 22, 312; Claus, *B.* 20, 1374).—2. From acetophenone by treatment with fuming HNO_3 and reduction of the resulting $C_{16}H_{10}N_2O_4$ by zinc-dust and HOAc (Hollemann, *B.* 20, 3361).—3. By the action of KOHAq on di-benzoyl-propionic acid suspended in alcohol (Paal, *B.* 21, 3056).

Properties.—Needles, v. sol. ether.

Oxim $C_2H_4(CPh:NOH)_2$. [204°].

Phenyl-hydrazide $C_2H_4(CPh:N_2HPh)_2$. [180°]. Needles, v. sol. ether.

DI-PHENYL ETHYLENE DIKETONE CARBOXYLIC ACID *v.* PHENACYL-BENZOYL-ACETIC ETHER.

Di-phenyl-ethylene diketone di-*o*-carboxylic acid $C_{18}H_{14}O_6$ *i.e.* $C_2H_4(CO.C_6H_4.CO_2H)_2$ [172°]. Obtained by boiling di-phthalyl-ethane with alkalis (Gabriel a. Michael, *B.* 10, 1561, 2199; Roser, *B.* 17, 2622; 18, 803, 3115; Baumann, *B.* 20, 1486). Prisms (from water), v. sol. alcohol. Reconverted by conc. H_2SO_4 into di-phthalyl ethane $C_2H_4(C_2O_2C_6H_4)_2$. A boiling alcoholic solution of phenyl-hydrazine forms $C_{30}H_{22}N_4O_2$ [237°]. Hydroxylamine at 100° gives rise to $C_2H_4\left(C\lessdot\substack{C_6H_4\\N.O}>CO\right)_2$ [270°] (Baumann, *B.* 20, 1492).—Ag_2A'': small plates, sl. sol. hot water.

(*a*)-*Anhydride* $C_{18}H_{12}O_5$. [230°]. Got by heating the acid alone, or together with diphthalyl-ethane, by heating it for a short time with HCl. Needles (from alcohol).

(*β*)-*Anhydride* $C_{18}H_{12}O_5$. [202°]. Formed by more prolonged heating of the acid with HCl, and also, together with the (*a*)-isomeride, by heating the acid by itself. Prisms (from alcohol). Both anhydrides are reconverted into the acid by boiling alkalis, and into di-phthalyl-ethane by elimination of H_2O.

Isomeride *v.* DI-BENZOYL-SUCCINIC ACID.

PHENYL-ETHYLENE OXIDE $\substack{CH_2\\CHPh}>O$. (260° at 50 mm.). Formed by heating di-oxy-ethyl-benzene with dilute H_2SO_4 (Breuer a. Zincke, *B.* 11, 1402). Oil. Converted by PBr_5 into $CHPhBr.CH_2Br$.

Tetra-phenyl-ethylene oxide *v.* BENZPINACOLIN.

PHENYL-ETHYLENE SULPHIDE $\substack{CH_2\\CHPh}>S$. S.G. $\frac{16}{}$ 1·099. Formed from $PhCHBr.CH_2Br$ by successive treatment with alcoholic KSHAq (Spring a. Marsenille, *Bl.* [3] 7, 13). Oil with strong smell, sol. alcohol-ether. Oxidised by CrO_3 to benzoic acid.

Di-phenyl-ethylene sulphide $\substack{CHPh\\CHPh}>S$. [169°]. A product of the distillation of benzyl sulphide (Barbier, *J.* 1876, 421). Needles.

Di-phenyl-ethylene disulphide $C_2H_4(SPh)_2$. [65°]. Formed from NaSPh and $C_2H_4Br_2$ (Ewerlöf, *B.* 4, 716). Needles, insol. water.

DI-PHENYL-ETHYLENE DISULPHONE $C_2H_4(SO_2C_6H_5)_2$. [180°].

Formation.—1. By oxidation of $C_2H_4(SPh)_2$ (Ewerlöf, *B.* 4, 717).—2. By boiling sodium benzene sulphinate (100 pts.) with $C_2H_4Br_2$ (58 pts.) in alcohol (Otto, *B.* 13, 1279; *J. pr.* [2] 30, 174). 3. By adding $CH_3.CCl_2.CO_2Na$ (1 mol.) to $C_6H_5.SO_2Na$ (2 mols.) in weak alcoholic solution, kept neutral by Na_2CO_3 (Otto, *J. pr.* [2] 40, 531). 4. By heating $CH_3.CCl_3$ with $C_6H_5.SO_2Na$ at 160° (Otto, *B.* 21, 1691).

Properties.—Triclinic needles or plates, sl. sol. water, m. sol. alcohol, v. sol. HOAc.

Reactions.—1. *Sodium-amalgam* reduces it to alcohol and $C_6H_5SO_2Na$, which is finally reduced to C_6H_5SNa.—2. *Chlorine* in diffused daylight forms $C_2H_4Cl_2$ and benzene sulphonic chloride. In sunlight the products are $C_2H_4Cl_2$, SO_2Cl_2, and chlorinated benzenes.—3. Boiling aqueous KOH splits it up into $C_6H_5SO_2K$ and $C_6H_5.SO_2.C_2H_4.OH$. Conc. KOHAq forms a compound [88°] crystallising from alcohol.—4. Aqueous NH_3 forms $C_6H_5.SO.ONH_4$ and $(C_6H_5.SO_2.CH_2.CH_2)_2NH$ [78°] which yields $B'HCl$ [193°], $B'_2H_2PtCl_6$, a nitrate [190°], and the derivatives $(C_6H_5.SO_2.CH_2.CH_2)_2NMe$ and $(C_6H_5.SO_2.CH_2.CH_2)_2NMeHCl$ [221°].—5. Aqueous *ethylamine* forms $C_6H_5.SO_2NH.Et$ and $C_6H_5.SO_2.C_2H_4NHEt$, an oil which yields B'HCl [130°].—6. Alcoholic KCy forms $C_6H_5SO_2K$ and $C_2H_4(CN)_2$.

PHENYL-ETHYLENE-THIO-UREA $CS{<}\begin{matrix}NPh\\NH\end{matrix}{>}C_2H_4$. [155°]. Formed from phenyl-ethylene-diamine and CS_2 (Newman, *B.* 24, 2191). White plates, v. sol. alcohol.

Di-phenyl-ethylene-ψ-thio-urea $C_2H_4{<}\begin{matrix}NPh\\S\end{matrix}{>}C{:}NPh$. [136°]. (above 300°). Formed by heating di-phenyl-thio-urea with ethylene bromide (Will, *B.* 14, 1490; 15, 343). Plates (from alcohol). $KClO_3$ and HClAq form $C_{15}H_{14}N_2SO_3$ [187°] (Andreasch, *M.* 4, 134).—$B'H_2SO_4$: thick prisms, v. sol. water.

Di-phenyl-ethylene-di-thio-di-urea $C_{16}H_{18}N_4S_2$ *i.e.* $C_2H_4(NH.CS.NHPh)_2$. [193°]. Formed from $C_2H_4(NH_2)_2$ and phenyl-thio-carbimide in alcohol (Lellmann a. Würthner, *A.* 228, 234). White scales, insol. alcohol, sl. sol. HOAc. Decomposed by heat, giving di-phenyl-thio-urea and a crystalline body [164°].

PHENYL-ETHYLENE-UREA $C_2H_4{<}\begin{matrix}NPh\\NH\end{matrix}{>}CO$. [161°]. Formed from phenyl-ethylene-diamine hydrochloride and potassium cyanate, NH_3 being given off (Newman, *B.* 24, 2192). Plates, v. sol. alcohol, insol. cold water.

Di-phenyl-ethylene-urea $\begin{matrix}CH_2.NPh\\CH_2.NPh\end{matrix}{>}CO$. [209°]. Formed by the action of $COCl_2$ in benzene on $C_2H_4(NHPh)_2$; an intermediate body being $C_{31}H_{28}N_4Cl_2O_3$ (Michler a. Keller, *B.* 14, 2183; Hanssen, *B.* 20, 784). Plates.

PHENYLETHYL-ETHYL-PYRIDINE $C_{15}H_{17}N$ *i.e.* $N{\ll}\begin{matrix}C(CH_2.CH_2Ph).CH\\CH{:}CEt\text{———}CH\end{matrix}$ (316° cor.). S.G. $\frac{0}{4}$ 1·016. Formed by reducing styryl-ethyl-pyridine with HIAq at 165° (Plath, *B.* 21, 3093; 22, 1057). Oil, v. sl. sol. water, v. sol. alcohol and ether, volatile with steam. Yields $C_{15}H_{15}Br_2N$ [128°] whence AgOAc forms $C_{15}H_{15}(OAc)_2N$ (315°-320°). — $B'_2H_2PtCl_6$. [168°]. Yellow needles. — $B'HHgCl_3$. [136°]. Needles. — $B'HAuCl_4$ aq: crystalline mass.

Hexahydride $C_{15}H_{23}N$. (314°). S.G. $\frac{0}{4}$ ·9668. Got by reducing the preceding body in alcohol with Na. Oil, sl. sol. water, miscible with alcohol and ether.

PHENYL-ETHYL-FURFURANE $C_6H_5.CH_2.CH_2.C_4H_3O$. (241°). A product of the action of Na on an alcoholic solution of $C_4H_3O.CH{:}CPh.CN$, which is formed by condensation of furfuraldehyde with phenyl-acetonitrile (Freund a. Immerwahr, *B.* 23, 2848). Oil, smelling like CH_2Ph_2.

DI-PHENYL-ETHYL-GUANIDINE $C_{15}H_{17}N_3$ *i.e.* NHEt.C(NPh).NHPh. Got from phenyl-ethyl-cyanamide and aniline at 100° (Weith, *B.* 8, 1531). Crystalline.—$B'_2H_2PtCl_6$.

PHENYL-ETHYL-HYDANTOÏN $C_{11}H_{12}N_2O_2$ *i.e.* $CHPh{<}\begin{matrix}CO.NEt\\NH.CO\end{matrix}$. [94°]. Formed from phenyl-hydantoïn, alcoholic KOH, and EtI (Pinner, *B.* 21, 2325). Prisms, v. sol. alcohol, sl. sol. cold water. Decomposed by baryta into ethylamine and phenyl-amido-acetic acid.

Phenyl-ethyl-ψ-hydantoïn $CHPh{<}\begin{matrix}CO.NEt\\O-C{:}NH\end{matrix}$. Separates from a dilute alkaline solution of the preceding isomeride on standing. Slender needles, insol. water, nearly insol. alcohol. Decomposed by heating with baryta-water into NH_3, NH_2Et, and α-oxy-phenyl-acetic acid.

***u*-PHENYL-ETHYL-HYDRAZINE** $C_8H_{12}N_2$ *i.e.* $NPhEt.NH_2$. (230°). Formed by reducing the nitrosamine of ethyl-aniline with zinc-dust, HOAc, and alcohol (Fischer, *B.* 8, 1642; *A.* 199, 325; Philips, *B.* 20, 2485). Formed also from EtBr and $NPhNa.NH_2$ in benzene (Michaelis a. Philips, *A.* 252, 270). Oil. Reduces Fehling's solution on warming. Oxidised by HgO to diphenyl-di-ethyl-tetrazone NPhEt.N:N.NPhEt [108°]. $SOCl_2$ forms oily NPhEt.N:SO (Michaelis, *B.* 22, 2231).—B'HCl. Plates.

Acetyl derivative NEtPh.NHAc. [80°].

Ethylo-bromide $NH_2.NPhEt_2Br$. Trimetric prisms (from alcohol); $a{:}b{:}c = ·822{:}1{:}·827$. V. e. sol. water, insol. ether. Decomposes at 193°. Insol. KOHAq. Converted by moist Ag_2O into a caustic hydroxide. Yields also $(NH_2.NPhEt_2)_3H_5Fe_2Cy_{12}\,2aq$ (Fischer, *A.* 190, 187).

Ethylo-chloride $NH_2.NPhEt_2Cl$. [198°]. Needles, v. e. sol. water. $B'_2Et_2PtCl_6$.

Ethylo-iodide $NH_2.NPhEt_2I$. [145°].

***s*-Phenyl-ethyl-hydrazine** NHPh.NHEt. Formed, together with the preceding isomeride, by heating phenyl-hydrazine with EtBr. The crude product is dissolved in water mixed with NaOHAq, and the ppd. oil extracted with ether. The ethereal solution is freed from phenyl-hydrazine by HCl and the filtrate oxidised by HgO. On addition of HCl it deposits di-phenyl-di-ethyl-tetrazone, and the mother-liquor yields by steam-distillation oily $C_6H_5.N{:}NEt$ (175°-185°). The NPh:NEt is then reduced by sodium-amalgam (Ehrhardt a. Fischer, *B.* 11, 613).

Properties.—Oil, sol. alcohol and ether. Readily reduces Fehling's solution and HgO. Zinc-dust and HOAc yield aniline and ethylamine. —$B'H_2C_2O_4$: needles, v. sol. hot water.

DI-PHENYL-ETHYLIDENE-DIAMINE *v.* *Ethylidene-di-aniline*, vol. ii. p. 496.

DI-PHENYL-ETHYLIDENE-DI-ETHYL-DIAMINE $C_{18}H_{24}N_2$ *i.e.* $CHMe(NPhEt)_2$. Formed from ethyl-aniline and aldehyde (Schiff, *A.* 140, 95; *cf.* Schultz, *B.* 16, 2601). Thick liquid.—$B'_2H_2PtCl_6$.

PHENYL-ETHYLIDENE DI-ETHYL DI-SULPHONE $CH_3.CPh(SO_2Et)_2$. [101°]. Formed from benzylidene di-ethyl di-sulphone, MeI, and EtONa (Fromm, *A.* 253, 154). Needles.

PHENYL-ETHYLIDENE-HYDRAZINE $CH_3.CPh{:}N.NH_2$. (255°). Formed from acetophenone and hydrazine hydrate (Curtius, *J. pr.* [2] 44, 540). Liquid. Yields $CH_3.CPh{:}N.N{:}CHPh$ [59°] and $N_2(CPh.CH_3)_2$ [121°].

DI-PHENYL ETHYLIDENE DISULPHONE $CH_3.CH(SO_2Ph)_2$. [102°]. Got by oxidising $CH_3.CH(SPh)_2$ or $CH_3.C(SPh)_2.CO_2H$ with dilute (1 p.c.) $KMnO_4$ (Escales a. Baumann, *B.* 19, 2815). Needles or thin lamellæ, insol. water, acids, and alkalis, sl. sol. alcohol and ether. Not attacked by alcoholic potash at 140°.

PHENYL-ETHYLIDENE-DI-THIO-DI-GLYCOLLIC ACID $CH_3.CPh(S.CH_2.CO_2H)_2$.

[186°]. Got by the action of ZnCl$_2$ on a mixture of acetophenone and thioglycollic acid (Bongartz, *B.* 21, 483). Needles, sol. hot water, CHCl$_3$, and HOAc.

PHENYL-ETHYL-IMESATIN *v. Di-phenyl-di-ethyl-diamide* of ISATIN.

PHENYL ETHYL KETONE $C_9H_{10}O$ *i.e.* $C_6H_5.CO.C_2H_5$. *Propiophenone.* [21°]. (218° cor.) (M. a. G.). V.D. 4·64 (obs.). S.G. ^{0} 1·009 (W.).

Formation.—1. By distilling a mixture of calcium benzoate and propionate (Barry, *B.* 6, 1006). 2. From BzCl and ZnEt$_2$ (Freund, *A.* 118, 20; Kalle, *A.* 119, 166). 3. By the action of Na on a mixture of BzCl and EtI (Bechi, *B.* 12, 463).—4. By the action of propionyl chloride on benzene in presence of AlCl$_3$ (Morley a. Green, *B.* 17, 3018; Pampel a. Schmidt, *B.* 19, 2896).—5. By the decomposition of propylene phenyl-ethyl-ketate by HI or H$_2$SO$_4$ (Morley a. Green).—6. By oxidising CHPhEt.OH (Wagner, *J. R.* 16, 325).—7. From benzoyl cyanide and ZnEt$_2$, either directly or by oxidising the product (Frankland a. Louis, *C. J.* 37, 715).—8. From phenylallylene (Körner, *B.* 21, 277).

Properties.—Tables. Does not combine with NaHSO$_3$. Yields benzoic acid on oxidation. Reduced by sodium-amalgam to CHPhEt.OH (211°).

Oxim CPhEt:NOH. Oil.

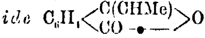
Phenyl hydrazide. Oil.

Phenyl ethyl diketone $C_6H_5.CO.CO.C_2H_5$. *Propionyl-benzoyl.* (239°). Got by distilling its mono-oxim (obtained from ethyl benzoyl-acetic ether) with dilute H$_2$SO$_4$ (Müller a. Pechmann, *B.* 22, 2131). Pungent liquid, volatile with steam, m. sol. water.

Reference.—NITRO- and OXY- PHENYL ETHYL KETONE.

PHENYL ETHYL KETONE DIBROMIDE *v.* DI-BROMO-CUMENE.

PHENYL ETHYL KETONE *o*-CARBOXYLIC ACID $C_2H_5.CO.C_6H_4.CO_2H$. *Propionyl-benzoic acid.* [92°]. Formed by boiling phthalyl-propionic acid with KOHAq (Gabriel, *B.* 11, 1014; 19, 840). Needles (from dilute alcohol).—AgA'.

Anhydride  $C_6H_4<\begin{array}{l}C(CHMe)\\CO\text{———}\end{array}>O$. [69°]. Formed by heating phthalic anhydride with succinic acid and NaOAc (G.). Formed also by distilling the anhydride of the dicarboxylic acid (Roser, *B.* 18, 3117). Plates (from water). Combines with N$_2$O$_4$ forming $C_{10}H_8N_2O_6$ [90°].

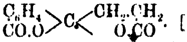
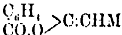
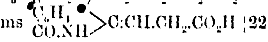
Amide $C_6H_4(CO.NH_2).CO.C_2H_5$. [159°]. Formed from the anhydride and alcoholic NH$_3$.

Isomerides *v.* BENZOYL-PROPIONIC ACID, vol. i. p. 487.

Phenyl ethyl ketone dicarboxylic acid $C_6H_5.CO.CH_2.CH(CO_2H)_2$. *β-Benzoyl-isosuccinic acid.* [180°]. Obtained by saponifying its ether which is formed from ω-bromo-acetophenone and sodium malonic ether (Bischoff, *B.* 16, 1044; 19, 9[illegible]; Kues a. Paal, *B.* 18, 3321). Needles, v. sol. alcohol and ether. Yields β-benzoyl-propionic acid when heated.—Ag$_2$A'': needles.—Et$_2$A'': oil.

Phenyl hydrazide $C_6H_5.C(N_2HPh).CH_2.CH(CO_2H)_2$. [120°].

Phenyl ethyl ketone dicarboxylic acid $C_6H_4(CO_2H).CO.CH_2.CH_2.CO_2H$. [137°]. Formed by boiling its dilactone with water or aqueous alkalis. Small six-sided prisms, re-converted by heat into the dilactone.—CaA''.—BaA''.—Ag$_2$A''.

Dilactone  $\begin{array}{l}C_6H_4\\CO.O\end{array}>C<\begin{array}{l}CH_2.CH_2\\O.CO\end{array}$. [120°]. A product of the action of phthalic anhydride on succinic acid and NaOAc at 250° (Roser, *B.* 17, 2770; 18, 804, 3115). Needles, sl. sol. cold water. At 260° it gives off CO$_2$ and changes to  $\begin{array}{l}C_6H_4\\CO.O\end{array}>C:CHMe$. HIAq and P at 190° reduce it to $C_6H_4(CO_2H).CH_2.CH_2.CH_2.CO_2H$. Cold NH$_3$Aq forms  $\begin{array}{l}C_6H_4\\CO.NH\end{array}>C:CH.CH_2.CO_2H$ [225°]. Boiling alcoholic NH$_3$ forms $C_{11}H_9NO_4$ [c. 205°]. Sodium-amalgam reduces it to phthalyl-propionic acid $C_{11}H_{10}O_4$. Phenyl hydrazine forms $C_{17}H_{14}N_2O_3$ [210°] which gives CaA'$_2$ aq.

Isomeride *v.* BENZOYL-SUCCINIC ACID.

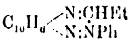
Phenyl ethyl ketone tetracarboxylic acid $C_6H_4(CO_2H).CO.C(CO_2H)_2.CH_2.CO_2H$. Formed by the action of chloro-acetic ether on $C_{17}H_{19}NaO_7$ which is got from phthalyl-malonic ether and NaOEt (Wislicenus, *A.* 212, 58). Oil.—Ag$_4$A^{IV}.

PHENYLETHYL METHYL KETONE *v.* BENZYL-ACETONE.

Diphenylethyl methyl ketone $CH_3.CPh_2.CO.CH_3$. [41°]. (311° i.V.). A product of the action of zinc and HCl on an alcoholic solution of acetophenone (Zincke a. Thörner, *B.* 11, 1989). Prisms (from alcohol).

PHENYLETHYL-METHYL-PYRIDINE $C_{14}H_{15}N$ *i.e.* $C_2H_4Ph.C_5H_3MeN$. (290°–295°). S.G. $\frac{0}{4}$ 1·0283. Formed by reducing styryl-methyl-pyridine with HIAq at 160° (Bachér, *B.* 21, 3076). Oil, volatile with steam. $B'_2H_2PtCl_6$. [168°].—$B'HHgCl_3$ aq. [95°]. Silky needles.—$B'C_6H_3N_3O_7$. [156°]. Yellow needles

Hexahydride $C_{14}H_{21}N$. (c. 288°). S.G. $\frac{0}{4}$ ·9775. Got by reducing styryl-methyl-pyridine in alcohol with Na. Liquid, v. sl. sol. water.

PHENYL-ETHYL-(β)-NAPHTHOTRIAZINE DIHYDRIDE $C_{19}H_{17}N_3$ *i.e.*  $C_{10}H_6<\begin{array}{l}N:CHEt\\N:NPh\end{array}$ [219°]. Formed by adding propionic aldehyde to benzene-azo-(β)-naphthylamine in alcohol (Goldschmidt a. Poltzer, *B.* 21, 1006). White needles, v. sol. alcohol. B'HCl. [258°].—$B'_2H_2PtCl_6$. Small yellow crystals.

PHENYL-ETHYL-OXAMIDE $C_{10}H_{12}N_2O_2$ *i.e.* NHPh.CO.CO.NHEt. [170°]. Formed by the action of ethylamine on phenyloxamic ether or of aniline on ethyloxamic ether (Wallach, *A.* 184, 66; 214, 259). Needles (from alcohol). Converted by PCl$_5$ (2 mols.) into a base which forms the salt $(C_{10}H_9N_2Cl)_2H_2PtCl_6$.

Di-phenyl-di-ethyl-oxamide *v.* vol. iii. p. 654.

PHENYL-ETHYL-PHENOL *v.* OXY-DI-PHENYL-ETHANE.

PHENYL-*p*-ETHYL-PHENYL-ETHANE $C_6H_5.CH_2.CH_2.C_6H_4.C_2H_5$. (294°). Formed by reduction of $C_6H_5.CH_2.CO.C_6H_4Et$ with HI and P (Söllscher, *B.* 15, 1681). Liquid.

Isomeride. Got by the action of zinc-dust on a mixture of ethyl-benzene and α-bromo-ethyl-benzene (Radziszewski, *B.* 6, 811; 7, 140). Gives *p*-benzoyl-benzoic acid on oxidation.

PHENYL-ETHYLPHENYL-ETHYLENE $C_6H_5.CH:CH.C_6H_4Et$. [90°]. Formed by boiling $CH_2Ph.CH(OH).C_6H_4Et$[1:4] with dilute H$_2$SO$_4$ (Söllscher, *B.* 15, 1681). Plates.

PHENYL *p*-ETHYLPHENYL KETONE $C_6H_5.CO.C_6H_4Et$. (331°) at 720 mm. Prepared by the action of $AlCl_3$ on a mixture of BzCl and ethylbenzene (Söllscher, *B.* 15, 1682; Smith, *B.* 24, 4029). Liquid, sol. alcohol and ether. Yields two oxims [108°] and [142°], both giving the same acetyl derivative [95°].

PHENYL-ETHYL-PHENYL METHANE *v.* BENZYL-ETHYL-BENZENE.

PHENYL - ETHYLPHENYL - THIO - UREA $NHPh.CS.NH.C_6H_4Et$. [104°]. Formed from *p*-ethyl-phenyl-thiocarbimide and aniline in alcohol (Mainzer, *B.* 16, 2020). Plates.

PHENYL-DI-ETHYL-PHOSPHINE $PEt_2C_6H_5$. (222° cor.). S.G. ^{13} ·957. Formed from $C_6H_5PCl_2$ and $ZnEt_2$ (Michaelis, *B.* 8, 493; *A.* 181, 345). Oil. Absorbs oxygen from air, yielding $OPEt_2C_6H_5$ [56°]. Combines also with Cl and S forming crystalline $C_{10}H_{15}PCl_2$ and $C_{10}H_{15}PS$. — $B'2HCl$. — $B'_2H_2PtCl_6$. — $B'HI$. — $B'EtI$. [115°]. — $B'_2Et_2PtCl_6$. — $B'MeI$. [95°]. — $B'_2Me_2PtCl_6$.

Di-phenyl-ethyl-phosphine $PEtPh_2$. (298°). Formed from Ph_2PCl and $ZnEt_2$ (Michaelis a. Link, *A.* 207, 214). Liquid, sol. alcohol and ether. Yields $OPEtPh_2$ on oxidation. EtI yields Ph_2PEt_2I [204°] which gives $(Ph_2PEt_2Cl)_2PtCl_4$ [218°]. MeI gives $Ph_2PEtMeI$ [181°] S. 1·5 at 22°; 50 at 100°, which gives $(Ph_2PEtMeCl)_2PtCl_4$ [220°] and $Ph_2PEtMe.O.C_6H_2(NO_2)_3$ [86°].

Di-phenyl-ethyl-phosphine oxide $PEtPh_2O$. [121°]. Formed as above, and also by the action of Ag_2O on Ph_3PEtI (Michaelis a. Soden, *A.* 229, 317). Prisms, sol. ether and ligroïn.

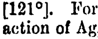
PHENYL-DI-ETHYL PROPENYL TRISULPHONE $PhSO_2CH_2.CMe(SO_2Et)_2$. [128°]. Got from EtSH and $PhS.CH_2.CO.CH_3$, the product being oxidised (Autenrieth, *B.* 24, 169). Plates.

Di-phenyl ethyl propenyl trisulphone $EtSO_2.CH_2.CMe(SO_2Ph)_2$. [139°]. Made in like manner from PhSH and $EtS.CH_2.CO.CH_3$. Needles (Autenrieth, *B.* 24, 1513).

TRI - PHENYL - ETHYL - PROPYL - DI - THIO - BIURET $C_2S_2N_3Ph_3EtPr$. The (α)- compound [166°] is formed by the action of di-phenyl-propyl-thio-urea on ClCS.NPhEt, while the (β)-compound [165°] is got from di-phenyl-ethyl-thio-urea and ClCS.NPhPr (Billeter a. Strohl, *B* 21, 109). Both crystallise in needles, v. sol. hot alcohol.

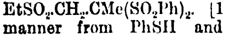
DI - PHENYL - ETHYL - PROPYL - THIO - UREA NPhEt.CS.NPhPr. [66°]. Formed by the action of $CSCl_2$ on propyl-aniline followed by ethyl-aniline or *vice versâ* (Billeter a. Strohl, *B.* 21, 103).

PHENYL-ETHYL-PYRAZOLE $C_{11}H_{12}N_2$ *i.e.*



$NPh{<}\begin{matrix}CEt{:}CH\\ N{=}CH\end{matrix}$. (274°). S.G. ^{15} 1·064. Formed from phenyl-hydrazine and propionyl-acetic aldehyde (Claisen a. Stylos, *B.* 21, 1148). Oil.

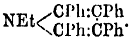
PHENYLETHYL-PYRIDINE



$CH{<}\begin{matrix}CH{:}CH\\ CH.N\end{matrix}{>}C.CH_2.CH_2Ph$. [−3°]. (289° cor.). S.G. $\frac{0}{4}$ 1·0465. Formed by reducing styryl-pyridine with HI (Baurath, *B.* 21, 821). Liquid, sl. sol. water, volatile with steam. — $B'_2H_2PtCl_6$. [186°]. — $B'HAuCl_4$. [150°]. Long yellow needles. — $B'HHgCl_3$. [149°].

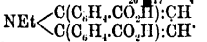
Hexahydride $C_{13}H_{19}N$. (288° cor.). S.G. $\frac{0}{4}$ ·9874. Got by reducing the preceding base in alcohol with Na. Liquid, smelling like piperidine, sl. sol. water. Turns moist litmus blue. Has toxic properties similar to those of coniine. Forms an oily nitrosamine. Yields pyridine carboxylic acid on oxidation. — $B'HCl$. [155°]. — $B'_2H_2PtCl_6$. [189°]. — $B'HAuCl_4$. [134°].

TETRA-PHENYL-ETHYL-PYRROLE



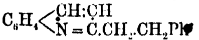
$NEt{<}\begin{matrix}CPh{:}CPh\\ CPh{:}CPh\end{matrix}$. [221°]. Formed by heating bidesyl with aqueous $NEtH_2$ at 150° (Fehrlin, *B.* 22, 555). Needles (from chloroform) or plates (from HOAc).

DI-PHENYL-ETHYL-PYRROLE DI-*o*-CARBOXYLIC ACID $C_{20}H_{17}NO_4$ *i.e.*



$NEt{<}\begin{matrix}C(C_6H_4.CO_2H){:}CH\\ C(C_6H_4.CO_2H){:}CH\end{matrix}$. [220°]. Formed by heating $C_2H_4(CO.C_6H_4.CO_2H)_2$ with ethylamine solution (Baumann, *B.* 20, 1488). Yellow plates (from alcohol), insol. water. — Ag_2A''.

PHENYLETHYL-QUINOLINE



$C_6H_4{<}\begin{matrix}CH{:}CH\\ N{=}C.CH_2.CH_2Ph\end{matrix}$. [c. 30°]. Formed by reducing styryl-quinoline with HI (Heymann a. Königs, *B.* 21, 1426). Crystals. — Picrate. [c. 130°]. Yellow prisms, sl. sol. alcohol.

PHENYL-ETHYL SULPHIDE Ph.S.Et. (204° i.V.) at 744 mm. S.G. ^{19} :1·032. Formed by heating PhSNa with EtI in sealed tubes at 120° (Beckmann, *J. pr.* [2] 17, 457). Obtained also by the action of H_2S at 50° on $C_6H_5.SO.OEt$ (Otto a. Rössing, *B.* 20, 2275) and by the action of EtSH on $C_6H_5.N_2Cl$ (Stadler, *B.* 17, 2078). Liquid, with nasty smell.

Sulphonic acid $C_2H_5.S.C_6H_4.SO_3H$. Formed by boiling $C_2H_5S.N_2.C_6H_4.SO_3Na$ with alcohol. — NaA′: plates.

Phenyl ethyl disulphide PhS_2Et. Formed together with Et_2S_2 by heating $C_6H_5SO_2H$ with EtSH at 100° (Otto a. Rössing, *B.* 19, 3135; 20, 189). Heavy oil. Decomposed by alcoholic potash into EtSH, Ph_2S_2, $C_6H_5SO_2H$, and ethane sulphinic acid.

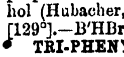
PHENYL ETHYL SULPHONE $C_8H_{10}SO_2$ *i.e.* $C_6H_5.SO_2.C_2H_5$. [43°]. (above 300°). Formed from $C_6H_5SO_2Na$ and EtBr or $CH_3.CBr_2.CO_2Na$ (Otto, *B.* 13, 1274; *J. pr.* [2] 40, 535). Formed also from $CH_3.CH(SO_2Ph).CO_2H$ by the action of alkalis and by oxidising PhSEt with dilute $KMnO_4$ (Beckmann, *J. pr.* [2] 17, 458). Monoclinic plates (Fock, *B.* 19, 1230), sol. hot water, v. sol. alcohol.

α-Carboxylic acid $C_6H_5.SO_2.CHMe.CO_2H$. *Phenyl sulphono-propionic acid.* [116°]. Formed by saponifying its ether, which is got from $C_6H_5SO_2Na$ and $CH_3.CHBr.CO_2Et$ (Otto, *J. pr.* [2] 40, 548). Groups of needles, v. sol. hot water. — NaA′. — BaA'_2 2aq: leafy aggregates.

Ethyl ether EtA′. [c. 17°]. Oil.

β-Carboxylic acid $C_6H_5.SO_2.CH_2.CH_2.CO_2H$. [124°]. Formed from benzene sulphinic acid and β-iodo-propionic acid (Otto, *B.* 21, 95). Plates, sl. sol. cold water, m. sol. ether.

PHENYL-ETHYL-THIAZOLE $C_{11}H_{11}NS$ *i.e.*



$N{<}\begin{matrix}CEt.S\\ CPh{:}CH\end{matrix}$. (296° cor.). Formed from thio-propionamide and bromo-acetophenone in alcohol (Hubacher, *A.* 259, 231). Oil. — $B'_2H_2PtCl_6$. [129°]. — B′HBr. [70°]. White needles.

TRI-PHENYL-DI-ETHYL-DI-THIO-BIURET NPhEt.C(NPh).S.CS.NPhEt. [158°]. Formed from NPhEt.CS.Cl (2 mols.) and aniline (1 mol.)

Billeter a. Strohl, *B.* 21, 108). Yellow needles, l. sol. alcohol.

PHENYL-ETHYL-THIOCARBAMIC ACID NPhEt.CS.OH.

Ethyl ether EtA. [18°]. (143° at 12 mm.). S.G. ^{15} 1·066. Formed from NPhEt.CS.Cl nd NaOEt (Billeter a. Strohl, *B.* 20, 1629; 21, 04). Crystals.

Phenyl-ether PhA′. [69°]. Formed from he chloride and phenol. Flat needles.

Chloride NPhEt.CS.Cl. [57°]. Formed rom ethyl-aniline and $CSCl_2$. Prisms (from igroïn). Converted by alcohol into $(NPhEt.CS)_2O$ 143°], S. (alcohol) 7 at 15°.

Phenylethyl-thiocarbamic acid. Phenyl-thylamine salt $C_2H_4Ph.NH.CS.SNH_3.C_2H_4Ph$ [130°]. Formed rom phenylethylamine and CS_2 (Neubert, *B.* 19, 825). Sol. hot water and alcohol.

Phenyl-ethyl-di-thio-carbamic acid NPhEt.CS.SH.

Ethyl ether EtA′. [67°]. (305°–315°). Formed by heating NPh:C(NPhEt).SEt with CS_2 at 160° (Bernthsen a. Friese, *B.* 15, 568, 533). Formed also from NPhEt.CSCl and NaSEt (B. a. S.). Prisms (from ether). Forms a crystalline compound with MeI.

Phenyl ether PhA′. [127°]. Formed from NPhEt.CS.Cl and PhSH (B. a. S.). Needles.

PHENYL-ETHYL-THIO-SEMI-CARBAZIDE NHEt.CS.NH.NHPh. [122°]. Formed from ethyl-thiocarbimide and phenyl-hydrazine (Dixon, *C. J.* 55, 302). White crystals, v. sl. sol. water. $FeCl_3$ gives a red colour changing to blackish-green.

Isomeride NHPh.CS.NH.NHEt. [110°]. Formed from phenyl-thiocarbimide and ethyl-hydrazine (Fischer, *A.* 199, 296). Needles.

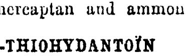
Di-phenyl-ethyl-thio-semi-carbazide NPhEt.NH.CS.NHPh. [149°]. Formed from α-phenyl-ethyl-hydrazine and phenyl-thiocarbimide (Michaelis a. Philips, *A.* 252, 273).

PHENYLETHYL-THIOCARBIMIDE $C_2H_4Ph.NCS$. Formed from phenylethyl-amine by successive treatment with CS_2 and $HgCl_2$ (Neubert, *B.* 19, 1825). Yellow oil.

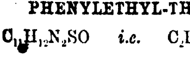
PHENYL ETHYL DITHIOCARBONATE CS(OEt)(SPh). Formed by mixing solutions of $C_6H_5.N_2Cl$ and potassium ethyl dithiocarbonate at 0° (Leuckart, *J. pr.* [2] 41, 186). Reddish-yellow oil, sl. sol. water, slightly volatile with steam. Converted by heating with alcoholic NH_3 into phenyl mercaptan and ammonium sulphocyanide.

PHENYLETHYL-THIOHYDANTOÏN

$C_{11}H_{12}N_2SO$ *i.e.*

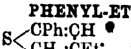


$C_2H_4Ph.N:C\left<\begin{matrix}S-CH_2\\NH.CO\end{matrix}\right.$ or



$CS\left<\begin{matrix}N(C_2H_4Ph).CH_2\\NH\text{——}CO\end{matrix}\right.$. The hydrochloride B′HCl [138°] is formed from phenylethyl-thio-urea and chloro-acetic acid (Neubert, *B.* 19, 1822).

PHENYL-ETHYL-THIOPHENE $C_{12}H_{12}S$ *i.e.*



$S\left<\begin{matrix}CPh:CH\\CH:CEt\end{matrix}\right.$ [40°]. Obtained by heating $CH_2Bz.CHEt.CO_2Na$ with P_2S_5 (Dittrich a. Paal, *B.* 21, 3457). Small plates. Gives a cherry-red colour with isatin and H_2SO_4 and a bluish-green colour with phenanthraquinone and HOAc.

u-PHENYL-ETHYL-THIO-UREA $C_9H_{12}N_2S$ i.e. $NPhEt.CS.NH_2$. [1[illegible]8°]. Formed from ethyl-aniline hydrochloride and potassium sulphocyanide (Gebhardt, *B.* 17, 2094). Large pearly prisms (from alcohol).

Benzoyl derivative NPhEt.CS.NHBz. [134°]. Formed from ethylaniline and benzoyl-thiocarbimide (Dixon, *C. J.* 55, 305). Pale lemon-yellow prisms, insol. water, sol. alcohol.

s-Phenyl-ethyl-thio-urea NHPh.CS.NHEt. [99°]. Formed from phenyl-thiocarbimide and NH_2Et and from ethyl-thiocarbimide and aniline (Weith, *B.* 8, 1524; Michael a. Palmer, *Am.* 6, 260). Monoclinic crystals.

Phenylethyl-thio-urea $NH_2.CS.NH.C_2H_4Ph$. [123°]. Formed from phenylethyl-amine hydrochloride and potassium sulphocyanide (Neubert, *B.* 19, 1822). Plates (from dilute alcohol).

Phenyl-ethyl-ψ-thio-urea NHPh.C(SEt):NH. Formed from phenyl-thio-urea and EtI (Bertram, *B.* 25, 55). Yields mercaptan on treatment with alkalis.—B′HI. [103°].—$B'C_6H_3N_3O_7$. [196°].

Phenyl-di-ethyl-ψ-thio-urea NPhEt.C(SEt):NH. Formed from the preceding body and EtI (B.).—B′HI.—$B'_2H_2PtCl_6$. [148°].—$B'C_6H_3N_3O_7$. [170°].

Phenyl-tri-ethyl-ψ-thio-urea NPhEt.C(SEt):NEt. (c. 275°). Got from the preceding and EtI (B.).—$B'C_6H_3N_3O_7$. [c. 96°].—$B'_2H_2PtCl_6$. [135°].

Di-phenyl-ethyl-thio-urea NHPh.CS.NPhEt. [89°]. Formed from phenyl-thiocarbimide and ethyl-aniline (Gebhardt, *B.* 17, 2090). Crystals.

Di-phenyl-ethyl-ψ-thio-urea NHPh.C(SEt):NPh. [79°]. Formed from di-phenyl-thio-urea and EtBr (Rathke, *B.* 14, 1776) and by the action of mercaptan on $C(NPh)_2$ in the cold (Will, *B.* 15, 1308). Needles (from dilute alcohol). Decomposed by heat into $C(NPh)_2$ and EtSH. Cl passed into a solution of its hydrochloride yields ethane sulphonic acid. B′HCl.—$B'_2H_2PtCl_6$2aq.—B′HI aq. [157·5°] (Bernthsen, *B.* 15, 266, 567).

Di-phenyl-di-ethyl-thio-urea $CS(NEtPh)_2$. [75·5°]. Formed from NPhEt.CSCl and ethyl-aniline at 100° (Billeter, *B.* 20, 1631). White tables (from ligroin) or needles (from alcohol).

Di-phenyl-di-ethyl-thio-urea $CS(NH.C_2H_4Ph)_2$. [84°]. Formed from phenyl-ethyl-amine and alcoholic CS_2 (Neubert, *B.* 19, 1824). Plates (from alcohol), insol. water.

Acetyl derivative $C_{19}H_{22}N_2SO$. [73°].

Di-phenyl-di-ethyl-ψ-thio-urea NPhEt.C(SEt):NPh. Oil. The hydro-iodide, got by heating di-phenyl-ethyl-ψ-thio-urea with EtI at 130°, is crystalline (B. a. F.).

u-PHENYL-ETHYL-UREA $NPhEt.CO.NH_2$. [62°]. Formed from ethyl-aniline hydrochloride and potassium cyanate (Gebhardt, *B.* 17, 2095).

s-Phenyl-ethyl-urea NPhH.CO.NEtH. [99°]. Formed from ethyl cyanate and aniline (Wurtz, *C. R.* 32, 417). Needles (from dilute alcohol). Yields a nitrosamine NPhH.CO.NEt.NO [60°] crystallising in monoclinic prisms (E. Fischer, *A.* 199, 286).

Phenylethyl-urea $NH_2.CO.NHC_2H_4Ph$. [112°]. Formed from β-phenyl-ethyl-amine and potassium cyanate (Spica, *G.* 9, 568). Flat prisms, m. sol. cold water.

Phenyl-di-ethyl-urea $NHPh.CO.NEt_2$. [85°]. Formed from phenyl cyanate and $NHEt_2$ (Gebhardt, *B.* 17, 3039). Needles.

Di-phenyl-ethyl-urea NHPh.CO.NPhEt. [91°]. Got from phenyl cyanate and ethyl-aniline (Gebhardt, *B.* 17, 2093). Prisms.

s-**Di-phenyl-di-ethyl-urea** $CO(NPhEt)_2$. [79°]. Formed from NPhEt.COCl and ethyl-aniline at 130° (Michler, *B.* 9, 712). Crystals.

u-**Di-phenyl-di-ethyl-urea** $NPh_2.CO.NEt_2$. [54°]. Formed from $NPh_2.COCl$ and $NHEt_2$.

Diphenyldiethyl-urea $NH_2.CO.N(C_2H_4Ph)_2$. [109°]. Formed from diphenyldiethylamine hydrochloride and potassium cyanate in aqueous solution (Spica, *G.* 9, 568). Prisms, sol. hot Aq.

Tri-phenyl-ethyl-urea $NPh_2.CO.NPhEt$. [89°]. Formed from NPh_2COCl and ethyl-aniline (M.). Formed also from NPhEt.COCl and diphenylamine (Kaufmann, *B.* 14, 2185).

PHENYL-FORMAMIDE *v.* vol. ii. p. 568.

DI-PHENYL-FORMAMIDINE $C_{13}H_{12}N_2$ *i.e.* CH(NPh)(NHPh). *Di-phenyl-methenyl-diamine.* Mol. w. 196. [138°].

Formation.—1. By heating chloroform with aniline for 12 hours at 190° (Hofmann, *Pr.* 9, 229).—2. By heating aniline with phenyl-carbamine, with orthoformic ether, or with formic acid (Weith, *B.* 9, 454; Wichelhaus, *B.* 2, 116).—3. By passing gaseous HCl into heated formic anilide (Wallach, *B.* 15, 208).—4. From formic anilide and PCl_5 (Wallach, *A.* 214, 233). 5. From CH(NPh)SEt and aniline (Wallach a. Wüsten, *B.* 16, 146).—6. From aniline and $CH(NH_2Cl)OEt$ (Pinner, *B.* 16, 358).

Properties.—Needles (from ether). Yields B'HCl and $B'_2H_2PtCl_6$.

PHENYL-FORMAMIDOXIM C_7H_8NO *i.e.* CH(NOH).NHPh. [116°]. Formed from thio-formanilide and hydroxylamine (Müller, *B.* 22, 2411). Needles, m. sol. water.—B'HCl: needles.—$B'_2H_2PtCl_6$: yellow needles.

Benzoyl-derivative CH(NOBz)(NHPh). [145°]. Needles, m. sol. alcohol and ether.

DI-PHENYL-FORMAZIDINE $C_{13}H_{14}N_4$ *i.e.* $CH(N_2HPh).N_2H_2Ph$. [185°]. Formed from $CH(NH_2Cl).OEt$ and phenyl-hydrazine (Pinner, *B.* 17, 2002). Yellow plates, v. sol. hot alcohol.

PHENYL-FORMYLACETIC ETHER $CHO.CHPh.CO_2Et$. (145° at 16 mm.). Got, together with an isomeride [71°], by the action of NaOEt on a mixture of formic and phenyl-acetic ethers (Wislicenus, *B.* 20, 2931). Liquid. $FeCl_3$ colours its alcoholic solutions bluish-violet. Phenyl-hydrazine forms oxy-di-phenyl-pyrazole.

DI-PHENYL-FUMARAMIC ACID *v.* FUMARIC ACID.

PHENYL-FUMARIC ACID $C_{10}H_8O_4$ *i.e.* $CO_2H.CPh:CH.CO_2H$. [161°]. Got by heating bromo-cinnamic ether with alcoholic KCy for 8 hours at 150° (Barisch, *J. pr.* [2] 20, 186). Got also by heating $CO_2H.CPh(OH).CH_2.CO_2H$ (Alexander, *A.* 258, 82). Nodules (from water).—BaA'': scales.—Ag_2A'': amorphous pp.

Di-phenyl-fumaric acid $CO_2H.CPh:CPh.CO_2H$. [c. 260°]. Formed from its ether, which is got, together with di-phenyl-maleïc ether, by the action of Na on α-bromo-phenyl-acetic ether (Rügheimer, *B.* 15, 1626). Crystals, decomposing at 260° into water and di-phenyl-maleïc anhydride.

Nitrile CN.CPh:CPh.CN. [158°]. Got by adding alcoholic NaOEt to α-chloro-phenyl-acetonitrile (Michael a. Jeanprêtre, *B.* 25, 1680).

DI-PHENYL FURAZANE $\begin{matrix}CPh{:}N\\CPh{:}N\end{matrix}{>}O$. [94°] Formed by heating the (α)-di-oxim of benzil with water at 210° (Dodge, *A.* 264, 180). Crystals At 300° it forms di-benzenyl-azoxim. H_2SO_4 and HNO_3 give a di-nitro derivative [220°].

DI-PHENYL-FURFURANE $\begin{matrix}CH{:}CPh\\CH{:}CPh\end{matrix}{>}O$. [91°]. (345°). Formed by heating $CPh{:}C.CH(CO_2H).CO.C_6H_5$ or $CH_2Bz.CH_2Bz$ with conc. HClAq at 160° for 3 hours (Kapf a. Paal, *B.* 21, 1490, 3057). Got also by heating its dicarboxylic acid (W. H. Perkin, jun., a. Schlosser, *C. J.* 57, 954). Plates, insol. water.

Tetrahydride $C_{16}H_{16}O$. (321°). Got by reducing with Na and alcohol. Oil.

Octohydride $C_{16}H_{20}O$. Oil.

Tri-phenyl-furfurane $C_{22}H_{16}O$ *i.e.* $\begin{matrix}CPh{:}CH\\CPh{:}CPh\end{matrix}{>}O$. [93°]. Mol. w. 263 by Raoult's method (calc. 296). Formed by boiling CPhBz:CHBz with HIAq (Japp a. Klingemann, *C. J.* 57, 675). Got also from desyl-acetophenone by successive treatment with H_2SO_4 and water (Smith, *C. J.* 57, 645). Needles (from alcohol).

Tetra-phenyl-furfurane *v.* LEPIDEN.

DI-PHENYL-FURFURANE CARBOXYLIC ACID $\begin{matrix}CO_2H.C{:}CPh\\HC{:}CPh\end{matrix}{>}O$. [217°]. Formed by boiling $CPh{:}C.CHBz.CO_2H$ with conc. HClAq and alcohol (Kapf a. Paal, *B.* 21, 1489, 3059). Formed also by heating the dicarboxylic acid (W. H. Perkin, jun., a. Schlosser, *C. J.* 57. 952). Needles (from alcohol), insol. water. May be distilled. Br yields $C_{17}H_{12}Br_4O_3$.—NaA': needles.

Ethyl ether EtA'. [82°]. Formed by boiling $CH_2Bz.CHBz.CO_2Et$ with alcohol and HClAq. Crystals (from ether). Yields on reduction a tetrahydride which does not react with AcCl.

Di-phenyl-furfurane dicarboxylic acid $C_{18}H_{12}O_5$ *i.e.* $\begin{matrix}CO_2H.C{:}CPh\\CO_2H.C{:}CPh\end{matrix}{>}O$. [23[illegible]°]. Formed by dissolving di-benzoyl-succinic ether in H_2SO_4 and boiling the product with alcoholic potash (W. H. Perkin, jun., *C. J.* 47, 262; 49, 168; 57, 951). Needles, sol. alcohol and ether. $FeCl_3$ gives an orange colour in its alcoholic solution. Yields acetophenone on distilling with soda-lime.—Ag_2A''.

Ethyl ether Et_2A''. [86°]. Formed from dibenzoyl-succinic acid and H_2SO_4. Yellow prisms, v. sol. alcohol. Its solution in H_2SO_4 turns violet on heating.

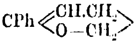
Anhydride $C_{18}H_{10}O_4$. [255°]. Formed by heating the acid alone or with Ac_2O. Plates, sl. sol. hot alcohol. Its alcoholic solution exhibits violet fluorescence.

PHENYL-FURFURYL-ACRYLIC ACID. *Nitrile.* $C_4H_3O.CH{:}CPh.CN$. [43°]. Formed from phenyl-acetonitrile, furfuraldehyde, and NaOEt in alcohol (Frost, *A.* 250, 159). Yields $C_4H_3O.CHBr.CBrPh.CN$ [114°] crystallising in orange plates.

Reference.—NITRO-PHENYL-FURFURYL-ACRYLIC ACID.

PHENYL-FURFURYL-(β)-NAPHTHO-TRIAZINE. *Dihydride* $C_{21}H_{15}N_3O$ *i.e.* $C_{10}H_6{<}\begin{matrix}N.CH.C_4H_3O\\N.NPh\end{matrix}$. [241°]. Formed by warming benzene-azo-(β)-naphthylamine with furfuraldehyde in alcohol (Goldschmidt a. Poltzer, *B.* 24, 1007). Needles.—B'HCl: plates.—$B'_2H_2PtCl_6$. Light-yellow crystalline pp.

(β)-**PHENYL-(γ)-FURFURYL-PROPYL-AMINE** $C_4H_3O.CH_2.CHPh.CH_2NH_2$. (283°). Formed from phenyl-acetonitrile and furfuraldehyde, the product of condensation of these bodies $C_4H_3O.CH{:}CPh.CN$ being reduced by Na and dry alcohol (Freund a. Immerwahr, *B.* 23, 2850). Oil, with alkaline reaction. Converted by nitrous acid into the liquid alcohol $C_4H_3O.CH_2.CHPh.CH_2OH$. Phenyl thiocarbimide forms $C_4H_3O.C_3H_5Ph.NH.CS.NHPh$ [113°].—B'HCl. [176°]. Crystalline, v. sol. water. Reacts with potassium cyanate forming $C_4H_3O.C_3H_5Ph.NH.CO.NH_2$ [101°].—Mercury double salt: [175°]; needles.—Picrate [152°]. Yellow crystalline powder.

PHENYL-FURIDANE. *Dihydride*  $\mathrm{CPh}<\begin{matrix}\mathrm{CH.CH_2}\\ \mathrm{O-CH_2}\end{matrix}>\mathrm{CH_2}$. (250° at 721 mm.). Formed by heating its carboxylic acid at 200° (Perkin, *C. J.* 51, 731). Oil. HBr forms $C_6H_5.CO.C_4H_8Br$.

PHENYL-FURIDANE DIHYDRIDE CARBOXYLIC ACID $\mathrm{CO_2H.C}<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CPh.O}\end{matrix}>\mathrm{CH_2}$. *Phenyldehydrohexone carboxylic acid.* [c. 144°]. Formed by saponifying its ether, which is got by the action of NaOEt on a mixture of trimethylene bromide and benzoyl-acetic ether (Perkin, *C. J.* 51, 726). Monoclinic prisms (from ether); *a*:*b*:*c* = 2·638:1:3·398; β = 74° 44'.—AgA': needles (from water).

Ethyl ether EtA'. [60°]. Prisms.

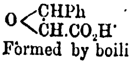
PHENYL-GLUTARIC ACID $C_{11}H_{12}O_4$ *i.e.* $CHPh(CH_2.CO_2H)_2$. [138°]. Formed by heating sodium malonic ether with alcohol and cinnamic ether at 100°, saponifying the resulting ether $CH(CO_2Et)_2.CHPh.CHNa.CO_2Et$, and heating the acid at 110° (Michael, *J. pr.* [2] 35, 352; *Am.* 9, 116). Needles, sl. sol. water, m. sol. alcohol.—AgA': amorphous pp.

Di-phenyl-glutaric acid $CH_2(CHPh.CO_2H)_2$. [164°]. Formed by saponifying its nitrile (Zelinsky a. Feldmann, *B.* 22, 3292). Needles.

Nitrile $CH_2(CHPh.CN)_2$. [71°]. Formed by heating $CH_2Ph.CN$ with CH_2I_2 and dry NaOH.

PHENYL-GLYCERIC ACID *v.* DI-OXY-PHENYL-PROPIONIC ACID.

TRI-PHENYL GLYCERYL TRIKETONE $CH_2Bz.CHBz.CH_2Bz$. *Tri-benzoyl-propane.* [137°]. Formed from tricarballylic chloride, benzene, and $AlCl_3$ (Emery, *B.* 21, 601). Straw-yellow needles. Yields a phenyl-hydrazide [57°–60°].

PHENYL-GLYCIDIC ACID $C_9H_8O_3$ *i.e.*  $\mathrm{O}<\begin{matrix}\mathrm{CHPh}\\ \mathrm{CH.CO_2H}\end{matrix}$. *Phenyl-pyruvic acid?* [155°] Formed by boiling benzoyl-imido-phenyl-propionic acid $\mathrm{NBz}<\begin{matrix}\mathrm{CHPh}\\ \mathrm{CH.CO_2H}\end{matrix}$ with aqueous HCl or with KOH (Plöchl, *B.* 16, 2817; 19, 3167). Formed also by boiling phenyl-oxalacetic acid with dilute H_2SO_4 (W. Wislicenus, *B.* 20, 592). Plates, v. e. sol. alcohol and ether. $FeCl_3$ colours its alcoholic solution green. Sodium-amalgam reduces it to α-oxy-phenyl-propionic acid. Yields an oxim and a phenyl-hydrazide $CH_2Ph.C(N_2HPh)CO_2H$ [161°]. Tolylene-*o*-diamine forms a quinoxaline (Erlenmeyer, jun., *B.* 19, 2576; 20, 2465; 22, 1482). Aniline forms $C_2H_2Ph(NHPh)(OH).CO_2H$.

(β)-Phenyl-glycidic acid. Formed from $C_6H_5.CH(OH).CHCl.CO_2H$ and cold alcoholic potash (Glaser, *A.* 147, 98). Oil, crystallising at 0°. Decomposes, even at 15°, into phenyl-acetic aldehyde and CO_2. Boiling dilute H_2SO_4 forms $CHPh(OH).CH(OH).CO_2H$ and phenyl-acetic aldehyde (Erlenmeyer a. Lipp, *A.* 219, 181). Yields β-oxy-phenyl-propionic acid on reduction with sodium-amalgam.—NaA'.—KA'.—AgA': crystalline powder.

Ethyl ether EtA'. (280° cor.). Oil.

References.—NITRO- and OXY- PHENYL-GLYCIDIC ACID.

PHENYL-GLYCOCOLL *v.* PHENYL-AMIDO-ACETIC ACID.

PHENYL-GLYCOL *v.* DI-OXY-ETHYL-BENZENE.

PHENYL-GLYCOLLIC ACID *v. Phenyl-derivative* of GLYCOLLIC ACID and MANDELIC ACID.

Di-phenyl-glycollic acid *v.* BENZILIC ACID.

PHENYL-GLYCOLLIC ACRYLIC ACID *v. Carboxy-methyl derivative* of COUMARIC ACID.

PHENYLGLYCOLYL-TROPEÏNE $C_{16}H_{21}NO_3$. *Homo-atropine.* [98°]. Formed by heating tropine mandelate with HClAq (Ladenburg, *A.* 217, 82). Deliquescent prisms (from ether), m. sol. water. Less poisonous than atropine.—$B'HAuCl_4$.—B'HBr.—$B'C_6H_3N_3O_7$. Yellow plates.

TETRA-PHENYL-GLYCOSINE *v.* GLYCOSINE.

PHENYL-GLYOXAL $C_6H_5.CO.CHO$. (142° at 125 mm.). Formed by allowing a mixture of its mono-oxim (30 g.) with $NaHSO_3$ (120 g. of a 35 p.c. solution) to stand till all is dissolved, and then adding H_2SO_4 and distilling (Müller a. von Pechmann, *B.* 20, 2904; 22, 2557). Oil. Forms a crystalline hydrate [73°]. Converted by HNO_3 into phenyl-glyoxylic acid, and by potash into mandelic acid. Ammonia forms $C_{22}H_{19}N_3O$ or $C_{22}H_{17}N_3O$ crystallising in plates [193°] which can be distilled. Hydroxylamine gives $C_{16}H_{13}N_3O_3$, [219°], sol. alkalis.

Mono-oxim $C_6H_5.CO.CH{:}NOH$. *Nitroso-acetophenone.* [128°]. Formed from acetophenone, isoamyl nitrite, and alcoholic NaOEt (Claisen, *B.* 20, 656, 2194; Braun, *B.* 22, 556). Monoclinic tables (from chloroform), sl. sol. cold water, v. sol. alkalis. Yields $C_6H_5.CO.CN$ on warming with Ac_2O. Boiling NaOHAq forms NaCy and NaOBz. Its acetyl derivative is converted by NaOHAq into $CHBz(OH).CO.CO.C_6H_5$ [170°] crystallising in minute needles (Söderbaum, *B.* 24, 1386, 3034).

Di-oxim $C_6H_5.C(NOH).CH(NOH)$. *Anti-phenyl-amphi-glyoxim.* [162°] (S.); [168°] (R.). Formed by the action of hydroxylamine on the mono-oxim, or on mono- or di-bromo-acetophenone (Schramm, *B.* 16, 2183; Strassmann, *B.* 22, 419; Russanoff, *B.* 24, 3501). Small needles, v. sol. alcohol, insol. $CHCl_3$; subliming below 160°. N_2O_4 gives $C_6H_5.C_2HN_2O_2$ [c. 90°] crystallising in colourless prisms (Scholl, *B.* 23, 3504). By dissolving in ether and treating with HCl it is converted into an isomeride [180°]. This body, called phenyl-anti-glyoxim, is v. sol. Ac_2O and yields a di-acetyl derivative [92°]. Phenyl-anti-glyoxim is only stable in acid solutions being readily re-converted into the original di-oxim [168°]. By treatment of the di-oxim [168°] NaOHAq and CO_2 at −10° there is formed a second isomeride [148°-154°] called phenyl-syn-glyoxim which yields an oily di-acetyl derivative.—$AgC_8H_7N_2O_2$. Curdy pp.

Phenyl-hydrazide $C_6H_5.C(N_2HPh).CHO$. [148°]. Yellow plates (M. a. P.).

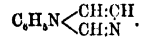
Phenyl-hydrazide $C_6H_5.CO.CH:N_2HPh$. [129°]. Formed by the action of warm dilute KOHAq on the compound got by treatment of sodium benzoylacetic ether with diazobenzene chloride (Stierlin, *B.* 21, 2123). Yellow plates.

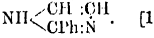
p-Tolyl-hydrazide $CHBz:N_2H.C_6H_4Me$. Got in like manner, using *p*-diazotoluene chloride. Yellowish-brown plates, v. sol. ether.

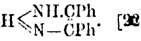
Di-phenyl-di-hydrazide $C_6H_5.C(N_2HPh).CH(N_2HPh)$. [152°]. Got by heating phenyl-glyoxal or, better, the phenyl-hydrazide of benzoyl-carbinol with phenyl-hydrazine hydrochloride and NaOAc at 100° (Laubmann, *A.* 243, 247). Yellow plates.

Di-phenyl-di-methyl-di-hydrazide $C_6H_5.C(N_2MePh).CH(N_2MePh)$. [151°]. Formed from ω-bromo-acetophenone and phenyl-methyl-hydrazine (Culmann, *B.* 21, 2597). Prisms.

Di-phenyl-glyoxal *v.* BENZIL.

PHENYL-GLYOXALINE $C_9H_8N_2$ *i.e.*  $C_6H_5N{<}\begin{array}{l}CH:CH\\CH:N\end{array}$. [13°]. (276°). Formed by warming sulphydro-phenyl-glyoxaline [181°] with dilute HNO_3 or HClAq (Wohl a. Marckwald, *B.* 22, 576, 1353). Crystalline, miscible with alcohol.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$.—Picrate $B'C_6H_3N_3O_7$. [152°]. Yellow needles (from alcohol).—B_2AgNO_3.—B'MeI. Syrup.

Phenyl-glyoxaline  $NH{<}\begin{array}{l}CH:CH\\CPh:N\end{array}$. [148°]. (c. 340°). Formed by distilling its dicarboxylic acid, which is got from di-nitro-tartaric acid, benzoic aldehyde, and NH_3 (Maquenne, *C. R.* 111, 742). Plates (from benzene).—$B'_2H_2C_2O_4$. Needles.—$B'_2H_2PtCl_6$.

Di-phenyl-glyoxaline  $CH{<}\begin{array}{l}NH.CPh\\N-CPh\end{array}$. [227°]. Formed by the action of formic aldehyde and ammonia on benzil (Japp, *C. J.* 51, 559). Dimorphous. Crystallises with di-phenyl-methyl-glyoxaline as $(C_3N_2H_2Ph_2)C_3N_2HMePh_2$ [218°]. —$B'_2H_2PtCl_6$: small flat yellow needles.

Tri-phenyl-glyoxaline *v.* *Lophine*, vol. i. p. 474.

PHENYL-GLYOXIM *v.* *Oxim* of PHENYL-GLYOXAL.

PHENYL-GLYOXYLIC ACID $C_8H_6O_3$ *i.e.* $C_6H_5.CO.CO_2H$. *Benzoyl-formic acid.* [66°].

Formation.—1. From benzoyl cyanide and conc. HClAq in the cold (Claisen, *B.* 10, 429, 844, 1663; 12, 626, 1505) or HOAc saturated with HCl (Buchka, *B.* 20, 395).—2. From di-oxy-ethyl-benzene (phenyl-glycol) and nitric acid of S.G. 1·38 (Zincke, *A.* 216, 305).—3. By saponifying its ether, which is got by heating $COCl.CO_2Et$ with $HgPh_2$ for several hours at 150°; the yield being 40 p.c. of the theoretical (Claisen a. Morley, *B.* 11, 1596).—4. By oxidising acetophenone with alkaline $KMnO_4$ at 0°; the yield being 20 p.c. of the theoretical amount (Glückmann, *M.* 11, 248).

Properties.—Prisms, v. e. sol. water and ether. Decomposed by distillation into benzoic acid and CO, and partly also into benzoic aldehyde and CO_2. Phenyl-hydrazine added to its solution in dilute HCl forms a bulky yellow pp. of phenyl-hydrazide (Ebers, *A.* 227, 340). Whe mixed with benzene (containing thiophene) i gives with conc. H_2SO_4 a red colour changing t violet. On adding water, the layer of benzen becomes crimson.

Reactions.—1. *Sodium-amalgam* reduces i to mandelic acid.—2. HI and P at 160° reduc it to phenyl-acetic acid.—3. *Phenyl mercapta* and gaseous HCl form $C_6H_5.C(SPh)_2.CO_2H$ [142°], sl. sol. benzene (Baumann, *B.* 18, 891). Phenyl mercaptan alone forms a crystallin powder $C_6H_5.C(OH)(SPh).CO_2H$ [69°].

Salts.—NaA'.—KA'aq: dimetric tables.—NH_4A'.—CaA'_2aq: flat prisms.—BaA'_2.—SrA'_2aq—CuA'_2.—$ZnA'_2 2aq$.—PbA'_2.—PbA'_2aq.—AgA'

Methyl ether MeA'. (218°).

Ethyl ether EtA'. (257°). S.G. $^{17.5}$ 1·121. Forms a crystalline compound with $NaHSO_3$. Reacts in alcoholic solution with hydrazine hydrate forming $C_8H_{12}N_4O_2$ [120°] and $C_{20}H_{20}N_2O$ [135°] (Curtius, *J. pr.* [2] 44, 566).

n-Propyl ether PrA'. (174° at 60 mm.).

Isobutyl ether. (174° at 38 mm.).

Isoamyl ether. (182° at 40 mm.).

(α)-*Amide* $C_6H_5.CO.CONH_2$. [91°]. Formed from benzoyl cyanide and cold HClAq. On solution and re-ppn. by CO_2 it forms an unstable hydrate $C_8H_7NO_2aq$ [65°] (so-called (β)-amide).

(γ)-*Amide* $(C_8H_7NO_2)_2$. [134°]. Formed by adding an alcoholic solution of the (α)-amide to dilute HClAq (Claisen). Formed also, together with the (α)-amide, by the action of HOAc saturated with HCl upon BzCy (Buchka). Prisms.

Nitrile *v.* BENZOYL CYANIDE.

(α)-*Oxim* $C_6H_5.C(NOH).CO_2H$. *Isonitroso-phenyl-acetic acid.* [127°]. Formed by the action of hydroxylamine on the Na salt (A. Müller, *B.* 16, 1617) or on the acid at 0° (Hantzsch, *B.* 23, 2333; 24, 42). Thick prisms, v. e. sol. water. Yields α-amido-phenyl-acetic acid on reduction.—KA'aq: very soluble crystals.—$BaA'_2 1\frac{1}{2}aq$.—AgA'.

Acetyl derivative. [119°]. Prisms.

(β)-*Oxim* $C_6H_5.C(NOH).CO_2H$. [145°]. Formed by the action of HCl on an ethereal solution of the (α)-oxim. Formed also by warming phenyl-glyoxylic acid with hydroxylamine and potash. White needles composed of dimetric prisms.

Acetyl derivative. [125°]. Tables.

Methyl ether of the oxim $CPh(NOH).CO_2Me$. [139°]. Got from the Ag salt and MeI (Müller, *B.* 16, 2987). Converted by NaOEt and MeI into $CPh(NOMe).CO_2Me$ [56°], sol. alcohol, insol. alkalis.

Ethyl ether of the oxim $CPh(NOH).CO_2Et$. [113°]. Formed from phenyl-glyoxylic ether and hydroxylamine (Gabriel, *B.* 16, 519). Needles (from hot water).

Nitrile of the oxim $C_6H_5.C(NOH).CN$. [129°]. Formed from phenyl-acetonitrile, amyl nitrite, and alcoholic NaOEt (Frost, *A.* 250, 163; Meyer, *B.* 21, 1306). Formed also by the action of hydroxylamine on dibromo-acetophenone in dilute alcohol at 60° (Russanoff, *B.* 24, 3505). Thin plates, v. sol. alcohol.—$C_6H_5.C(NONa).CN$: yellow powder, v. sol. water. Yields an acetyl derivative [68°].—KA'.—CuA'_2.—$Pb_2A'_2O$.—AgA'.

Phenyl hydrazide $C_6H_5.C(N_2HPh).CO_2H$. [153°]. (F.); [153°-164°] (Von Pechmann, *B.* 25, 1054). Yellow needles, sl. sol. hot water

(Fischer, *B.* 17, 578; Ebers, *A.* 227, 340). May be reduced to $C_6H_5.CH(N_2H_2Ph).CO_2H$ [158°], and finally to aniline and α-amido-phenyl-acetic acid.

Phenyl-methyl-hydrazide $C_6H_5.C(N_2MePh).CO_2H$ [116°]. Plates (from alcohol). Its amide $C_6H_5.C(N_2MePh).CONH_2$ [156°] is crystalline.

Phenyl-ethyl-hydrazide $C_6H_5.C(N_2EtPh).CO_2H$. [109°]. Formed, together with its amide $C_6H_5.C(N_2EtPh).CO.NH_2$ [111°], by the action of phenyl-ethyl-hydrazine in dilute HOAc on phenyl-glyoxylic acid. Yellow plates, sl. sol. water. Yields ethyl-aniline and benzoic aldehyde when heated with conc. HClAq.

References. — AMIDO-, NITRO-, and OXY-PHENYL-GLYOXYLIC ACID.

PHENYL - GLYOXYLIC *o* - CARBOXYLIC ACID $C_6H_4(CO_2H).CO.CO_2H$. [140°]. Formed by oxidising the oxyquinone $C_{16}H_{10}O_3$ or indo-naphthene dihydride carboxylic acid with alkaline $KMnO_4$ (Scherks, *B.* 18, 378; *cf.* Zincke, *A.* 226, 53; 240, 142). Yields CO_2 and phthalic anhydride on heating. May be reduced to phthalide carboxylic acid.—K_2A''. BaA'' 2aq. —$Cu_2A''(OH)_2$ 6aq.—Ag_2A'': crystalline pp.

PHENYL-DIGUANIDE $C_8H_{11}N_5$ *i.e.* $NH:C(NHPh).NH.C(NH_2):NH$. [c. 237°]. Formed by the action of alcoholic ammonia and $AgNO_3$ or $HgCl_2$ on guanyl-phenyl-thio-urea (Bamberger, *B.* 13, 1582). Formed also by heating aniline hydrochloride with di-cyan-di-amide in alcohol at 100° (Smolka a. Friedrich, *M.* 9, 232). Plates, v. sol. water and alcohol; absorbs CO_2 from air. When boiled with baryta-water it yields NH_3, aniline, phenyl-urea [147°], phenyl-guanidine, guanidine, and urea (Emich, *M.* 12, 15).—B'HCl: prisms. Yields phenyl-carbamine when warmed with alcoholic potash and $CHCl_3$.

Salts. — $B'HNO_3$. [209°].— $B'_2H_2SO_4$. — $Cu(C_8H_{10}N_5)_2$ $1\frac{1}{2}$aq: red powder, sol. hot water. — $CuA'_2H_2Cl_2$ $1\frac{1}{2}$aq. — $CuA'_2H_2SO_4$ $1\frac{1}{2}$aq. — $CuA'_2H_2CrO_4$ aq. — NiA'_2. — $NiA'_2H_2Cl_2$. — $NiA'_2H_2SO_4$ $1\frac{1}{2}$aq.—CoA'_2 $1\frac{1}{2}$aq. $CoA'_2H_2Cl_2$ $\frac{1}{2}$aq. —$CoA'_2H_2SO_4$ aq: crimson needles.

(*a*)-**Di-phenyl-diguanide** $C_{14}H_{15}N_5$ *i.e.* $NPh:C(NHPh).NH.C(NH_2):NH$. Formed by the action of $AgNO_3$ and aniline on guanyl-phenyl-thio-urea (Bamberger, *B.* 13, 1581). White solid, m. sol. water and alcohol, alkaline in reaction.—$B'HNO_3$. [231°]. White needles.

(*β*)-**Di-phenyl-diguanide** $NH:C(NPh_2).NH.C(NH_2):NH$. [c. 162°]. Formed by heating diphenylamine hydrochloride with di-cyan-di-amide (Emich, *M.* 12, 21). Thin needles, with alkaline reaction.—$B'HNO_3$. [203°]. Prisms.—$B'_2 3H_2SO_4$.

Tri-phenyl-diguanide $C_{20}H_{19}N_5$. [138°]. Formed from guanyl-tri-phenyl-thio-urea, NH_3, and $AgNO_3$. Formed also from di-phenyl-guanidine and phenyl-cyanamide [78°] in ether (Rathke a. Oppenheim, *B.* 23, 1672). Prisms (from alcohol). With CS_2 at 100° it yields tri-phenyl-thio-ammeline $C_{21}H_{17}N_5S$. — B'HCl: prisms, v. sol. alcohol.—$B'_2H_2PtCl_6$.

PHENYL-GUANIDINE $C_7H_9N_3$ *i.e.* $NH:C(NH_2)(NHPh)$. Formed by desulphuration of phenyl-thio-urea in presence of alcoholic NH_3 (Feuerlein, *B.* 12, 1602). Formed also by the action of baryta-water on phenyl-diguanide (Emich, *M.* 12, 11). Decomposes on standing into phenylcyanamide and ammonia.—*Picrate* $B'C_6H_3N_3O_7$. [208°-214°] (Prelinger, *M.* 13, 99).

Di-phenyl-guanidine $C_{13}H_{13}N_3$ *i.e.* $NH:C(NHPh)_2$. *Melaniline.* [147°]. S. (90 p.c. alcohol) 9·25 at 21°.

Formation.—1. From aniline and CyCl or CyBr (Hofmann, *A.* 67, 129; 74, 8; Weith a. Ebert, *B.* 8, 912).—2. By the action of PbO on a solution of di-phenyl-urea in alcoholic NH_3 (Hofmann, *B.* 2, 452, 688; Weith, *B.* 7, 937; Rathke, *B.* 12, 772).—3. By boiling phenyl-thio-urea with HgCl(NHPh) and alcohol (Forster, *B.* 7, 291; *A.* 175, 35).—4. Together with thio-urea, by the action of aniline on mercuric fulminate (Steiner, *B.* 7, 1244; 8, 518).—5. By combination of di-phenyl-cyanamide with NH_3 (Weith, *B.* 7, 10).

Properties.—Monoclinic prisms (Arzruni, *P.* 152, 281), sl. sol. cold water.

Reactions.—1. Ac_2O at 100° yields acetyl-phenyl-urea [183°]. At 150° the product is acetyl-di-phenyl-urea [115°] (McCreath, *B.* 8, 1181).—2. *Phenyl thiocarbimide* forms, in the cold, NHPh.CS.NPh.C(NH).NHPh [150°], a weak base, sl. sol. benzene.—3. HClAq at 250° forms CO_2, NH_3, and aniline.—4. *Cyanogen* passed into its alcoholic solution forms $C_{15}H_{13}N_5$ which crystallises from alcohol in yellowish needles [154°], decomposed by HClAq into crystalline melanoximide $C_{15}H_{11}N_3O_2$, which is split up by alcoholic potash into oxalic acid and diphenylguanidine, and by alcoholic HCl into NH_3 and di-phenyl-parabanic acid.

Salts.—The hydrochloride is gummy. —$B'HAuCl_4$: golden needles.—$B'_2H_2PtCl_6$.— B'HBr: stellate groups of needles, v. sol. water. — B'HI. — $B'HNO_3$. — B'_2AgNO_3: geodes. — $B'_2H_2SO_4$: stellate groups of plates.—$B'H_2C_2O_4$. —Sulphocyanide: [115°]; m. sol. water.

Di-benzoyl derivative $C_{27}H_{21}N_3O_2$. [102°]. Monoclinic (McCreath, *B.* 8, 383).

Tri-phenyl-guanidine $C_{19}H_{17}N_3$ *i.e.* $NPh:C(NHPh)_2$. Mol. w. 287. [143°]; [147°] (F. a. W.). S. (alcohol) 4·5 at 0°.

Formation.—1. By adding I to an alcoholic solution of di-phenyl-thio-urea alone or mixed with aniline (Hofmann, *B.* 2, 453).—2. From di-phenyl-thio-urea and HgCl(NHPh) (Forster, *B.* 7, 291).—3. From di-phenyl-cyanamide $C(NPh)_2$ and aniline (Weith, *B.* 7, 10).—4. Together with phenyl-thiocarbimide by heating di-phenyl-cyanamide with di-phenyl-urea (Weith, *B.* 9, 810).—5. By boiling di-phenyl-urea with inverted condenser (Barr, *B.* 19, 1765).—6. By heating di-phenyl-thio-urea with aniline, with Cu, or with $PbCl_2$ (Merz a. Weith, *Z.* [2] 4, 513, 609; 5, 583, 659; Girard, *Bl.* [2] 46, 506), or with $HgCl_2$ at 145° (Buff, *B.* 2, 498).—7. By heating di-phenyl-cyanamide (2 mols.) with phenylene-*o*-diamine (1 mol.) at 210° (Keller, *B.* 24, 2505). 8. By the action of aniline on CCl_4 or chloropicrin (Hofmann; Basset, *C. J.* 18, 31).—9. By the action of PCl_3 (1 mol.) on a mixture of di-phenyl-urea (3 mols.) and aniline (3 mols.).—10. By the action of PCl_3 (2 mols.) and CO_2 (3 mols.) on aniline (9 mols.) at 170° (Merz a. Weith, *Z.* [2] 6, 160).—11. By fusing di-phenyl-urea with NaOH (Hentschel, *J. pr.* [2] 27, 500). 12. From phenyl thiocarbimide by chlorinating and heating the product $NPh:CCl_2$ with aniline (Sell a. Zierold, *B.* 7, 1231). The base got is possibly an isomeric tri-phenyl-guanidine.—13. A product of the action of $CSCl_2$ on $CS(NHPh)_2$ and benzene (Freund a. Wolf, *B.* 25, 1464).

Properties.—Trimetric six-sided prisms (from alcohol); *a*:*b*:*c* = ·670:1:·558, nearly insol. boiling water. Occurs also in an amorphous form (Giraud, *Bl.* [2] 46, 505). Decomposed above 250° into aniline and $C(NPh)_2$. $KClO_3$ (1½ pt.) and HCl give a greenish solution, depositing dark flakes which dissolve in alcohol with violet colour.

Reactions.—1. CS_2 at 170° forms $CS(NPhH)_2$ and phenyl thiocarbimide.—2. H_2S passed through it at 170° forms aniline and di-phenyl-urea (Merz a. Weith, *Z.* [2] 6, 72).—3. *Water* at 175° forms aniline and di-phenyl-urea.—4. Conc. KOHAq or conc. HClAq yield aniline and CO_2 on heating.—5. *Cyanogen* passed into the alcoholic solution forms crystals of $C_{21}H_{17}N_5$ which is decomposed by HClAq into NH_4 and the **oxalyl-derivative** $C(NPh)<\begin{matrix}NPh.CO\\NPh.CO\end{matrix}$ [c. 230°] which is itself decomposed by boiling with alcohol and HClAq into aniline and di-phenyl-parabanic acid (Hofmann, *B.* 3, 761; Stojentin, *J. pr.* [2] 32, 1).—6. *Chloro-glyoxylic ether* $COCl.CO_2Et$ forms a **carbonyl derivative** $C(NPh)<\begin{matrix}NPh\\NPh\end{matrix}>CO$ which forms the salts B′HCl [190°] and $B'HNO_3$ [185°] (Stojentin).—7. $COCl_2$ forms the above (?) carbonyl derivative $C_{20}H_{15}N_3O$, which crystallises from CS_2 in tables [134°] and forms a hydrate B′aq [141°] (Michler a. Keller, *B.* 14, 2181).

Salts.—B′HCl aq. [242°] (Weith, *B.* 9, 810); [245°] (F. a. W.). S. 2 at 0°.—$B'HNO_3$: laminæ.—$B'_2H_2PtCl_6$. S. ·09 at 0°.—$B'H_2SO_4$: broad needles.—B′HOAc.—$B'H_2C_2O_4$: laminæ.—$B'C_6H_3N_3O_7$. [178°]. S. ·0082 at 15° (Prelinger, *M.* 13, 98).

Acetyl derivative $C(NPh)(NPhAc)_2$. [131°]. Crystals (MacCreath, *B.* 8, 383).

Benzoyl derivative $C(NPh)(NPhBz)_2$. [185°]. Plates (from alcohol).

(β)-Tri-phenyl-guanidine $C(NH)(NHPh)(NPh_2)$. [131°]. Formed by heating phenyl-cyanamide (cyanilide) CN.NHPh with diphenylamine at 125° (Weith a. Schröder, *B.* 8, 912). Regular tablets, nearly insol. water. Its solution in conc. H_2SO_4 becomes violet on heating.

Reactions.—1. Conc. HClAq or KOHAq at 260° forms CO_2, NH_3, aniline, and $NHPh_2$.—2. CS_2 at 160° forms the sulphocyanide, H_2S, phenyl-thiocarbimide and $NHPh_2$.

Salts.—B′HCl aq. S. (of B′HCl) 28·4 at 23°.—$B'_2H_2PtCl_6$: crystalline.

Dicyanide $C_{21}H_{17}N_5$. [173°]. A product of the action of cyanogen as an alcoholic solution of aniline (Hofmann, *A.* 66, 129; *B.* 3, 763). Got also by boiling the compounds of cyanogen with di-phenyl-guanidine or (α)-tri-phenyl-guanidine with aniline hydrochloride (Landgrebe, *B.* 10, 1593; 11, 973). Dark-brown needles (containing ½aq) with violet iridescence (from alcohol).—B′HCl 3aq: brown needles.

Tetra-phenyl-guanidine $C(NH)(NPh_2)_2$. [131°]. Formed by passing gaseous cyanogen chloride through diphenylamine at 160° (Weith, *B.* 7, 843). Pyramids (from ligroïn), insol. water, v. sol. alcohol and ether. Conc. H_2SO_4 forms a colourless solution turned violet-red by heat. CS_2 at 260° forms tetra-phenyl-thio-urea. Solid KOH at 200°, and conc. HClAq at 340°, yield NH_3, CO_2, and $NHPh_2$.

Salts.—B′HCl 5aq. Efflorescent tablets.—$B'_2H_2PtCl_6$.—$B'HNO_3$.

References.—DI-BROMO-, DI-CHLORO-, DI-IODO-, and NITRO- PHENYL-GUANIDINES.

DI-PHENYL-GUANIDINE CARBOXYLIC ACID $C(NH)(NHPh).NH.C_6H_4.CO_2H$. *Phenyl-guanido-benzoic acid.* [165°]. Formed by heating *m*-cyanamido-benzoic acid or cyancarbimido-amido-benzoic acid with aniline (Traube, *B.* 15, 2120; Griess, *B.* 16, 336). Crystals (containing aq), nearly insol. alcohol and ether, sol. hot water, aqueous alkalis and acids.—HA′HCl aq.

Reference.—AMIDO-DI-PHENYL-GUANIDINE CARBOXYLIC ACID.

PHENYL-GUANIDO-ACETIC ACID $C_9H_{11}N_3O_2$ *i.e.* $C(NH)(NHPh).NH.CH_2.CO_2H$. [260° uncor.] Formed from phenyl-cyanamide and glycocoll (Berger, *B.* 13, 992). Crystals.

DI-PHENYL-DI-GUANIDO-DI-TOLYL-SULPHIDE $S(C_7H_6.NH.C(NH).NHPh)_2$. *Thio-p-tolyl-di-phenyl-di-guanidine.* [153°]. Formed by heating di-phenyl-di-uramido-di-tolyl sulphide with alcoholic NH_3 and HgO (Truhlar, *B.* 20, 675). Small white needles (from ether-ligroïn). V. sol. alcohol, benzene, and ether.—$B''H_2Cl_2PtCl_4$: yellow amorphous powder.

Tetra-phenyl-di-guanido-di tolyl-sulphide $S(C_7H_6.NH.C(NPh).NHPh)_2$. *Thio-p-tolyl-tetra-phenyl-di-guanidine.* [106°]. Formed by heating di-phenyl-di-uramido-di-tolyl sulphide with aniline and HgO (T.). Amorphous powder.

PHENYL-HEPTADECYL-THIO-UREA $C_6H_5NH.CS.NHC_{17}H_{35}$. [79°]. Formed by boiling heptadecyl-thiocarbimide with aniline and alcohol (Turpin, *B.* 21, 2491).

PHENYL-HEPTADECYL-UREA $C_{24}H_{42}N_2O$ *i.e.* $C_6H_5NH.CO.NHC_{17}H_{35}$. [99°]. Formed by heating heptadecylamine hydrochloride with $COCl_2$ in benzene at 100°, the product being heated with aniline (Turpin, *B.* 21, 2492).

PHENYL-HEPTANE *v.* HEPTYL-BENZENE.

Di-phenyl-heptane $C_6H_{13}.CHPh_2$. [14°]. (191° at 13 mm.). Formed from $C_6H_{13}.CHCl_2$, benzene, and $AlCl_3$ (Anger, *Bl.* [2] 47, 48; Krafft, *B.* 19, 2986). Needles.

PHENYL-HEPTENOIC ACID $C_{13}H_{16}O_2$ *i.e.* $Ph.CEt:CEt.CO_2H$ (?) Oil. Got by passing CO over a heated mixture of NaOEt and sodic cinnamate (M. Schroeder, *A.* 221, 52).

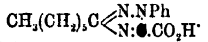
PHENYL HEPTYL KETONE CARBOXYLIC ACID $C_6H_5.CO.CH_2.CH(C_5H_{11}).CO_2H$. [103°]. Formed by heating phenacyl-isoamyl-malonic acid (Paal a. Hofmann, *B.* 23, 1504). Plates, insol. water, sl. sol. ligroïn. On repeated distillation it yields an oily lactone (310°–320°).

Ethyl ether EtA′. (260°). Oil.

PHENYL-HEXINENE *v.* BUTENYL-STYRENE.

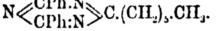
DI-PHENYL-HEXOIC ACID. *Nitrile.* $CH_2Ph.CPhPr.CN$. [63°]. (330°–340°). Formed from $C_6H_5.CHPr.CN$, benzyl chloride, and NaOH (Rossolymo, *B.* 22, 1236). Needles.

TETRA-PHENYL-HEXUNENE $\begin{matrix}CPh\\CPh\end{matrix}>CH.CH<\begin{matrix}CPh\\CPh\end{matrix}$. [260°]. Formed by heating di-benzyl-carbinol with MeI at 265° (Bogdanowska, *B.* 25, 1273). Needles, insol. alcohol and ether, sol. $CHCl_3$.

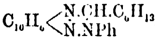
PHENYL-HEXYL-TRIAZOLE CARBOXYLIC ACID  $CH_3(CH_2)_5C\left\langle\begin{matrix}N.NPh\\N:C.CO_2H\end{matrix}\right.$ [126°]. Obtained by saponifying its nitrile, which is got from phenyl-hydrazine dicyanide and heptoic aldehyde (œnanthol) (Bladin, *B.* 25, 186). Silvery plates, v. sol. alcohol.—CuA'_2 aq.—HA'HCl.

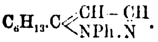
Amide. [82·5°]. White plates.

Thio-amide $C_{11}H_{18}N_2.CS.NH_2$. [77°]. Formed from the crude nitrile and alcoholic ammonium sulphide. Yellow plates, sol. alcohol.

DI-PHENYL-HEXYL-TRICYANIDE  $N\left\langle\begin{matrix}CPh.N\\CPh:N\end{matrix}\right\rangle C.(CH_2)_5.CH_3$. [44°]. (265° at 15 mm.). Got from heptoyl chloride, benzonitrile, and $AlCl_3$ at 70° (Krafft a. Hanssen, *B.* 22, 808).

PHENYL HEXYL KETONE $C_6H_5.CO.C_6H_{13}$. [17°]. (267°) at 740 mm. Formed by the action of $AlCl_3$ on a mixture of benzene and heptoyl chloride (Auger, *Bl.* [2] 47, 50; Krafft, *B.* 19, 2987). Leaflets. Yields an oxim [55°].

PHENYL-HEXYL-(β)-NAPHTHOTRIAZINE. *Dihydride* $C_{23}H_{25}N_3$ *i.e.*  $C_{10}H_6\left\langle\begin{matrix}N.CH.C_6H_{13}\\N.NPh\end{matrix}\right.$. [176·5°]. Formed by heating benzene-azo-(β)-naphthylamine with œnanthol and alcohol (Goldschmidt a. Poltzer, *B.* 24, 1007). Needles, sol. alcohol.—B'HCl. [226°]. White needles.—$B'_2H_2PtCl_6$. [225°]. Granules.

PHENYL-HEXYL-PYRAZOLE $C_{15}H_{20}N_2$ *i.e.*  $C_6H_{13}.C\left\langle\begin{matrix}CH-CH\\NPh.N\end{matrix}\right.$. (319°). Formed from heptoyl-acetic aldehyde and phenyl-hydrazine (Claisen a. Stylos, *B.* 21, 1149). Oil.

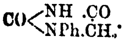
PHENYL-HEXYL-THIO-UREA $C_{13}H_{20}N_2S$ *i.e.* $CS(NHPh).NH.CH_2.CHEt_2$. [53°]. Formed from hexylamine and phenyl-thiocarbimide (Freund a. Herrmann, *B.* 23, 195). Prisms.

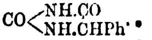
PHENYL-HEXYL-UREA $C_{13}H_{20}N_2O$ *i.e.* $CO(NHPh).NH.CH_2.CHEt_2$. [70°]. Formed from hexylamine and phenyl cyanate (Freund a. Herrmann, *B.* 23, 194). Needles.

PHENYL-HOMO-ITAMALIC ACID *v.* OXY-BENZYL PYROTARTARIC ACID.

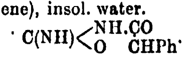
PHENYL-HYDANTOÏC ACID $NH_2.CO.NH.CHPh.CO_2H$. [178°]. Got by boiling (α)-phenyl-hydantoïn with baryta (Pinner, *B.* 21, 2326). Prisms, sl. sol. cold water.

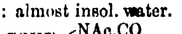
Amide $NH_2.CO.NH.CHPh.CO.NH_2$. [223°]. Formed by adding the compound got from urea and the cyanhydrin of benzoic aldehyde to H_2SO_4 and pouring into water at 0° (Pinner a. Spilker, *B.* 22, 697). Prisms (from dilute alcohol). Yields phenyl-hydantoïn on heating.

PHENYL-HYDANTOÏN $C_9H_8N_2O_2$ *i.e.*  $CO\left\langle\begin{matrix}NH\ .CO\\NPh.CH_2\end{matrix}\right.$. [192°]. Formed by fusing urea with phenyl-amido-acetic acid (Schwebel, *B.* 10, 2045). Needles, v. sl. sol. water, sol. alkalis.

(α)-Phenyl-hydantoïn  $CO\left\langle\begin{matrix}NH.CO\\NH.CHPh\end{matrix}\right.$. *Di-oxy-phenyl-glyoxaline.* [178°]. Formed by heating the cyanhydrin of benzoic aldehyde with mandelic nitrile at 100° (Pinner, *B.* 21, 2321). Formed also from phenyl-uramido-acetic ether and KOH (Kossel, *B.* 24, 4150). Needles (from HClAq). KOH and MeI yield $C_9H_7MeN_2O_2$ [162°], crystallising in needles.—KA': needles, v. sol. water.

Acetyl derivative $C_9H_7AcN_2O_2$. [145°]. Small needles (from benzene), insol. water.

Phenyl-ψ-hydantoïn  $C(NH)\left\langle\begin{matrix}NH.CO\\O\quad CHPh\end{matrix}\right.$. [above 300°]. Got by dissolving (α)-phenyl-hydantoïn in alcoholic potash and then adding HCl. Crystalline.—KA': almost insol. water.

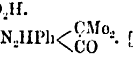
Acetyl derivative  $C(NH)\left\langle\begin{matrix}NAc.CO\\O\quad CHPh\end{matrix}\right.$. White prisms (Pinner a. Spilker, *B.* 22, 698). Decomposes at about 290°.

PHENYL-HYDRAZIDO-ACETIC ACID $C_6H_5NH.NH.CH_2.CO_2H$. [159°]. Formed by reducing the phenyl-hydrazide of glyoxylic acid (Elbers, *A.* 227, 353). Formed also by reducing phenyl-osotriazole carboxylic acid with sodium-amalgam (Pechmann, *A.* 262, 288). Hexagonal tables, sol. hot water. Re-oxidised by Fehling's solution to $NHPh.N:CH.CO_2H$.

u-**Phenyl-hydrazido-acetic acid** $NH_2.NPh.CH_2.CO_2H$. [131°]. Got by saponifying its ether [127°], which is formed by heating phenyl-hydrazine with chloro-acetic ether at 100° (Reissert a. Kayser, *B.* 24, 1519). Needles.

PHENYL-HYDRAZIDO-BUTYRIC ACID $C_{10}H_{14}N_2O_2$ *i.e.* $CHEt(N_2H_2Ph).CO_2H$. Formed by reducing the phenyl-hydrazide of ethyl-glyoxylic acid (Japp a. Klingemann, *A.* 247, 217). Needles (from MeOH). Softens at 165°.

Phenyl-hydrazido-isobutyric acid $CMe_2(N_2H_2Ph).CO_2H$.

Anhydride  $N_2HPh\left\langle\begin{matrix}CMe_2\\CO\end{matrix}\right.$. [175°]. Got by gently heating the nitrile with H_2SO_4 and pouring into water (Reissert, *B.* 17, 1458). Crystals, v. sol. alcohol.—B'HCl: crystals.

Nitrile $CMe_2(N_2H_2Ph).CN$. [70°]. Got by heating the cyanhydrin of acetone with phenyl-hydrazine at 100°. Needles, v. sol. alcohol.

Imide $(CMe_2(N_2H_2Ph).CO)_2NH$. [117°]. Got by passing HCl into an alcoholic solution of the nitrile.—$B'''H_3Cl_3$: crystals.

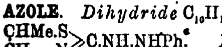
Phenyl-hydrazido-butyric acid $NH_2.NPh.CHMe.CH_2.CO_2H$. [111°]. Formed from potassium β-bromo-butyrate, phenyl-hydrazine and NaOAc in aqueous solution (Lederer, *J. pr.* [2] 45, 87). Plates (from alcohol), v. sol. hot Aq. Converted by conc. H_2SO_4 into oxy-phenyl-methyl-pyrazole dihydride.

PHENYL - β - HYDRAZIDO - CROTONIC ETHER $CH_3.C(NH.NHPh):CH.CO_2Et$. [50°]. Formed from acetoacetic ether (1 mol.) dissolved in ether by adding phenyl-hydrazine (Nef, *A.* 266, 70; *cf.* Knorr, *A.* 238, 147). Colourless needles, v. e. sol. ether, sl. sol. ligroïn. Turns yellow in air. Split up by conc. HClAq into phenyl-hydrazine and acetoacetic ether. When heated *in vacuo* at 200° it changes to oxy-phenyl-methyl-pyrazole. Conc. H_2SO_4 followed, after 10 minutes, by water forms methyl-indole carboxylic ether [134°]. HgO oxidises it to the azo-compound $CH_3.C(N_2Ph):CH.CO_2Et$ crystallising from light petroleum in red needles [51°]. AcCl forms a di-acetyl derivative $CH_3.C(NAc.NAcPh):CH.CO_2Et$ (245°–250° at 150 mm.).

PHENYL-HYDRAZIDO-METHYL-QUINOLINE $C_9H_5MeN(N_2H_2Ph)$. [197°]. Formed from

(*Py.* 3) methyl-quinoline and phenyl-hydrazine (Ephraim, *B.* 24, 2820).

PHENYL - HYDRAZIDO - METHYL - THIAZOLE. *Dihydride* $C_{10}H_{13}N_3S$ *i.e.*



$$\begin{matrix}CHMe.S\\CH_2—N\end{matrix}\!\!>C.NH.NHPh.$$

Phenyl-propylene-ψ-thio-semicarbazide. [93°]. Formed by heating phenyl-allyl-thio-urea with conc. HClAq at 100° (Arenarius, *B.* 24, 269). Yellowish plates (from ligroïn).—B'HCl. [202°]. Concentric crystals. —*Picrate.* [167°].

PHENYL - HYDRAZIDO - PHENYL - ACETIC ACID $C_{14}H_{14}N_2O_2$ *i.e.* NHPh.NH.CHPh.CO_2H. [158°]. Got by reducing the phenyl-hydrazide of phenyl-glyoxylic acid (Elbers, *A.* 227, 315). Crystalline, v. sl. sol. cold water, v. sol. alcohol.

PHENYL-HYDRAZIDO-PROPIONIC ACID $C_9H_{12}N_2O_2$ *i.e.* NH_2.NPh.CHMe.CO_2H. [187°]. Formed by boiling its amide with NaOHAq (Reissert, *B.* 17, 1454; 20, 3110; 22, 2924). The ether is got by heating lactic ether with phenyl-hydrazine. Needles. Yields phenyl-α-amido-propionic acid on reduction.

Ethyl ether EtA'. [116°].—EtA'HCl.

Nitrile. [58°]. Formed by heating CH_3.CH(OH).CN with phenyl-hydrazine at 100°.

Amide. [124°]. White crystals.

Phenyl-hydrazido-propionic acid NHPh.NH.CHMe.CO_2H. [172°]. Formed by reducing the phenyl-hydrazide of pyruvic acid with sodium-amalgam (Fischer a. Jourdan, *B.* 16, 2244; Japp a. Klingemann, *B.* 20, 3284; *A.* 247, 211). Needles (from MeOH). Re-oxidised by cold Fehling's solution to NHPh.N:CMe.CO_2H.

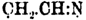
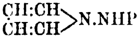
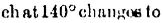
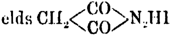
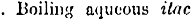
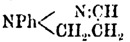
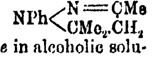
PHENYL-HYDRAZIDO-QUINOLINE C_9H_6N.NH.NHPh. [191°]. Formed from (*Py.* 3)-chloro-quinoline and phenyl-hydrazine (Ephraim, *B.* 24, 2818). Needles, v. sol. chloroform. Reduced by HI and P to (*Py.* 3)-amido-quinoline.

PHENYL-HYDRAZINE $C_6H_8N_2$ *i.e.* NHPh.NH_2. [23°]. (241·5° i.V.) at 750 mm. S.G. $\frac{22.7}{4}$ 1·097 (E. Fischer, *A.* 236, 198). H.C.v. 805,240. H.C.p. 806,300. H.F. 34,200 (from diamond) (Petit, *A. Ch.* [6] 17, 168).

Formation.—(E. Fischer, *B.* 8, 589, 1005, 1641; 9, 111, 880; *A.* 190, 67).—By the action of zinc and HOAc on diazo-benzene anilide or diazo-benzene diethylamide.

Preparation.—1. A cold solution of $7\frac{1}{2}$ pts. of sodium nitrite in 50 pts. of water is slowly added to a well-cooled mixture of 10 pts. of aniline and 200 pts. of HCl (30 p.c.). To the diazo-benzene chloride solution so prepared a cold solution of 45 pts. of stannous chloride in 45 pts. of HCl is now added, when the mixture immediately becomes a thick magma of phenyl-hydrazine hydrochloride, which is filtered off, basified, and distilled (Meyer a. Lecco, *B.* 16, 2976).—2. Aniline (28 g.) is dissolved in K_2CO_3 (21 g.) and water (500 c.c.) by passing in SO_2. The solution is mixed with a cold solution of $NaNO_2$ (25 g.) exactly neutralised by HOAc. After two hours the product is warmed till dissolved, acidified by HOAc, and reduced with zinc-dust and HClAq (Reychler, *B.* 20, 2463). By adding diazo-benzene nitrate to a cold aqueous solution of $KHSO_3$, heating the resulting $C_6H_5.N_2.SO_3K$ with excess of $KHSO_3$, and decomposing the C_6H_5.NH.NH.SO_3K, thus formed, by heating with HClAq.

Properties.—Oil, solidifying to monoclinic tables; v. sl. sol. hot water, almost insol. KOHAq. Miscible with alcohol, ether, benzene, and $CHCl_3$. Volatile with steam. Reduces Fehling's solution in the cold, N, aniline, and benzene being formed. When heated for a long time at 150° it is gradually split up into aniline, NH_3, benzene, and N (Reissert a. Kayser, *B.* 23, 3703). Reduces SeO_2 to Se (Hinsberg, *A.* 260, 42). Gives benzene and N when boiled with $CuSO_4$. It is very poisonous.

Reactions.—1. H_2O_2 forms benzene and diazo-benzene imide PhN_3 (Wurster, *B.* 20, 2633).—2. Yellow HgO added to its ethereal solution forms aniline, N, and $HgPh_2$ (Fischer, *A.* 199, 320). HgO added to a solution of the sulphate forms diazo-benzene sulphate and imide.—3. $SOCl_2$ in ether forms in the cold NPhH.N:SO, which crystallises in yellow prisms [105°]; v. sol. ether, volatile with steam. Thionyl-phenyl-hydrazine is hardly attacked by HCl, but is converted by NaOHAq into phenyl-hydrazine and Na_2SO_3. Br forms NPhBr.NBr_2. AcCl forms diazo-benzene chloride, S, and HOAc (Michaelis, *B.* 22, 2228; *A.* 270, 115).—4. SO_2 passed into an ethereal solution of phenyl-hydrazine forms NHPh.$NH_2.SO_2$ as a crystalline pp. SO_2 passed into an alcoholic solution of phenyl hydrazine forms $(NHPh.NH_2)_2SO_2$; v. sol. water and alcohol, insol. ether, crystallising in tables which shrink together at 70°, but decompose at a higher temperature (Michaelis a. Ruhl, *B.* 23, 474). SO_2 passed into a benzene solution at 75° forms NHPh.N:SO, which when heated with phenyl-hydrazine gives Ph_2S_2, benzene, and N.—5. Dry CO_2 forms solid phenyl-hydrazine phenyl-carbazate $(NHPh.NH_2)_2CO_2$ or $N_2PhH_2.CO.O.N_2PhH_4$, which is crystalline; sl. sol. water and ether, decomposed by hot water.—6. CS_2 forms the corresponding $N_2PhH_2.CS.S.N_2PhH_4$ [97°], which at 110° splits up into H_2S and di-phenyl-thiocarbazide. COS forms crystalline $COS(N_2H_3Ph)_2$ (Fischer, *B.* 22, 1935).—7. *Zinc-dust* and conc. HClAq slowly form aniline and NH_3.—8. Excess of phenyl-hydrazine acts upon *iodine*, forming HI, aniline, and PhN_3 (Fischer, *B.* 10, 1335). Excess of I forms iodo-benzene, N, and HI (E. von Meyer, *J. pr.* [2] 36, 115). This reaction may be used for the volumetric estimation of phenyl-hydrazine.—9. *Sulphur* above 80° forms aniline, H_2S, N, Ph_2S_2, Ph_2S, PhSH, benzene, and NH_3.—10. *Nitrous acid* forms PhN_3. KNO_2 added to the hydrochloride at 0° forms a yellow crystalline pp. of NPh(NO)NH_2.—11. *Alcoholic potash* and *chloroform* form, on heating, $C_{14}H_{12}N_4$ [180°], mol. w. 236. This body crystallises in white needles; sol. alcohol, scarcely affected by HClAq at 200°, and yielding crystalline $C_{14}H_{11}N_4.NO_2$ and $C_{14}H_{11}N_4.SO_3H$ (Ruhemann a. Elliott, *C. J.* 53, 850).—12. EtBr forms NPhEt.NH_2, NPhH.NHEt, and $NPhEt_2Br.NH_2$.—13. Aqueous *diazobenzene nitrate* added to a cold solution of the hydrochloride ppts. PhN_3, aniline nitrate remaining in solution.—14. Reacts with aldehydes and ketones, forming phenyl-hydrazides; *e.g.* (Fischer, *B.* 17, 572) $CH_3.CHO + NPhH.NH_2 = H_2O + CH_3.CH:N.NHPh$. Thus a solution of phenyl-hydrazine hydrochloride (2 pts.) and crystallised sodium acetate (3 pts.) in water (20 pts.) gives a pp. of the phenyl-hydrazide when added to an aqueous solution of an aldehyde or ketone, either in the cold, or, in the case of aromatic compounds, on warming. These phenyl-hydrazides are decomposed by acids into the original components, and, in alcoholic solution, by sodium-amalgam and HOAc into aniline and a base. The phenyl-hydrazides of ketones are converted by $ZnCl_2$ into derivatives of indole. The phenyl-hydrazides of aldehydes and ketones are described under the aldehydes and ketones from which they are derived.—15. *Diketones* containing the group CO.CHX.CO yield derivatives of phenyl-pyrazole. Saturated γ-diketones in ethereal solution usually form a mono- or di- phenyl-hydrazide; in HOAc the product is the anhydride of the mono-phenyl-hydrazide, a derivative either of  $\begin{matrix}CH_2.CH:N\\CH:CH.NPh\end{matrix}$ or of  $\begin{matrix}CH:CH\\CH:CH\end{matrix}\!\!>N.NHPh$ (Klingemann, *A.* 269, 108).—16. *Acetoacetic ether* forms a phenyl-hydrazide, which at 140° changes to oxy-phenyl-methyl-pyrazole  $NPh<\begin{matrix}CO.CH_2\\N\ :CMe\end{matrix}$ by loss of alcohol. *Acetyl-propionic acid* forms the compound $CH_3.C(N_2HPh).CH_2.CH_2.CO_2H$ [108°]. *Benzoylacetic ether* forms two compounds [132°] and [165°] (Bender, *B.* 21, 2495).—**17.** Reacts with *sugars* as with aldehydes; thus a solution of glucose gives $CH_2(OH).(CH(OH))_4.CH:N_2HPh$ [145°] on heating with phenyl-hydrazine, while galactose gives $C_6H_{12}O_5(N_2HPh)$ [158°] (Fischer, *B.* 20, 824). On heating these compounds with aqueous phenyl-hydrazine acetate at 100° 'osazones' are formed, *e.g.* phenyl-glucosazone $CH_2OH.(CH.OH)_3.C(N_2HPh).CH:N_2HPh$ [204°] and the isomeric phenyl-galactosazone [c. 191°]. 18. By heating with phenyl-hydrazine hydrochloride and NaOAc *arabinose* is converted into $C_{17}H_{20}N_4O_3$ [158°]; *formose* into $C_{18}H_{22}N_4O_4$ [c. 144°]; *acrose* (the product of the action of NaOHAq on glyceric aldehyde) into $C_{18}H_{22}N_4O_4$ [c. 217°] and an isomeride [159°].—19. Phenyl hydrazine acetate reacts with the *product of oxidation of glycerin* with Na_2CO_3Aq and Br forming glycerosazone $C_{15}H_{16}N_4O$ crystallising from benzene in yellow plates [131°] (Fischer a. Tafel, *B.* 20, 1089, 3386).—20. *Erythrite*, after oxidation by dilute HNO_3, yields with phenyl-hydrazine hydrochloride and NaOAc the compound $C_4H_6O_2(N_2HPh)_2$ [167°]. 21. *Mannite* on oxidation with HNO_3 yields levulose (mannitose) and mannose, which with phenyl-hydrazine forms $C_{12}H_{18}N_2O_5$ [195°-200°] (Fischer, *B.* 21, 1805).—22. The acetate reacts with the *product of oxidation of dulcite* by bromine and Na_2CO_3Aq with formation of the 'phenyldulciteosazone' $C_{18}H_{22}N_4O_4$ [206°].—23. *Isodulcite* heated with phenyl-hydrazine hydrochloride and sodium acetate at 100° forms 'phenyl-isodulcite-osazone' $C_{18}H_{22}N_4O_3$ or $C_6H_{10}O_3(N_2HPh)_2$ [180°]. Solutions of *isodulcite* and phenyl-hydrazine form, on mixing, $C_6H_{12}O_4(N_2HPh)$ [159°] (Fischer a. Tafel, *B.* 20, 2574; Raymann, *Bl.* [2] 47, 760).—24. *Sorbin* heated with aqueous phenyl-hydrazine hydrochloride and NaOAc at 100° forms the osazone $C_{18}H_{22}N_4O_4$ [164°].—25. *Milk sugar* heated with aqueous phenyl-hydrazine hydrochloride and NaOAc forms $C_{24}H_{32}N_4O_9$ [200°] and $C_{24}H_{30}N_4O_8$ [224°].—26. *Maltose* forms $C_{21}H_{32}N_4O_9$ [191°].—27. The acetate gives with *glyoxylic, phenyl-glyoxylic*, and *pyruvic acids* the corresponding phenyl-hydrazides [137°], [153°], and [192°] respectively.—28. Phenyl-hydrazine in HOAc (50 p.c.) gives with a dilute solution of *gluconic, galactonic, and arabinose carboxylic acids* compounds $C_6H_{11}O_6.N_2H_2Ph$ [200°], [203°], and [216°] respectively (Fischer a. Passmore, *B.* 22, 2760). These compounds are m. sol. hot water. *Saccharic acid* gives a similar compound $C_6H_{11}O_5N_2H_2Ph$ [165°] which, as well as the compounds from mucic and meta-saccharic acid, is almost insoluble. The compound from mucic acid melts at 240°. All these compounds contain the group CO.NH.NHPh. Compounds containing this group are also obtained by the action of phenyl-hydrazine and dilute HOAc at 100° on *formic, succinic, malic, tartaric, cinnamic*, and *gallic acids*, but not from *glycollic, lactic*, and *glyceric acids*. The compounds got from succinic, malic, gallic, and tartaric acid melt at 218°, 223°, 187°, and 240° respectively. Acetyl-phenyl-hydrazine is produced when aqueous phenyl-hydrazine acetate is heated at 130°; and a similar reaction occurs with benzoic, glyceric, and lactic acids. Compounds containing the group CO.NH.NHPh give a reddish-violet colouration with H_2SO_4 and a little $FeCl_3$, and they are readily decomposed by KOHAq and by baryta into phenyl-hydrazine and a salt of the acid (Fischer, *B.* 22, 2728).—29. *Glucose carboxylic lactone* yields $C_7H_{13}O_7.N_2H_2Ph$ [172°], while *mannose carboxylic acid* gives an isomeric body [223°].—30. The acetate gives with *rhamnose carboxylic acid* the compound $C_7H_{13}O_7N_2H_2Ph$ [c. 210°], while 31. *Malonic acid* heated at 100° with phenyl-hydrazine and dilute HOAc forms $C_{15}H_{18}N_4O_2$ [143°] and $CO_2H.CH_2.CO.N_2H_2Ph$ [154°], which when heated with water and phenyl-hydrazine at 200° yields  $CH_2<\begin{matrix}CO\\CO\end{matrix}\!\!>N_2HPh$ [128°].—32. *Lactic ether* forms, on heating, phenyl-hydrazido-propionic ether. *a-Oxy-butyric acid* at 160° forms $C_{10}H_{11}N_2O_2$ [152°], while mandelic acid yields $C_{14}H_{11}N_2O_2$ [182°] (Reissert a. Kayser, *B.* 22, 2924).—33. *γ-Oxy-valeric lactone* at 100° forms $C_5H_8O_2N_2PhH_3$ [79°] (Wislicenus, *B.* 20, 402).—34. *Benzoyl-carbinol* gives $N_2HPh:CPh.CH_2OH$ [112°] and the 'osazone' $N_2HPh:CPh.CH:N_2HPh$ [192°] (Laubmann, *A.* 243, 244).—35. Boiling aqueous *itaconic acid* forms the acid  $NHPh.N<\begin{matrix}CH_2.CH.CO_2H\\CO\ .\ CH_2\end{matrix}$ [194°] (Scharfenberger, *A.* 254, 150).—36. *Cinnamic acid* forms $C_{13}H_{14}N_2O$ [183°], which on distillation yields $C_{15}H_{12}N_2O$ [251°] (Knorr, *B.* 20, 1107).—37. *Acrolein* reacts forming phenyl-pyrazole dihydride  $NPh<\begin{matrix}N:CH\\CH_2.CH_2\end{matrix}$ [52°] (274°) (Fischer a. Knoevenagel, *A.* 239, 194).—38. *Mesityl oxide* yields phenyl-tri-methyl-pyrazole  $NPh<\begin{matrix}N=CMe\\CMe_2.CH_2\end{matrix}$ (F. a. K.).—39. *Chloro-acetone* in alcoholic solution at −18° forms $C_{24}H_{26}N_6$ [158°] which yields an acetyl derivative $C_{24}H_{25}AcN_6$ [220°] (Bender, *B.* 21, 2496). *s-Tetra-chloro-acetone* forms $C_{15}H_{12}N_4$ [126°] converted by fuming HNO_3 into $C_{15}H_{10}N_6O_5$ [235°] and by $SnCl_2$ to two bases $C_{15}H_{11}N_4$ [77°] and [193°] (Levy a. Witte, *A.* 252, 343; Zincke a. Kegel, *B.* 22, 1478).—40. *Tetra-bromo-di-benzyl-ketone* heated with alcoholic phenyl-hydrazine at 150° forms $C_3Ph_2(N_2Ph)_2$ [70°] (Bourcart, *B.* 22, 1369).—41. *Di-bromo-aceto* *phenone* forms $N_2HPh:CPh.CH:N_2HPh$ [148°], crystallising from alcohol in yellow prisms (B.). 42. *Bromo-acetyl-propionic ether* mixed with an alcoholic solution of phenyl-hydrazine forms $CH_3.C(N_2HPh).CH:CH.CO_2Et$ [117·5°], which on reduction with tin and HCl forms methyl-indole carboxylic acid (Bender). Bromo-acetyl-propionic acid forms $CH_3.C(N_2HPh).CH:CH.CO_2H$ [157°] (Decker, *B.* 21, 2937). — 43. *Di-chloro-maleïc imide* at 100° forms $C_4O_2(N_2H_2Ph)_2NH$ crystallising from acetone in orange-red needles (Ciamician, *B.* 22, 2495).—44. *Amides* react thus: $N_2H_3Ph + R.CO.NH_2 = NH_3 + R.CO.N_2H_2Ph$ (Just, *B.* 19, 1201).—45. *Carbamic ether* forms, on heating, di-phenyl-carbazide $CO(NH.NHPh)_2$ [151°] (Skinner a. Ruhemann, *B.* 20, 3372).—46. Reduces *alloxan* to alloxantin, N and benzene being formed (Pellizzari, *G.* 17, 254). In this reaction the first product is the compound $CO{<}\begin{matrix}NH.CO\\NH.CO\end{matrix}{>}C(OH).N_2H_2Ph$ (Skinner a. Ruhemann, *C. J.* 53, 550).—47. *Parabanic acid* with phenyl-hydrazine hydrochloride and NaOAc yields $C_{15}H_{20}N_6O_4$ [170°], which on boiling with water forms $NH_2.CO.NH.CO.CO.N_2H_2Ph$ [215°] (S. a. K.).—48. *Urea* heated with phenyl-hydrazine hydrochloride at 160° forms phenyl-urazole $NPh{<}\begin{matrix}NH.CO\\CO.NH\end{matrix}$ [263°]. — 49. Reduces *nitroso-aniline* to *p*-phenylene-diamine and $C_{12}H_{12}N_4O$ (Fischer, *B.* 21, 2610). —50. The acetate (2 mols.) acting on *nitroso-dimethyl-aniline* (3 mols.) forms $C_{14}H_{16}N_4O$ [103°]. An ethereal solution of phenyl-hydrazine converts nitroso-di-methyl-aniline into di-methyl-amido-benzene-azo-di-methyl-aniline and phenylene-di-methyl-diamine. In alcoholic solution there is formed $NHPh.C_6H_4.NMe_2$ [130°] which yields a nitrosamine $C_{14}H_{15}N_3O$ [116°] (O. Fischer, *B.* 21, 2609).—51. *Di-nitroso-acetone* (1 mol.) mixed with phenyl-hydrazine (1 mol.) in hot alcoholic solution forms $CH(NOH).C(N_2HPh).CH(NOH)$ [145°]. Di-nitroso-acetone boiled with excess of phenyl-hydrazine acetate forms $C_{15}H_{12}N_4$ crystallising in yellow plates [122°].—52. *Diazo-acetic ether* at 100° gives off N and forms a colourless compound [136°]. — 53. *p-Diazo-benzene sulphonic acid* forms the compound $N_3C_6H_4.SO_3N_2H_4Ph$ aq crystallising in plates (Griess, *B.* 20, 1528).—54. *Di-acetyl-succinic ether* fused with phenyl-hydrazine at 100° forms $CO_2Et.CH(CMe:N_2PhH).CHAc.CO_2Et$ [91°] and $CO_2Et.CH(CMe:N_2PhH).CH(CMe:N_2PhH).CO_2Et$ which on heating with toluene at 180° gives di-oxy-di-phenyl-di-methyl-dipyrazyl (*q.v.*). — 55. *Dioxims* form additive compounds; *e.g. glyoxim* yields $C_2H_2(NOH)_2N_2H_3Ph$ [110°], *di-phenyl-glyoxim* yields $C_2Ph_2(NOH)_2N_2H_3Ph$ [150°], while the *di-oxim of (β)-naphthoquinone* forms $C_{10}H_6(NOH)_2N_2H_3Ph$ [138°] (Polonowsky, *B.* 21, 182).—56. *Phloroglucin* kept for five days with an alcoholic solution of phenyl-hydrazine in the cold forms $C_6H_3(OH)(N_2H_2Ph)_2$ [144°] which may be oxidised by $FeCl_3$ to $C_6H_3(OH)(N_2Ph)_2$ [177°] (Baeyer *B.* 22, 2891).—57. *Thio-acetoacetic ether* forms $S(CH{<}\begin{matrix}CO-NPh\\CMe:N\end{matrix})_2$ [183°], together with the compounds $NHPh.N:C{<}\begin{matrix}CO-NPh\\CMe:N\end{matrix}$ [156°], $S_2(CH{<}\begin{matrix}CO-NPh\\CMe:N\end{matrix})_2$ and di-oxy-di-phenyl-di-methyl-dipyrazyl (Sprague, *C. J.* 59, 332).—5 *Cyanogen* passed into an emulsion of pheny hydrazine in cold water forms the dicyanide (*infra*). - 59. *Cyanogen* passed into an alcoholi solution forms $PhN_2H_2.C(NH).C(NH).N_2PhH$ [225°], crystallising in white plates (fro alcohol). The same compound is formed by th action of phenyl-hydrazine on cyananiline. I gives a rose-red colour with alcoholic NH Conc. H_2SO_4 is coloured indigo-blue. Dry HC forms the hydrochloride $C_{14}H_{16}N_6 2HCl$ [188 Dilute HCl forms $PhN.NH.CO.C(NH).NHNHP$ [180°].—60. *Cyananiline* in chloroform solutio forms, after boiling, matted needles of the com pound $C_{21}H_{23}N_8Cl_2$ [200°-212°]. This body i perhaps $(PhH_2N_2.CHCl.C_{14}H_{15}N_6)2HCl$ (Senf *J. pr.* [2] 35, 533).—61. PCl_3 in ether form amorphous $NHPh.N:P.NH.NHPh$ converted b water into $(NHPh.NH)_2POH$, a yellowish-whit powder [92°] which reduces Fehling's solutio in the cold (Michaelis a. Oster, *A.* 270, 126) This body is split up by acids into phenyl-hydrazine and H_3PO_3, but is attacked by alkali with difficulty. Benzoic aldehyde produce $NPhH.N:CHPh$ and H_3PO_3.—62. $POCl_3$ forms $PO(NH.NHPh)_3$ [196°], easily decomposed by acids and alkalis (Michaelis, *A.* 270, 135).—63. $PSCl_3$ forms, in like manner, $PS(NH.NHPh)_3$ [154°].—64. $AsCl_3$ forms $(N_2PhH_3)_3AsCl_3$, an amorphous powder decomposed at 236°.—65. BCl_3 forms, in like manner, $(N_2PhH_3)_3BCl_3$, v. sol. water, decomposed at 242°.—66. $C_6H_5PCl_2$ in ether forms $NHPh.N.PC_6H_5$ [152°] crystallising from EtOAc in plates (Michaelis a. Oster, *A.* 270, 129). It reduces hot Fehling's solution, and is split up by acids into $PhPO_2H_2$ and phenyl-hydrazine.

Salts.—B'HCl. Plates, m. sol. water. Got by ppg. an alcoholic solution of the base by HCl, and washing the pp. till it is colourless.—B'HBr. Needles (from water).—$B'_2H_2SO_4$. Plates, v. sol. water.—$B'C_6H_3N_3O_7$. Yellow needles.—$B'_2H_2C_2O_4$. Plates.—**Benzene sulphinate**; [131°] (Escales, *B.* 18, 895).—**Di-nitro-(α)-naphthol sulphonate**: light-brown needles, sl. sol. hot water (Richardson, *C. N.* 58, 39).—**Sulphocyanide**: sparingly soluble plates. Changes at 160°-170° into phenyl-thio-semicarbazide. — $B'H_3PO_3$. [118°] (Michaelis, *A.* 270. 127, 133).—$B'_2H_3PO_3$. [121°]. — $B'C_6H_5PH_2O_2$. [135°].

Sodium derivative $C_6H_5NNa.NH_2$. Formed by dissolving 8 g. of sodium in 70 g. of warm phenyl-hydrazine. The H evolved reduces some of the phenyl-hydrazine to NH_3 and aniline; when the reaction is complete the aniline and excess of phenyl-hydrazine are distilled off by heating the product in an oil-bath to 200°-210° (not higher) in a current of H. It is a yellow hygroscopic powder. When finely divided it sometimes takes fire in the air. Decomposed by water into phenyl-hydrazine and NaOH. Readily reacts with alkyl haloids, giving unsymmetrical phenyl-alkyl-hydrazines (Michaelis, *B.* 19, 2448; *A.* 252, 266).

Formyl derivative NHPh.NH.CHO. [145°]. Formed by heating formamide with phenyl-hydrazine at 180°. White scales.

Acetyl derivative NHPh.NHAc. [128·5°]. Formed by heating phenyl-hydrazine with HOAc or acetamide (Fischer, *A.* 190, 129; Just. *B.*

19, 1201). Formed also from the sodium- derivative and Ac$_2$O at 0° (Michaelis a. Schmidt, *A.* 252, 301). Six-sided prisms, sl. sol. cold water.

Di-acetyl derivative NPhAc.NHAc. [108°]. Formed from NPhNa.NH$_2$ and AcCl in ether. Tables or needles, v. e. sol. alcohol. Completely reduces hot Fehling's solution.

Chloro-acetyl derivative NHPh.NH.CO.CH$_2$Cl. [115°]. Formed from the base and CH$_2$Cl.COCl in ether (Gattermann, *B.* 25, 1081).

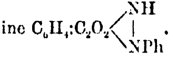
Propionyl derivative NHPh.NH.CO.Et. [158°] (Freund a. Goldschmidt, *B.* 21, 2161).

n-Butyryl derivative. [114°]. Scales, v. sol. ether (Michaelis a. Schmidt, *A.* 252, 308).

Isovaleryl derivative NHPh.NH.CO.CH$_2$Pr. [101°]. Formed from the base and aceto-valeric anhydride (Autenrieth, *B.* 20, 3190). Plates, v. sl. sol. cold ligroïn.

Hexoyl derivative. [117°]. Needles.

s-Benzoyl derivative NHPh.NHBz. [169°]. Formed from phenyl-hydrazine by adding BzCl in ether at 0° (Fischer, *A.* 190, 125), or by heating with benzamide (Just, *B.* 19, 1203). Formed also by warming phenyl-hydrazine with BzCy (Hausknecht, *B.* 22, 329). Prisms, sl. sol. hot water. Yields NPhMe.NHBz on methylation. Reduces HgO. Phthalic anhydride at 180° forms an addition-compound C$_{21}$H$_{16}$N$_2$O$_4$ [172°], crystallising from alcohol in prisms. It is probably CO$_2$H.C$_6$H$_4$.CO.NPh.NHBz. At 250° it splits up into benzoic acid and (*β*)-phthalyl-phenyl-hydrazine



$$C_6H_4{:}C_2O_2\left\langle\begin{array}{l}NH\\ \,|\\ NPh\end{array}\right.$$

u-Benzoyl derivative NPhBz.NH$_2$. [70°]. A product of the action of BzCl in benzene on NPhNa.NH$_2$ at 0° (Michaelis a. Schmidt, *B.* 20, 43, 1718; *A.* 252, 310). Needles (from water). Reduces hot Fehling's solution but not HgO. Conc. HCl at 150° gives HOBz and phenyl-hydrazine. HNO$_2$ forms in acid solution benzanilide and N$_2$O, but in neutral solution it forms N$_3$Ph and HOBz. Reacts like phenyl-hydrazine with aldehydes and ketones; thus acetone yields NPhBz.N:CMe$_2$ [115·5°], acetophenone forms NPhBz.N:CMePh [124°], and benzoic aldehyde gives NPhBz.N:CHPh [122°]. Salts.—B'HCl. [202°]. Needles, m. sol. HClAq. —NPhBz.NHNa. White pp., decomposed by water.—B'$_2$H$_2$SO$_4$. [191°]. Needles, sl. sol. cold water.—B'HNO$_3$. [145°].—B'C$_6$H$_3$N$_3$O$_7$. [122°].

Di-benzoyl derivative NPhBz.NHBz. [178°] (Fischer, *A.* 190, 128; M. a. S.). Prisms, v. sl. sol. water, sol. alkalis. On methylation it yields NPhBz.NHBz.—NPhBz.NBzNa: plates.

Benzoyl-acetyl derivative NPhBz.NHAc. [153°]. Got from NPhBz.NH$_2$ and Ac$_2$O. Needles (from dilute alcohol).

p-Nitro-benzoyl derivative NHPh.NH.CO.C$_6$H$_4$.NO$_2$. [198°]. Formed from phenyl-hydrazine and C$_6$H$_4$(NO$_2$)CN (Hausknecht, *B.* 22, 328). Yellowish-red needles.

o-Amido-benzoyl derivative. [170°]. Got by warming phenyl-hydrazine with an alcoholic solution of isatoic acid (Meyer, *J. pr.* [2] 33, 20). Yellow needles, v. sl. sol. ether.

m-Amido-benzoyl derivative NHPh.NH.CO.C$_6$H$_4$.NH$_2$. [151°]. Formed by heating phenyl-hydrazine (1 mol.) with *m*-amido-benzoic acid (1 mol.) at 165° (Pellizzari, *G.* 16, 200). Scales, insol. cold alkalis, sol. acids.

Amido-toluyl derivative [3:6:1] C$_6$H$_3$Me(NH$_2$).CO.N$_2$H$_2$Ph. [198°]. Formed from methyl-isatoic acid and phenyl-hydrazine (Panaotovitch *J. pr.* [2] 33, 68). Prisms (from chloroform), sl. sol. ether.

Phenyl-acetyl derivative N$_2$H$_2$Ph.CO.CH$_2$Ph. [169°]. Got by heating phenyl-acetic acid with phenyl-hydrazine at 150° (Bülow, *A.* 236, 196). Needles (from alcohol), sl. sol. water.

Cinnamoyl derivative N$_2$H$_2$Ph.CO.C$_2$H$_2$.Ph. [258°]. Got by heating cinnamic acid with phenyl-hydrazine at 190° (Knorr, *B.* 20, 1108). Forms, on distillation, a compound C$_{15}$H$_{12}$N$_2$O [258°], crystallising in needles with green fluorescence.

Oxalyl derivative C$_2$O$_2$(N$_2$H$_2$Ph)$_2$. [278°]. Described in vol. iii. p. 655.

Ethyl-malonyl derivative CHEt(CO.N$_2$H$_2$Ph)$_2$. [233°]. Got by heating ethyl-malonic amide with phenyl-hydrazine at 220° (Freund a. Goldsmith, *B.* 21, 1242). Needles (from HOAc). Converted by COCl$_2$ into C$_{19}$H$_{16}$N$_4$O$_4$ [113°].

Succinyl derivative C$_2$H$_4$:C$_2$O$_2$:(N$_2$H$_2$Ph)$_2$. [218°]. Formed from succinyl chloride (1 mol.) and phenyl-hydrazine (2 mols.). Formed also by heating C$_2$H$_4$:C$_2$O$_2$:S with phenyl-hydrazine and HOAc (Zanetti, *Rend. Accad. Linc.* [4] 5, i. 225). Plates (from HOAc) (Freund, *B.* 21, 2456; Fischer a. Passmore, *B.* 22, 2734). When succinic anhydride is heated with phenyl-hydrazine at 160° there is formed C$_2$H$_4$:C$_2$O$_2$:N.NHPh [155°], which yields a nitros-amine C$_2$H$_4$:C$_2$O$_2$:N$_2$Ph.NO [84°] (Hötte, *J. pr.* [2] 35, 293).

(a)-*Phthalyl derivative* C$_6$H$_4$:C$_2$O$_2$:N.NHPh. [179°]. Formed from phenyl-hydrazine and phthalyl chloride in ether (Pickel, *A.* 232, 233). Formed also by heating phenyl-hydrazine (1 mol.) with phthalimide (1 mol.) at 120° (Pellizzari, *G.* 16, 203; Just, *B.* 19, 1204); or with phthalic anhydride (1 mol.) at 150° (Hötte, *J. pr.* [2] 33, 99; 35, 268). Prepared by boiling an alcoholic solution of phthalic anhydride with phenyl-hydrazine. Colourless needles (from alcohol), insol. water and alkalis. Conc. H$_2$SO$_4$ forms a violet solution, turning brown. *Reactions.*—1. Converted by boiling alcoholic *potash* into N$_2$H$_2$Ph.CO.C$_6$H$_4$.CO$_2$H [166°], an acid of which the benzoyl derivative NHPh.NBz.CO.C$_6$H$_4$.CO$_2$H [172°] is formed by heating NHPh.NHBz with phthalic anhydride at 180°.—2. Boiling aqueous KOH or HClAq at 150° splits it up into phthalic anhydride and phenyl-hydrazine.—3. *Benzoyl chloride* at 160° forms C$_6$H$_4$:C$_2$O$_2$:N.NPhBz [193°].—4. *Nitrous acid* passed into its solution in diluted HOAc forms the nitramine C$_6$H$_4$:C$_2$O$_2$:N.NPh.NO$_2$ [148°]; but in boiling HOAc it forms the di-nitro- derivative C$_{14}$H$_8$N$_4$O$_6$ [182°]. Nitrous acid passed into phthalyl-phenyl-hydrazine suspended in ether forms the nitrosamine C$_6$H$_4$:C$_2$O$_2$:N.NPh(NO) [154°].—5. Alcoholic NH$_3$ at 80° forms unstable NH$_2$.CO.C$_6$H$_4$.CO.NH.NHPh [146°], which decomposes at 170° into NH$_3$ and (*β*)-phthalyl-phenyl-hydrazine [210°].

(β)-*Phthalyl derivative* $C_6H_4{:}C_2O_2{<}\begin{matrix}NH\\NPh\end{matrix}$. [210°]. Formed at the same time as the (α)-isomeride by heating phenyl-hydrazine with phthalimide or phthalic anhydride, being the chief product when the temperature is above 163° (Pellizzari, *G.* 16, 204; 17, 278; Hötte, *J. pr.* [2] 35, 284). Monoclinic tablets (from benzene) or prisms (from alcohol), v. sol. alkalis. Ammoniacal $AgNO_3$ ppts. $C_6H_4{:}C_2O_2{:}N_2PhAg$.

Reactions.—1. NaOMe and MeI at 100° form $C_6H_4{:}C_2O_2{:}N_2PhMe$ [125°], which is decomposed by conc. HClAq into phthalic acid and NHPh.NHMe.—2. KOEt and EtI give $C_8H_4O_2{:}N_2PhEt$ [106°].—3. BzCl at 200° forms $C_8H_4O_2{:}N_2PhAc$ [122°].

Phthalyl derivative $C_6H_4(CO.NH.NHPh)_2$. [191°]. Formed by heating phenyl-hydrazine (2 mols.) with phthalic anhydride (1 mol.) at 150° (H.). White tables. At 170° it gives the (β)-phthalyl derivative [210°].

Nitrosamine $NH_2.NPh.NO$. Formed by adding $NaNO_2$ to an aqueous solution of phenyl-hydrazine hydrochloride at 0° (Fischer, *A.* 190, 92). Pale-yellow plates. Very poisonous. Converted by hot alcoholic potash into diazobenzene-imide. Alcoholic HCl acts in like manner. Exhibits Liebermann's reaction.

Dicyanide $C_8H_8N_4$ *i.e.* $NH_2.NPh.C(NH).CN$? Separates as colourless flakes when cyanogen is passed into an emulsion of phenyl-hydrazine and cold water (Bladin, *B.* 18, 1544). Monoclinic laminæ, v. sol. alcohol and ether. Decomposes above 160°. Yields a formyl derivative $C_8H_7(CHO)N_4$ [193°].

Reactions.—1. By heating with Ac_2O it is converted into $C_{10}H_8N_4$ [108°], which on saponification yields an acid $C_{10}H_9N_3O_2$ [177°], which on heating loses CO_2, leaving oily $C_9H_9NO_3$ (c. 240°).—2. By heating with *propionic anhydride* it is converted into $C_{11}H_{10}N_4$ [38°].—3. By treatment with *nitrous acid*, followed by boiling with water, it yields $C_8H_5N_5$, crystallising in needles [56°], v. sl. sol. water.—4. *Acetic aldehyde* in alcohol and HCl give $CH_3.CH{:}N.NPh.C(NH).CN$ [96·5°], crystallising in pale-yellow plates, v. e. sol. alcohol and ether, insol. water; converted by alcoholic $AgNO_3$ into phenyl-methyl-triazole carboxylic nitrile [109°] (Bladin, *B.* 25, 184).—5. *Benzoic aldehyde* forms the corresponding $CHPh{:}N.NPh.C(NH).CN$ [129·5°], crystallising from alcohol in prisms, oxidised by $FeCl_3$ to $C_{15}H_{10}N_4$ [156°] (Bladin, *B.* 22, 796).—6. *Pyruvic acid* in alcohol forms the above phenyl-methyl-triazole carboxylic nitrile on warming gently (Bladin, *B.* 19, 2598).—7. Boiling *acetoacetic ether* forms the compound $CO_2H.CH_2.CMe{:}N.NPh.C(NH).CN$ [209°], the oily ether of this acid, and phenyl-methyl-triazole carboxylic nitrile $N{\ll}\begin{matrix}CMe.N\\NPh.C.CN\end{matrix}$ [109°] (Bladin, *B.* 25, 190). The acid forms the salts KA′ and NH_4A', and is converted by nitrous acid into $CO_2H.C(NOH).CMe{:}N.NPh.C(NH).CN$ [218°], and by potash into the compound $CO_2H.CH_2.CMe{:}N.NPh.CO.CN$ [188°], from which potassium nitrite and HClAq form $CO_2H.C(NOH).CMe{:}N.NPh.CO.CN$ [209°].

References.—AMIDO-, IODO-, NITRO-, and OXY PHENYL-HYDRAZINE.

u-Di-phenyl-hydrazine $NPh_2.NH_2$. [34·5°] (220° at 40 mm.) (Stahel, *A.* 258, 243). Formed by reducing di-phenyl-nitrosamine $NPh_2.NO$ in alcoholic solution with zinc-dust and HOAc (E. Fischer, *A.* 190, 174). Monoclinic tables (from ligroïn), partially decomposed on distillation into diphenylamine and NH_3. Conc. H_2SO_4 forms a deep-blue solution. Decomposed by nitrous acid into $NPh_2.NO$ and N_2O. Reduces HgO, forming in the cold crystalline tetra-phenyl-tetrazone $NPh_2.N{:}N.NPh_2$ [123°], but if the temperature rises the products are N and diphenylamine. Benzoic aldehyde forms $NPh_2.N{:}CHPh$ [122°]. With salicylic aldehyde, furfuraldehyde, glucose, mannose, galactose, and rhamnose it forms di-phenyl-hydrazides, melting at 139°, 90°, c. 162°, c. 155°, 157°, and 134° respectively.

Salts.—B′HCl. Needles, v. sl. sol. cold water.—$B'_2H_2SO_4$: needles, m. sol. dilute H_2SO_4.

Formyl derivative $NPh_2.NH.CHO$. [116·5°]. Formed by boiling the formyl derivative of phenyl-hydrazine with ammoniacal $CuSO_4$ (Gattermann, *B.* 25, 1075). Needles, sl. sol. hot water and ligroïn, v. sol. alcohol.

Acetyl derivative $NPh_2.NHAc$. [185°]. Formed by boiling NHPh.NHAc with HOAc and $Cu(OAc)_2$ (Tafel, *B.* 25, 413).

Propionyl derivative. [178°]. Needles.

Benzoyl derivative $NPh_2.NHBz$. [189°] (G.); [192°] (Fischer, *A.* 190, 178). Needles (from acetone), m. sol. alcohol.

Phthalyl derivative $C_8H_4O_2{:}N.NPh_2$. [155°]. Formed by heating di-phenyl-hydrazine with phthalic anhydride at 160° (Hötte, *J. pr.* [2] 35, 271).

s-Di-phenyl-hydrazine NHPh.NHPh. *Hydrazo-benzene.* Mol. w. 184. [131°]. H.C. 1,598,000 (from diamond) (Petit, *A. Ch.* [6] 17, 163). S. (alcohol) 5 at 16° (Moltschanowsky, *C. J.* 42, 965). Prepared by passing H_2S into a solution of azobenzene $Ph.N_2.Ph$ in alcoholic NH_3 (Hofmann, *Pr.* 12, 576). Formed also by reducing nitro-benzene with sodium-amalgam or zinc-dust (Alexejeff, *Z.* 1868, 497; Glaser, *A.* 142, 364). Laminæ, sl. sol. water, m. sol. alcohol and ether. Yields aniline and azobenzene on distillation.

Reactions.—1. HClAq converts it into the isomeric di-*p*-amido-diphenyl (benzidine). H_2SO_4 acts in like manner.—2. Readily *oxidised* to azobenzene, even by moist air.—3. *Nitrous acid*, passed into an alcoholic solution at 0°, yields a nitroso- compound which, when warmed, violently decomposes into NO and azobenzene (Baeyer, *B.* 2, 683).—4. On heating with BzCl it yields di-benzoyl-di-*p*-amido-diphenyl; formic acid gives di-formyl-di-*p*-amido-diphenyl (Stern, *B.* 17, 379); and phthalic anhydride yields di-phthalyl-di-amido-diphenyl (Bandrowski, *B.* 17, 1181).—5. Boiling *benzoic aldehyde* forms azobenzene, but benzoic aldehyde and $ZnCl_2$ gives $C_{12}H_8(N{:}CHPh)_2$ (Clève, *Bl.* [2] 45, 188). Benzoic aldehyde, heated with hydrazobenzene at 120°–150°, forms 'benzhydrazoïn' $CHPh{<}\begin{matrix}NPh\\NPh\end{matrix}$ [55°]. The *o*-nitro- derivative $C_6H_4(NO_2).CHN_2Ph_2$ of this body melts at 66°.—6. *Furfuraldehyde* forms

$C_4H_3O.CH<\begin{smallmatrix}NPh\\NPh\end{smallmatrix}$ [59°] (Cornelius a. Homolka, *B.* 19, 2240).—7. *Phenyl cyanate* (2 mols.) and some benzene at 150° forms the compound NHPh.CO.NPh.NPh.CO.NHPh [220°] (Goldschmidt a. Rosell, *B.* 23, 490).

Acetyl derivative NHPh.NPhAc. [159°]. Formed from *s*-di-phenyl-hydrazine and Ac_2O in the cold (Stern, *B.* 17, 380). Needles (from alcohol). Decomposed by heat into acetanilide and azobenzene.

Di-acetyl derivative NPhAc.NPhAc. [105°]. Formed from *s*-di-phenyl-hydrazine and Ac_2O (Schmidt a. Schultz, *B.* 12, 485; *A.* 207, 326). Yellowish trimetric crystals (from alcohol); *a:b:c* = ·67:1:·56, not affected by dilute HClAq.

Chloro-derivatives $C_6H_5NH.NHC_6H_4Cl$. [90°].—$N_2H_2(C_6H_4Cl[1:3])_2$ [91°].—$N_2H_2(C_6H_4Cl[1:4])_2$ [122°] (Claus a. Heumann, *B.* 13, 1181, 19, 1688; Laubenheimer, *B.* 8, 1624).

Bromo-derivative $C_6H_5.NH.NH.C_6H_4Br$. [115°]. Formed from benzene-azo-*p*-bromobenzene and alcoholic ammonium sulphide (Janowsky a. Erb, *B.* 20, 361). Tables. Converted by H_2SO_4 into bromo-benzidine.

Di-bromo- derivatives $N_2H_2(C_6H_4Br.)_2$. *o.* [82°]. *m.* [109°]. *p.* [130°] (J. a. E.; Gabriel, *B.* 9, 1406; Werigo, *A.* 165, 192).

Iodo- derivatives v. vol. iii. p. 41.

Nitro- derivatives v. vol. iii. p. 607.

Oxy- derivatives v. vol. iii. p. 743.

Chloro-nitro- derivative $NHPh.NHC_6H_3Cl(NO_2)$ [1:3:6]. [135°-140°]. Formed from chloro-di-nitro-benzene and phenyl-hydrazine in alcohol (Willgerodt a. Ferko, *J. pr.* [2] 37, 355). Red prisms.

p-Amido- derivative. The compound $NHPh.NH.C_6H_4.NHAc$ [146°] is got by treating $C_6H_5.N_2.C_6H_4NHAc$ with alcoholic ammonium sulphide (Schultz, *B.* 17, 463). Yellowish plates (from dilute alcohol). Re-oxidised to the azo- compound by air.

Di-m-amido- derivative $N_2H_2(C_6H_4.NH_2)_2$. [141°] (Gebek, *A.* 251, 193). Got by treatment of *m*-nitro-aniline with alcoholic potash and zinc-dust (Graeff, *A.* 229, 341), or with sodium-amalgam (Haarhaus, *A.* 135, 164). Golden needles (from alcohol). Yields $C_{12}H_9Br_5N_4$ [150°] and $C_{12}H_{12}Ac_2N_4$ [247°].—$B''H_2Cl_2$.—$B''H_2PtCl_6$.—$B''2HNO_3$.—$B''H_2SO_4$.—$B''H_2C_2O_4$. Prisms, v. sl. sol. water.

Di-p-amido- derivative. [145°]. Got by reducing $N_2(C_6H_4.NO_2)_2$ with alcoholic ammonium sulphide (Gerhardt a. Laurent, *A.* 75, 74; Lermontoff, *B.* 5, 232). Yellow crystals. Yields quinone on oxidation. — $B''H_2Cl_2$. — $B''2HNO_3$.

Di-diphenyl-hydrazine *v.* HYDRAZO-DIPHENYL.

PHENYL-HYDRAZINE *o*-CARBOXYLIC ACID $C_7H_8N_2O_2$ *i.e.* $NH_2.NH.C_6H_4.CO_2H$. *Hydrazido-benzoic acid.* Formed from *o*-amidobenzoic acid by diazotising and treating the product with Na_2SO_3 (E. Fischer, *B.* 13, 679; *A.* 212, 333). Needles, sol. hot water. Reduces Fehling's solution in the cold. — HA'HCl: needles, sol. hot water.

Anhydride $C_7H_6N_2O$. [242°]. Formed by heating the acid at 220°. Monoclinic plates (from alcohol); *a:b:c* = 1·072:1:·664; β = 75° 18'. Sublimes in white needles.—$NaC_7H_5N_2O$ *x*aq: silvery plates. — B'HCl: white needles. — $B'HgCl_2$: needles (from water). Yields an acetyl derivative $C_7H_4Ac_2N_2O$ [112°].

Phenyl-hydrazine *m*-carboxylic acid $N_2H_3.C_6H_4.CO_2H$. [186°]. Formed by the action of tin and HClAq on $C_6H_4(CO_2H).N{:}N.SO_3K$, which is got by warming the nitrate of *m*-diazobenzoic acid with aqueous K_2SO_3 (Griess, *B.* 9, 1657; Roder, *A.* 236, 164). Plates, sl. sol. hot Aq.

Reactions.—1. *Acetone* forms $C_{10}H_{12}N_2O_2$ [150°], which gives EtA' [91°].—2. *Benzoic aldehyde* forms $CHPh{:}N.NH.C_6H_4.CO_2H$ [172°].—3. *Pyruvic acid* reacts with formation of $CO_2H.CMe{:}N.NH.C_6H_4.CO_2H$ [208°], which forms whetstone-shaped crystals (containing aq), and gives EtA' [102°].—4. *Glucose*, heated with the hydrochloride and NaOAc, gives $C_{20}H_{22}N_4O_8$ [208°]. — 5. *Phenyl-thiocarbimide* forms the compound $C_{14}H_{13}N_3SO_2$ [205°].

Salts.—HA'HCl.—BaA'_2 4aq. Nodules.

Phenyl-hydrazine *p*-carboxylic acid $N_2H_3.C_6H_4.CO_2H$. [220°-225°]. Formed, in the same way as its isomerides, from *p*-amido-benzoic acid (Fischer, *A.* 212, 337). Needles or plates (from water).—HA'HCl: sl. sol. cold water.

***s*-Di-phenyl-hydrazine di-*o*-carboxylic acid** $C_{14}H_{12}N_2O_4$ *i.e.* $CO_2H.C_6H_4.NH.NH.C_6H_4.CO_2H$. Mol. w. 272. [205°]. Formed by reducing *o*-azoxy-benzoic acid with sodium-amalgam (Griess, *B.* 7, 1609; Homolka, *B.* 17, 1904). Small colourless plates. Oxidised by moist air to *o*-azobenzoic acid.

***s*-Di-phenyl-hydrazine di-*m*-carboxylic acid.** *Hydrazo-benzoic acid.* Formed by boiling *m*-azobenzoic acid with $FeSO_4$ and NaOHAq (Strecker, *A.* 129, 141). Insol. water, sl. sol. hot alcohol. In alkaline solutions it absorbs O, being oxidised to azobenzoic acid. Boiling conc. HClAq forms azobenzoic acid and amidobenzoic acid. Yields orange-red crystals of BaA''. On warming with $SnCl_2$ and HClAq at 100° it yields di-amido-diphenyl dicarboxylic acid and two other acids. One of these $C_{14}H_{10}N_2O_3$ crystallises from hot water in yellowish needles and forms BaA'_2 7aq and HA'HCl. The other acid $C_{14}H_{12}N_2O_4$ crystallises in yellow needles melting above 290°, and forms NaA' 4aq, BaA'_2 2aq, HA'HCl, HA'HBr, and $(HA')_2H_2SO_4$ (Kusseroff, *B.* 23, 913).

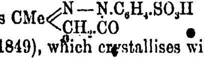
***s*-Di-phenyl-hydrazine di-*p*-carboxylic acid** $C_{14}H_{12}N_2O_4$. Formed by boiling *p*-azobenzoic acid with $FeSO_4$ and NaOHAq (Reichenbach a. Beilstein, *A.* 132, 137; Billfinger, *A.* 135, 152). Needles (from alcohol), easily oxidised in alkaline solution.

***s*-Di-phenyl-hydrazine tetra-carboxylic acid** $[1:4:2]C_6H_3(CO_2H)_2.NH.NH.C_6H_3(CO_2H)_2$ [2:1:4]. Formed by reducing azoxyterephthalic acid in alkaline solution with sodium-amalgam (Homolka a. Löw, *B.* 19, 1092). White crystalline pp., v. sol. alcohol and ether.

PHENYL-HYDRAZINE *m*-SULPHONIC ACID $C_6H_4(N_2H_3).SO_3H$. Formed from *m*-amidobenzene sulphonic acid by diazotisation and subsequent reduction by $SnCl_2$ at 0° (Limpricht, *B.* 21, 3409). Crystals (containing 2aq), sl. sol. cold water, nearly insol. alcohol. Converted in alcoholic solution by nitrous acid into $N_2C_6H_4SO_3H$.

Phenyl-hydrazine *p*-sulphonic acid $[1:4]C_6H_4(N_2H_3).SO_3H$.

Formation.—1. From diazobenzene *p*-sulphonic acid by warming with aqueous K_2SO_3 followed by HCl (E. Fischer, *A.* 190, 74).—2. By heating phenyl hydrazine sulphate with $ClSO_3H$ at 160° (Limpricht, *B.* 18, 2196).—3. Together with alcohol, by heating phenyl-hydrazine ethyl-sulphate at 160°.—4. By heating phenyl-hydrazine (1 pt.) with H_2SO_4 (6 pts.) at 100° (Gallinek a. Richter, *B.* 18, 3172).

Properties.—Needles (containing ½aq), sl. sol. water. By boiling with $CuSO_4$ it is neatly oxidised to N and benzene sulphonic acid. With acetoacetic ether and dilute (50 p. c.) HOAc at 155° it forms  $CMe\Big\langle\begin{matrix}N—N.C_6H_4.SO_3H\\CH_2.CO\end{matrix}$ (Möllenhoff, *B.* 25, 1849), which crystallises with aq.

Salts.—NaA′ 1½aq.—NH_4A'.—BaA'_2 5aq.—PbA'_2 2aq.—ZnA'_2 4aq: minute tables.

Phenyl-hydrazine ν-sulphonic acid. Potassium salt. $C_6H_5NH.NH.SO_3K$. Formed from diazobenzene nitrate and K_2SO_3 (Römer, *Z.* 1871, 481) and also by heating phenyl-hydrazine with $K_2S_2O_7$ (Fischer, *A.* 190, 97). Crystals (containing aq), sl. sol. cold water and alcohol. Oxidised by HgO to $C_6H_5.N_2.SO_3K$. Split up by boiling HClAq into phenyl-hydrazine and $KHSO_4$.

Phenyl-hydrazine disulphonic acid $NH_2.NH.C_6H_3(SO_3H)_2$. Two acids of this formula are got by further sulphonation of the *m*- and *p*- sulphonic acids respectively (L.). They both yield BaA″ and $BaH_2A''_2$.

s-Di-phenyl-hydrazine *m*-sulphonic acid $C_6H_5.NH.NH.C_6H_4.SO_3H$. Formed by heating the disulphonic acid with water at 200° for 3 days (Limpricht, *B.* 11, 1048). Yellow needles (containing 2½aq). — KA′ 4aq. — PbA'_2 3aq. — BaA'_2 4aq: yellow plates, v. sol. water.

Chloride $C_{12}H_{11}N_2SO_2Cl$. [240°].

Di-bromo- derivative $C_6H_4Br.NH.NH.C_6H_3Br.SO_3H$. Formed as a by-product in the oxidation of $C_6H_2Br_2(NH_2)SO_3H$ [1:3:6:4] by $KMnO_4$ (Limpricht, *B.* 18, 1425).—KA′ aq: long needles.

s-Di-phenyl-hydrazine di-*m*-sulphonic acid $N_2H_2(C_6H_4.SO_3H)_2$. S. ·079 at 22°. Formed by reduction of nitro-, azo-, or azoxy-benzene-sulphonic acid (Limpricht, *B.* 11, 1048; 21, 3409; 23, 1057; Bruhnemann, *A.* 202, 344; Mahrenholz a. Gilbert, *A.* 202, 337; Neumann, *B.* 21, 3419). White needles, v. e. sol. water, almost insol. alcohol and ether. Readily reduces ammoniacal $AgNO_3$ and Fehling's solution. HClAq immediately forms benzidine disulphonic acid.—K_2A'' aq.—BaA″ 2aq.

Amide $NH(C_6H_4.SO_2NH_2).NH.C_6H_4.SO_2NH_2$. [248°]. Formed by reducing $N_2(C_6H_4.SO_2NH_2)_2$ with zinc-dust and NH_3Aq or HOAc (Limpricht a. F. Meyer, *A.* 268, 132). White needles (from 50 p.c. acetic acid), almost insol. water, ether, and toluene. Reduces ammoniacal $AgNO_3$ forming a mirror. HClAq converts it into the amide of diamido-diphenyl (benzidine) disulphonic acid, *m*-amido-benzene sulphonic amide and $N_2(C_6H_4.SO_2NH_2)_2$. — $N_2H_2(C_6H_4.SO_2NHK)_2$ 1½aq. Thin needles or plates quickly oxidised by air.—$N_2H_2(C_6H_4.SO_2NHNa)_2$ 2½aq: needles.

s-Di-phenyl-hydrazine di-*p*-sulphonic acid $N_2H_2(C_6H_4.SO_3H)_2$. Obtained, in the same way as the preceding acid, from amido-benzene *p*-sulphonic acid.—$BaH_2A''_2$.—BaA″: crystalline.

Isomeride.—*V.* Benzidine tetrasulphonic acid, vol. i. p. 174.

DI-PHENYL-HYDRAZINE ν-DI-THIO-CARBOXYLIC ACID $NPh_2.NH.CS.SH$. [c. 109°]. Formed by dissolving $NPh_2.NH_2$ in CS_2 (Stahel, *A.* 258, 249). Golden prisms, v. sol. alcohol, insol. water.

s-Di-phenyl-hydrazine di-*m*-thiosulphonic acid $N_2H_2(C_6H_4.SO_2SH)_2$. Formed, together with $N_2(C_6H_4.SO_2.SH)_2$, by adding $N_2(C_6H_4.SO_2Cl)_2$ to a cold saturated solution of $Ba(SH)_2$ (Limpricht, *B.* 18, 1470; *A.* 220, 354). White amorphous pp., becoming sticky on boiling with water. Oxidised by $KMnO_4$ to $N_2(C_6H_4.SO_3H)_2$. — BaA″ 2aq: minute needles, sl. sol. cold water.

TRI-PHENYL-HYDRAZOÏN is *Benzhydrazoïn*, *v.* *s*-Di-phenyl-hydrazine, *Reaction* 5.

DI-PHENYL-HYDROQUINONE $C_{18}H_{14}O_2$ *i.e.* $C_6H_2Ph_2(OH)_2$ [5:2:4:1]. [219°]. Formed by reducing di-phenyl-quinone with aqueous SO_2 (Müller a. Pechmann, *B.* 22, 2131). Colourless cubes (from dilute alcohol).

PHENYL-IMESATIN *v.* Isatin.

PHENYL-IMIDO-DIACETIC ACID $NPh(CH_2.CO_2H)_2$. [150°-155°]. A product of the action of aniline on chloro-acetic acid (P. Meyer, *B.* 14, 1325; Hausdörfer, *B.* 22, 1796). Formed also by heating phenyl-amido-acetic acid with chloro-acetic acid and NaOAc at 120°-130° (H.). Needles, v. sol. hot water and alcohol. $NPhH_3A'$. Needles (from alcohol). Decomposes at 151°.

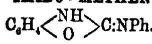
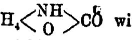
Mono-anilide $CO_2H.CH_2.NPh.CH_2.CO.NHPh$. [213°]. Formed together with the dianilide by heating the acid with aniline at 175°. Needles. Its ether $CO_2Et.CH_2.NPh.CH_2.CO.NHPh$ [122°] is got by heating the anilide of phenyl-amido-acetic acid (*q.v.*) with ether and NaOAc at 140°.

Di-anilide $NPh(CH_2.CO.NHPh)_2$. [218°]. Needles, v. sl. sol. alcohol.

TRI-PHENYL-TRI-IMIDO-BENZENE $C_{24}H_{21}N_3$ *i.e.* $C_6H_3(NHPh)_3$. [242°]. Formed by warming $C_6H_6Cl_6$ with aniline (Mohr, *M.* 11, 22). Golden plates, v. sol. chloroform, insol. water and alcohol. Conc. H_2SO_4 gives a dark-blue colour changed to violet by potash.

PHENYL-IMIDO-BENZYL-MALONIC ETHER $C_6H_5.C(NPh).CH(CO_2Et)_2$. [75°]. Formed, together with $(C_6H_5.C(NPh))_2C(CO_2Et)_2$, by the action of sodium malonic ether on the compound $C_6H_5.CCl:NPh$ (Just, *B.* 18, 2624). Decomposes at 150° into alcohol and oxy-phenyl-quinoline carboxylic ether.

DI-PHENYL IMIDO-DI-ETHYL DISULPHONE $NH(CH_2.CH_2.SO_2.C_6H_5)_2$. [78°]. Got by heating $C_2H_4(SO_2.C_6H_5)_2$ with NH_3Aq is sealed tubes (Otto, *J. pr.* [2] 30, 324). Triclinic plates (from alcohol).—Nitrate: [190°].—B′HCl. [193°].—$B'_2H_2PtCl_6$: plates, sl. sol. water.

PHENYL-IMIDO-METHENYL-*o*-AMIDO-PHENOL  $C_6H_4\Big\langle\begin{matrix}NH\\O\end{matrix}\Big\rangle C:NPh$. [c. 230°]. Formed by heating  $C_6H_4\Big\langle\begin{matrix}NH\\O\end{matrix}\Big\rangle CO$ with aniline at 210° (Von Chelmicki, *J. pr.* [2] 42, 440). Needles, insol. water, sl. sol. cold alcohol.

DI-PHENYL-DI-IMIDO-NAPHTHOL *v.* (β)-Naphthoquinone, *Reaction* 5.

PHENYL-IMIDO-DINAPHTHYL *v.* Phenyl dinaphthylene amine.

PHENYLIMIDO-PHENYL-METHYL-THI-ZOLE DIHYDRIDE $NPh{<}\begin{smallmatrix}C(NPh).S\\CMe=CH\end{smallmatrix}$. 138°]. Formed from di-phenyl-thio-urea and hloro-acetone (Traumann, *A.* 249, 51). Yel- wish prisms, insol. water, v. sol. ether.

DI-PHENYL-DI-IMIDO-DI-PHENYL-IAZTHIOLE TETRAHYDRIDE $C_{28}H_{20}N_4S$ *i.e.* ${<}\begin{smallmatrix}C(NPh).NPh\\C(NPh).NPh\end{smallmatrix}$. [131°]. Got by oxidising di-henyl-thio-urea with H_2O_2 (Hector, *B.* 23, 357).

PHENYL-IMIDO-PROPIONIC ACID $H_3.C(NPh).CO_2H$. *Anilpyruvic acid.* [122°]. ormed from aniline and pyruvic acid in ether Böttinger, *B.* 16, 1924; *A.* 188, 336; 263, 126). rystals, v. sol. water. Decomposed by boiling ater. Br yields $C_{15}H_{12}Br_3N_2O_2$ [264°].

Isomeride *v.* IMIDO-PHENYL-PROPIONIC ACID.

PHENYL-IMIDO-SUCCINIC ACID $O_2H.CH_2.C(NPh).CO_2H$. [150°]. Formed by ne action of dilute (1 p.c.) $KMnO_4$ on 'pyranil-yroic' acid (Anschütz, *B.* 22, 738; *cf.* Reissert, . 21, 1942). Decomposed on fusion.

PHENYL-IMIDO-THIAZOLE DIHYDRIDE $(NPh){<}\begin{smallmatrix}S-CH\\NH.CH\end{smallmatrix}$. [124°]. Formed from $H_2Cl.CHCl.OEt$ and phenyl-thio-urea (Näf, *A.* 5, 125). White needles, sol. alcohol. Yields nitrosamine $C_9H_7(NO)N_2S$ [58°].

Di-phenyl-imido-thiazole dihydride $(NPh){<}\begin{smallmatrix}S-CH\\NPh.CH\end{smallmatrix}$. [105°]. Formed from di-chloro-di-ethyl oxide and di-phenyl-thio-urea.

DIPHENYLINE *v.* DI-AMIDO-DIPHENYL.

PHENYL-INDAZINE $C_{13}H_{10}N_2$ *i.e.* $C_6H_4{<}\begin{smallmatrix}N\\CH\end{smallmatrix}{>}NPh$. [84°]. (345° uncor.). Formed by reducing *o*-nitro-benzyl-aniline with tin and HClAq (Paal, *B.* 23, 2640; 24, 961). Needles (from alcohol). Not affected by distillation over red-hot zinc-dust. Reduced to a dihydride [98°] by adding Na to its alcoholic solution. Yields a methylo-iodide B'MeI [188°].

PHENYL-INDOLE $C_6H_4{<}\begin{smallmatrix}CH\\NPh\end{smallmatrix}{>}CH$. (327° i.V.). Formed by heating its carboxylic acid [176°] (Fischer a. Hess, *B.* 17, 567; Pfülf, *A.* 239, 221). Oil, v. sol. alcohol. Its solution in HClAq colours pine-wood intensely violet.

Phenyl-indole $C_6H_4{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}CPh$. *Methyl-phenanthridine.* [186°]. (above 360°).

Formation.—1. By boiling ω-bromo-aceto-phenone or phenyl-ω-amido-acetophenone with aniline (Möhlau, *B.* 14, 173; 15, 2480; 18, 165). 2. By heating the phenyl-hydrazide of aceto-phenone or of phenyl-acetic aldehyde with $ZnCl_2$ at 180° (Fischer, *B.* 19, 1565; 21, 1071; *A.* 236, 135).—3. By passing benzylidene-*o*-toluidine through a red-hot tube (Etard, *Bl.* [2] 39, 531). 4. By the action of zinc-dust and NH_3Aq on $C_6H_4(NO_2).CH_2.CO.C_6H_5$ (Pictet, *B.* 19, 1065).

Properties.—Colourless plates, insol. water. May be sublimed. Colours pine-wood violet-blue. Yields $B'C_6H_3N_3O_7$ [127°]. Nitrous acid forms a nitroso-derivative $C_6H_4{<}\begin{smallmatrix}C(NO)\\NH\end{smallmatrix}{>}CPh$ [c. 258°], which yields B'HCl, $B'HNO_3$, and $NaC_{14}H_9N_2O$, and may be reduced to amido-phenyl-indole [174°].

Dihydride $C_{14}H_{13}N$. [46°]. Formed by boiling phenyl-indole with zinc-dust, alcohol, and HCl. Colours pine-wood orange. Yields a nitrosamine.

Phenyl-indole $C_6H_4{<}\begin{smallmatrix}CPh\\NH\end{smallmatrix}{>}CH$. [89°]. Formed by the action of alcoholic HCl on the phenyl-hydrazide of phenyl acetic aldehyde (Fischer, *B.* 21, 1811). White plates (from ligroïn), v. sol. alcohol. Converted by heating for fifteen minutes with $ZnCl_2$ into the preceding isomeride [186°]. Yields a picrate [107°] and a nitrosamine $C_6H_4{<}\begin{smallmatrix}CPh\\N(NO)\end{smallmatrix}{>}CH$ [61°] which gives Liebermann's reaction (Ince, *A.* 253, 37).

Di-phenyl-indole $C_6H_4{<}\begin{smallmatrix}CPh\\NH\end{smallmatrix}{>}CPh$. [123°]. Formed by heating the phenyl-hydrazide of de-oxybenzoïn with $ZnCl_2$ (Fischer, *B.* 19, 1566; *A.* 236, 136). Colourless crystals, v. sol. alcohol. Does not give the pine-wood reaction. Its picrate crystallises in dark-red needles.

Di-phenyl-indole $C_6H_4{<}\begin{smallmatrix}CH\\NPh\end{smallmatrix}{>}CPh$. (above 360°). Got by heating the *u*-di-phenyl-hydrazide of acetophenone with $ZnCl_2$ at 175° (Pfülf, *A.* 239, 223). Oil. Colours acidified pine-wood bluish-violet.

PHENYL-INDOLE CARBOXYLIC ACID $C_{15}H_{11}NO_2$ *i.e.* $C_6H_4{<}\begin{smallmatrix}C(CO_2H)\\N(C_6H_5)\end{smallmatrix}{>}CH$. [176°]. Formed by heating the di-phenyl-hydrazide of pyruvic acid with HOAc and HClAq (E. Fischer, *B.* 17, 567). Needles, v. sl. sol. water, v. sol. alcohol. NaOCl in the cold forms phenyl-ψ-isatin $C_6H_4{<}\begin{smallmatrix}CO\\NPh\end{smallmatrix}{>}CO$. [134°] (Pfülf, *A.* 239, 222).

PHENYL INDOXAZINE $C_6H_4{<}\begin{smallmatrix}CH\\O\end{smallmatrix}{>}N$. [84°]. Got from *o*-bromo-benzophenone and an alkaline solution of phenyl-hydrazine (Cathcart a. V. Meyer, *B.* 25, 1498). Large crystals.

PHENYL-INDULINE $C_{24}H_{17}N_3$ *i.e.* $\begin{smallmatrix}CH:CH——C:N\\C(NPh).CH:C.NPh\end{smallmatrix}{>}C_6H_4$. [231°]. Mol. w. (by Raoult's method) 320–370 (calc. 347). Formed from amido-phenyl-induline [152°] by treatment with nitrous acid (Fischer a. Hepp, *A.* 262, 257; 266, 263). Reddish tables, with blue reflex; v. sol. benzene, insol. ligroïn. Heated with HOAc (5 pts.) and HClAq (25 pts. of 20 p.c.) at 165° for six hours it forms: (*a*) $C_{24}H_{19}N_3O$ crystallising from benzene in steel-blue plates [218°], forming a brownish-red solution in HClAq, and converted by conc. HClAq at 200° into a compound $C_{18}H_{14}N_2O_2$; (*b*) the compound $C_{18}H_{14}N_2O_2$ [c. 280°] which crystallises from benzene or alcohol in brownish-yellow prisms or plates, and is both base and phenol. Its hydrochloride crystallises from conc. HClAq in prisms with green lustre; (*c*) *benzolindone* $C_{18}H_{12}N_2O$; (*d*) a body which dissolves in benzene with fiery brown fluorescence, and is perhaps carbazole-fluorindine (Fischer a. Hepp, *A.* 266, 249).

Benzolindone $C_{18}H_{12}N_2O$ *i.e.* $\begin{smallmatrix}CH:CH.C:N\\CO.CH:C.NPh\end{smallmatrix}{>}C_6H_4$. Formed by heating phenyl-induline with HOAc and HClAq at 160°–200° (Fischer a. Hepp, *A.* 266, 253). Lustrous brown plates, insol. alkalis, sol. dilute HClAq, forming a rose-coloured solution. Its solution in conc. H_2SO_4 is green. Yields phenazine on distillation with zinc-dust.

PHENYL IODIDE *v.* Iodobenzene.

PHENYL IODOMETHYL SULPHONE $C_6H_5.SO_2.CH_2I$. [64·5°]. Formed from benzene sulphinic acid, NaOEt, and CH_2I_2 at 100° (Michael a. Palmer, *Am.* 6, 253). Prisms (from alcohol). NaOEt at 75° gives phenyl-methyl sulphone and products of oxidation (Otto, *B.* 21, 654).

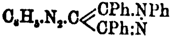
PHENYL-ITACONIC ACID $CHPh:C(CO_2H).CH_2.CO_2H$. [172°]. Formed by the action of Na or NaOEt on phenyl-paraconic acid (Fittig, *A.* 256, 68). Prisms, sl. sol. cold water. Yields phenyl-isocrotonic acid [179°] and γ-oxy-phenyl-butyric lactone [37°] when boiled with diluted H_2SO_4 (1:1). Br gives bromo-phenyl-paraconic acid $C_{11}H_9BrO_4$ [99°] and an isomeride [144°].—BaA″ 2½aq.—CaA″.—Ag_2A''.

Ethyl ether Et_2A''. (315° uncor.). Oil.

Di-PHENYL-KETONE *v.* Benzophenone.

Di-phenyl diketone *v.* Benzil.

Di-phenyl triketone $C_6H_5.CO.CO.CO.C_6H_5$. [70°]. (248° at 40 mm.). Formed by distilling $CBz_2Br.OAc$ *in vacuo.* Formed also by adding aqueous $NaNO_2$ to a solution of the mono-oxim in HOAc, and boiling (Pechmann, *B.* 22, 852; 23, 3375). Hygroscopic golden needles (from ligroïn), v. sol. all solvents. Give a blue colour with H_2SO_4 and benzene that contains thiophene.

Reactions.—1. Alkalis decompose it, forming benzoïn, benzoic acid, and $CBzPh(OH).CO_2H$ [118°].—2. *Phenyl-hydrazine* forms a phenyl-hydrazide $C_{21}H_{16}N_2O_2$ [c. 135°], benzene-azo-tri-phenyl-pyrazole  $C_6H_5.N_2.C<\begin{array}{l}CPh.NPh\\ CPh{:}N\end{array}$ [157°], and a third compound [223°].—3. *Aniline* gives rise to $CPh(NPh).C(OH)_2.COPh$ [100°] and $C(OH)_2(CPh:NPh)_2$ [148°].

Hydrate $Bz_2C(OH)_2$. [90°].

Mono-oxim $Bz_2C:NOH$. [146°]. Formed from Bz_2CH_2 and nitrous acid.

Tri-oxim $(C_6H_5.C(NOH))_2C:NOH$. [186°]. Formed from the triketone and hydroxylamine.

Di-phenyl tetraketone $C_6H_5.CO.CO.CO.CO.C_6H_5$. The hydrate [88°] of this body is formed by the action of conc. HNO_3 on phenyl-glyoxal (Abenius a. Söderbaum, *B.* 24, 3034).

DI-PHENYL-KETONE CARBOXYLIC ACID *v.* Benzoyl-benzoic acid.

Di-phenyl ketone dicarboxylic acid *v.* Benzophenone dicarboxylic acid.

Di-phenyl diketone *o*-carboxylic acid $C_6H_5.CO.CO.C_6H_4.CO_2H$. Formed by oxidising deoxybenzoïn *o*-carboxylic acid with alkaline $KMnO_4$ (Graebe, *B.* 21, 2003; 23, 1344). Occurs in a yellow modification [141·5°] and a white variety [125°–130°]. The yellow modification is nearly twice as sol. alcohol and chloroform as the white variety, and is converted into the white variety by dissolving in alkali and ppn. by acids. The white modification changes into the yellow one at 115°–125°.

Dicarboxylic acid *v.* Diphthalylic acid.

DI-PHENYL-KETOXIM *v. Oxim* of Benzophenone.

PHENYLLACTIC ACID *v.* Oxy-phenyl-propionic acid.

PHENYL-LACTIMIDE *v.* vol. i. p. 180.

PHENYL-LUTIDINE-CARBOXYLIC ACID *v.* Phenyl-di-methyl-pyridine-carboxylic acid.

PHENYL-LUTIDONE *v.* Oxy-phenyl-di-methyl-pyridine.

PHENYL-MALEÏC ACID $C_{10}H_8O_4$ *i.e.* $CO_2H.CPh:CH.CO_2H$. Formed by dissolving its anhydride in water and extracting with ether (Alexander, *A.* 258, 77). Prisms, m. sol. water. Begins to lose water below 100°.

Anhydride $\begin{array}{l}CH.CO\\ CPh.CO\end{array}\!>\!O$. [119·5°]. Formed by distilling phenyl-malic acid. Needles, insol. water, v. sol. chloroform and ether.

Di-phenyl-maleïc acid $CO_2H.CPh:CPh.CO_2H$. *Stilbene dicarboxylic acid.* Formed by saponification of its nitrile. Its ether is formed, together with di-phenyl-fumaric ether, by the action of Na on α-bromo-phenyl-acetic ether in ether (Reimer, *B.* 14, 1800; Rügheimer, *B.* 15, 1626). The free acid splits up at once, on liberation from its salts, into H_2O and anhydride. On distillation with lime it yields *s*-di-phenyl-ethylene.—K_2A'': needles, v. sol. water.—Ag_2A'': amorphous pp.—AgHA′: needles.

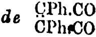
Ethyl ether Et_2A''. [54°]. Prisms.

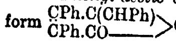
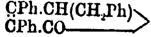
Imide $C_{16}H_{10}O_2(NH)$. [213°]. Needles, almost insol. water, v. sol. alcohol.

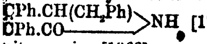
Phenylimide $C_{16}H_{10}O_2(NPh)$. [175°]. Formed by heating the anhydride with aniline at 120° (Anschütz a. Bendix, *A.* 259, 63).

Nitrile CN.CPh:CPh.CN. *Dicyanostilbene.* [158°]. Formed by heating α-bromo-phenyl-acetonitrile alone or with alcoholic KCy (Reimer, *B.* 14, 1798). Plates (from benzene).

Isonitrile. [242°]. Occurs in small quantity in the preparation of the nitrile by heating the product of bromination of phenyl-acetonitrile. Golden needles (from alcohol). Yields an acid [222°] on saponification.

Anhydride  $\begin{array}{l}CPh.CO\\ CPh.CO\end{array}\!>\!O$. [155°]. (236° at 15 mm.). Formed by adding HCl to solutions of salts of the acid, or by heating di-phenyl-fumaric acid at 260° (Reimer, *B.* 13, 742). Trimetric needles (from dilute alcohol), *a*:*b*:*c* = ·693:1:·385, insol. water, sol. CS_2. May be sublimed. Its alkaline solution reduces $AgNO_3$. Not changed by NaOHAq into the fumaroid form (Delisle, *A.* 269, 91). NaOHAq (15 p.c.) at 100° forms a polymeride melting much above 250°, insol. water and other solvents.

Reactions.—1. Reduced in alcoholic solution by zinc-dust and HCl to a mixture of the two di-phenyl-succinic acids.—2. Fuming HNO_3 gives rise to an amorphous di-nitro- derivative $(C_6H_4(NO_2))_2C_4O_3$.—3. *p-Tolyl-acetic acid* forms $C_4Ph_2O_2:CH.C_7H_7$ [165°], crystallising in yellow needles.—4. *Phenyl-acetic acid* and NaOAc at 225° form  $\begin{array}{l}CPh.C(CHPh)\\ CPh.CO\end{array}\!>\!O$ [176°], which may be reduced by HI and P to benzyl-di-phenyl-maleïde  $\begin{array}{l}CPh.CH(CH_2Ph)\\ CPh.CO\end{array}\!>\!O$ [128°] (Gabriel a. Cohn, *B.* 24, 3228, 3854). The compound $C_4Ph_2O_2(CHPh)$ combines with Br, forming $C_4Ph_2BrO_2(CHBrPh)$ [154°], which splits up at 155°–160° into HBr and $C_4Ph_2O_2(CBrPh)$ [165°]. The compound $C_4Ph_2HO_2(CH_2Ph)$ is converted by potash into $CO_2H.C_2Ph_2.CH(OH).CH_2Ph$ [174°], and by an alcoholic solution of $NEtH_2$ into $CO(NHEt).C_2Ph_2.CH(OH).CH_2Ph$ [196°]. The compound $C_4Ph_2O_2(CHPh)$ is converted by KOH into $C_4Ph_2O_2(OH).CH_2Ph$ [185°], and in benzene solution by HNO_2 into $C_4Ph_2O_2(OH).CH(NO_2)Ph$ [125°] (which yields an acetyl derivative [166°]), and the compound $C_4Ph_2O_2(NO_2).CH(NO_2)Ph$ [146°], which is converted by boiling alcohol into $C_4Ph_2O_2{:}C(NO_2)Ph$ [177°], a body that may be reduced by HI and P to iso-benzyl-diphenyl-maleïde [118°]. Benzyl-di-phenyl-maleïde is converted by alcoholic NH_3 at 180° into



$\left.\begin{array}{l}\mathrm{CPh.CH(CH_2Ph)}\\ \mathrm{CPh.CO}\end{array}\right\rangle\mathrm{NH}$ [170°], which yields a nitrosamine [136°].

PHENYL-MALIC ACID *v.* OXY-PHENYL-SUCCINIC ACID.

PHENYL-MALONAMIC ACID *v.* MALONIC ACID.

DI-PHENYL-MALONIC ACID. *Ethyl ether of the nitrile* $CPh_2(CN).CO_2Et$. [59°]. Formed from $CPh_2Cl.CO_2Et$ and $HgCy_2$ at 125° (Bickel, *B.* 22, 1537). Yellowish tables.

Reference.—DI-NITRO-PHENYL-MALONIC ETHER.

PHENYL-MANDELIC ACID *v. Phenyl derivative* of MANDELIC ACID.

PHENYL-MELAMINE *v.* vol. ii. p. 322.

PHENYL MERCAPTAN C_6H_5SH. *Thiophenol. Phenyl-sulphydrate.* Mol. w. 110. (168°) (L.); (172°) (F. a. C.). S.G. ^{24} 1·078.

Formation.—1. A product of the dry distillation of sodium benzene sulphonate (Kekulé, *Z.* 1867 194; Stenhouse, *A.* 149, 248; *Pr.* 17, 62). 2. Together with Ph_2S and diphenylene sulphide by heating benzene with S and $AlCl_3$ at 75° (Friedel a. Crafts, *C. R.* 86, 884; *A. Ch.* [6] 14, 437).—3. By distilling phenol (10 mols.) with P_2S_5 (1 mol.), the yield being 6 p.c. of the phenol used (Kekulé, *Z.* [2] 3, 193, 306; Beckmann, *J. pr.* [2] 17, 456).—4. From Ph_2S_2 and K_2S in alcohol (Otto a. Rössing, *B.* 19, 3129).—5. By distilling $C_6H_5.SO_2Na$ with NaSH (Stadler, *B.* 17, 2080).

Preparation.—Phenyl ethyl dithiocarbonate, or a mixture of diazobenzene chloride solution and potassium ethyl dithiocarbonate (xanthate) is boiled with alcoholic potash until the solution remains clear on addition of water. The alcohol is then distilled off and the residue dissolved in water, mixed with a little H_2SO_4 and zinc-dust (to prevent oxidation), and distilled with steam. The distillate is extracted with ether. The yield is 75 p.c. of the theoretical (Leuckart, *J. pr.* [2] 41, 187).

Properties.—Oil, v. sol. alcohol and ether. Smells like garlic. Attacks the skin. Conc. H_2SO_4 forms a violet solution, changing on warming through cherry-red to blue (Baumann, *H.* 5, 321; *cf.* Brunner, *B.* 4, 984).

Reactions.—1. Readily oxidised to Ph_2S_2.—2. CH_3CCl_3 and dilute (20 p.c.) NaOHAq form $CH_3.C(SPh)_3$, crystallising in white plates; v. sol. hot alcohol (Laves, *B.* 25, 353).—3. *Aceto-acetic ether* and dry hydrochloric acid form $CH_3.C(SPh)_2.CH_2.CO_2Et$ [58°], crystallising from alcohol in plates. Not attacked by boiling HClAq, but decomposed by alkalis into alcohol, PhSH, and $CH_3.C(SPh){:}CH.CO_2H$ [177°] (Escales a. Baumann, *B.* 19, 1790).—4. $NH_2.COCl$ forms $NH_2.CO.NH.CO.SPh$ [218°] (Gattermann, *A.* 244, 43).—5. *Acetone* and HCl in the cold give $Me_2C(SPh)_2$ [56°] (Baumann, *B.* 19, 2804), which is oxidised by $KMnO_4$ and H_2SO_4 to $Me_2C(SO_2Ph)_2$ [97°]. — 6. *Chloro-acetone* reacts on PhSNa in ether, forming acetonyl-phenyl-sulphide $PhS.CH_2.CO.CH_3$ [35°] (269°) S.G. $_{x}$ 1·244 (Delisle, *A.* 260, 252). This body crystallises in prisms, sl. sol. hot water, v. sol. alcohol; combines with $KHSO_3$, yields a phenyl-hydrazide [82·5°], and is converted by oxidation into $Ph.SO_2.CH_2.CO.CH_3$ [57°]. Acetonyl-phenyl sulphide may be converted by successive treatment with HCy, alcoholic hydrochloric acid, and alcoholic potash into the acid $PhS.CH_2.CMe(OH).CO_2H$ [97°], which yields CaA'_2 aq, BaA'_2 aq, and AgA′, and is oxidised by $KMnO_4$ to $Ph.SO_2.CH_2.CMe(OH).CO_2H$ [121°].—7. *Chloral* forms $CCl_3.CH(OH)(SPh)$ [53°], decomposed by heat into its components (Baumann, *B.* 18, 886).—8. Combines with *pyruvic acid*, forming $CH_3.C(OH)(SPh).CO_2H$ [87°], but in presence of gaseous HCl it forms the 'mercaptol' $CH_3.C(SPh)_2.CO_2H$ [117°] which is not attacked by boiling HClAq or alcoholic potash.—9. *Phenyl-glyoxylic acid* forms $C_6H_5.C(OH)(SPh).CO_2H$ converted by HCl gas into $C_6H_5.C(SPh)_2.CO_2H$ [143°] (Escales a. Baumann, *B.* 19, 1789).—10. *β-Acetyl-propionic acid* does not combine directly, but in presence of hydrochloric acid it forms $CH_3.C(SPh)_2.CH_2.CH_2.CO_2H$ [69°], which is not attacked by alkalis, but is decomposed by dilute acids into PhSH and acetyl-propionic acid (E. a. B.).—11. $CH_3.CO.CH_2SPh$ forms $CH_3.C(SPh)_2.CH_2.SPh$ [55°], crystallising in cubes; v. sol. alcohol, insol. water; converted by oxidation in $CH_3.C(SPh)(SO_2Ph).CH_2.SO_2Ph$ [157°], crystallising in needles, sl. sol. cold alcohol, split up by alkalis into $Ph.SO_2.CH_3$, PhSH, and $Ph.SO_2H$ (Autenrieth, *B.* 24, 170).—12. $CBr_2(SO_2Et)_2$ and NaOHAq form $PhS.CH(SO_2Et)_2$ [86°], crystallising in tables; v. sl. sol. hot water, v. sol. alkalis; converted by alcoholic NaOH and MeI into $PhS.CMe(SO_2Et)_2$ [113°], crystallising in white needles; m. sol. hot alcohol (Fromm, *A.* 253, 166; Laves, *B.* 25, 361). — 13. NaSPh reacts with isobutylene bromide, forming NaBr, Ph_2S_2, and isobutylene (Otto, *B.* 23, 1052).

Salts.—NaSPh. When Na is dissolved in an ethereal solution of PhSH containing phenol, a pp. of NaSPh is got while NaOPh remains in solution.—$Hg(SPh)_2$: colourless needles (from alcohol).—ClHgSPh: plates.—$Pb(SPh)_2$: yellow crystalline pp., split up on distillation into PbS and Ph_2S.—$Cu(SPh)_2$: pale-yellow powder.—AgSPh: pale-yellow crystalline pp.

Methyl ether PhSMe. (188°). Formed from $Pb(SPh)_2$ and MeI (Obermeyer, *B.* 20, 2926).

Ethyl ether PhSEt. (204°) at 744 mm. Formed from NaSPh and EtI at 120° (Beckmann, *J. pr.* [2] 17, 457), and by the action of PhSH on PhN_2Cl (Stadler, *B.* 17, 2078). Liquid with unpleasant smell.

Allyl ether v. PHENYL ALLYL SULPHIDE.

Acetyl derivative PhSAc. (229°). Formed from phenyl mercaptan and AcCl (Michler, *A.* 176, 177). Oil.

References. — AMIDO-, BROMO-, CHLORO-, CHLORO-NITRO-, NITRO-, and OXY- PHENYL-MERCAPTAN.

PHENYL-MERCAPTURIC ACID $C_{11}H_{13}NSO_3$ *i.e.* $NHAc.CMe(SPh).CO_2H$. [143°]. Formed by reducing bromo-phenyl-mercapturic acid with sodium-amalgam (Baumann, *B.* 15, 1732; 18, 258; *H.* 5, 335; 8, 190). Tetrahedra, m. sol. alcohol. Lævorotatory in alcoholic solution. Solutions of its salts are dextrorotatory. Decomposed by dilute H_2SO_4 into HOAc and phenyl-cysteïn.—BaA'_2 3aq: needles.

References.—Bromo- and Chloro- Phenyl-mercapturic acid.

PHENYL-MESITYL-CARBINOL *v.* Phenyl-tri-methyl-phenyl-carbinol.

PHENYL-MESITYL-CARBINOL CARBOXYLIC ANHYDRIDE *v.* Tri-methyl-phenyl-phthalide.

PHENYL MESITYL KETONE *v.* Phenyl tri-methyl-phenyl ketone.

PHENYL-METHACRYLIC ACID *v.* Phenyl-crotonic acid.

PHENYL-METHACRYLIC ALDEHYDE CHPh:CMe.COH. (150° at 100 mm.). Formed by adding NaOHAq to a mixture of benzoic aldehyde and propionic aldehyde (Miller a. Kinkelin, *B.* 19, 525). Oil. Reduces ammoniacal $AgNO_3$. Combines with bisulphite. Yields a phenyl-hydrazide [137°].

PHENYL-METHANE *v.* Toluene.

Di-phenyl-methane $C_{13}H_{12}$ *i.e.* CH_2Ph_2. Mol. w. 168. [25°]. (c. 263°).

Formation.—1. Together with $C_6H_4(CH_2Ph)_2$, by boiling benzyl chloride with benzene and zinc-dust (Zincke, *B.* 4, 298; *C. J.* 24, 508, 688). 2. By the action of H_2SO_4 and HOAc on a mixture of benzene and benzyl alcohol (Meyer a. Wurster, *B.* 6, 963).—3. By heating benzophenone with zinc-dust (Staedel, *B.* 6, 1401; 7, 1480; *cf.* Barbier, *C. R.* 79, 812), or by reducing it with HI and P (Graebe, *B.* 7, 1624), or Zn and H_2SO_4 (Zincke, *B.* 10, 1473).—4. From benzene, CH_2Cl_2, and $AlCl_3$ (Friedel a. Crafts, *Bl.* [2] 41, 324; *A. Ch.* [6] 11, 264).—5. From $CH_2(OMe)_2$, benzene, HOAc, and H_2SO_4 (Baeyer, *B.* 6, 221).—6. By distilling barium di-phenyl-acetate with soda-lime (Jena, *A.* 155, 86).

Preparation.—By adding $AlCl_3$ (35 g.) to a mixture of benzyl chloride (100 g.) and benzene (500 g.) (Friedel a. Crafts, *A. Ch.* [6] 1, 478; *Bl.* [2] 33, 337).

Properties.—Prisms, v. sol. alcohol and ether, smelling like oranges. According to Reissert (*B.* 23, 2242) it melts at 23°. Oxidised by chromic acid mixture to benzophenone. Yields diphenylene-methane when passed through a red-hot tube (Graebe, *B.* 7, 1623). Prolonged treatment with Cl in presence of I forms CCl_4 and C_6Cl_6 (Ruoff, *B.* 9, 1048).

Tri-phenyl-methane $C_{19}H_{16}$ *i.e.* $CHPh_3$. [92°]. (330°) (Schwarz); (355°) (K. a. F.).

Formation.—1. By heating $PhCHCl_2$ with $HgPh_2$ at 150° (Kekulé a. Franchimont, *B.* 5, 907).—2. By heating $Ph_2CH(OH)$ with benzene and P_2O_5 at 135° (Hemilian, *B.* 7, 1203).—3. By heating (β)-benzpinacolin $C_{26}H_{20}O$ with soda-lime at 300° (Thörner a. Zincke, *B.* 9, 65).—4. Together with a little CH_2Ph_2 by adding $AlCl_3$ to a mixture of chloroform and benzene (Friedel a. Crafts, *J. pr.* [2] 16, 233; *A. Ch.* [6] 1, 496). 5. With other products, by the action of $AlCl_3$ on benzene mixed with CH_2Cl_2, with CCl_4, with $PhCCl_3$, and with CPhHBr.CPhHBr (Magatti, *B.* 12, 1468; Schwarz, *B.* 14, 1526; Anschütz, *A.* 235, 208).—6. By heating benzoic aldehyde (100 g.) with benzene (147 g.) and $ZnCl_2$ (100 g.) at 260° for 7 hours (Griepentrog, *B.* 19, 1876; *A.* 242, 329).

Preparation.—$AlCl_3$ (500 g.) is slowly added to a mixture of benzene (1400 g.) and chloroform (400 g.). The mixture is finally heated on the water-bath, water is carefully added, and the oil dried and fractionally distilled. It is finally purified by conversion into the compound with benzene (Allen a. Kölliker, *A.* 227, 108; *cf.* Fischer, *A.* 194, 252; Schwarz, *B.* 14, 1516). If the benzene contains toluene the product will contain a homologue (Hanriot, *Bl.* [3] 1, 773).

Properties.—Plates (from alcohol), v. sol. benzene, ether, and $CHCl_3$, m. sol. cold alcohol. Crystallises from benzene in efflorescent rhombohedra $CHPh_3C_6H_6$ [76°]. Oxidised by chromic acid to tri-phenyl-carbinol [159°]. $AlCl_3$ at 120° decomposes it, but below 80° it forms CH_2Ph_2 (Friedel a. Crafts, *C. R.* 100, 692). On exhaustive chlorination with $SbCl_5$ it yields CCl_4 and C_6Cl_6 (Merz a. Weith, *B.* 16, 2876). Na has no action at 300°, but K at 200° forms a red substance ($CKPh_3$). K at 250° forms a dark mass, whence HClAq liberates $C_{19}H_{14}$ [148·5°] (360°) (Hanriot a. Saint-Pierre, *C. R.* 108, 1119; *Bl.* [3] 1, 774). The potassium derivative $CKPh_3$ absorbs CO_2 at 200°, yielding $CPh_3.CO_2H$ [264°]. Benzyl chloride acting on $CKPh_3$ forms the compound $CPh_3.CH_2Ph$ [140°]. BzCl forms $C_{26}H_{18}O$ [172°] which may be reduced by HI and P to $C_{26}H_{20}$ [234°].

References. — Amido-, Bromo-, Chloro-, Methyl-amido-, Nitro-, Nitro-amido-, Oxy-amido-, and Oxy- Phenyl-methane.

DI-PHENYL-METHANE DI-*o*-CARBOXYLIC ACID $CH_2(C_6H_4.CO_2H)_2$. [255°]. Formed by reducing the lactone of $CH(OH)(C_6H_4.CO_2H)_2$ with HI and P (Graebe a. Juillard, *A.* 242, 253). Crystals (from alcohol). Yields anthraquinone on heating at 280°.—BaA″ 6aq. S. 4·7.

Methyl ether Me_2A''. [44°].

Isomeride *v.* Benzyl-isophthalic acid.

Di-phenyl-methane tricarboxylic acid $CO_2H.CH(C_6H_4.CO_2H)_2$. [220°]. S. ·095 at 25°. Got by heating the lactone of the oxyacid $CO_2H.C(OH)(C_6H_4.CO_2H)_2$ with HI and P at 170° (Graebe a. Juillard, *A.* 242, 235). Crystals (containing aq). At 270° it forms a red compound $C_{15}H_8O_4$ [261°].

Methyl ether Me_3A'''. [145°].

Tri-phenyl methane *o*-carboxylic acid $CHPh_2.C_6H_4.CO_2H$. [162°].

Formation.—1. By the action of NaOH an zinc-dust on di-phenyl-phthalide (Baeyer, *B.* 1 644; *A.* 202, 52).—2. By heating phenyl phthalide with benzene and $AlCl_3$ (Gresly, *A* 234, 242).—3. By saponifying the nitrile, which is obtained from $CHCl_2.C_6H_4.CN$, benzene, an $AlCl_3$ (Drory, *B.* 24, 2572).

Properties.—Needles (from alcohol), insol water. May be sublimed. Yields tri-phenyl methane when heated with $Ba(OH)_2$. CrO_3 i HOAc oxidises it to diphenyl-phthalide.

Nitrile $CHPh_2.C_6H_4.CN$. [89°].

Tri-phenyl-methane-*p*-carboxylic acid [162°]. Obtained by saponifying the nitrile which is obtained by Sandmeyer's reaction from *p*-amido-tri-phenyl-methane [84°] (Fischer a Fränkel, *A.* 241, 364; Otto a. Fischer, *B.* 24, 729). Needles, v. sol. alcohol and ether.—AgA'.

An isomeric acid melting above 360° was obained by Oppenheimer (*B.* 19, 2029) by oxidising he corresponding aldehyde with Ag_2O.

Tri-phenyl-methane dicarboxylic acid $CHPh_2.C_6H_3(CO_2H)_2$ [1:2:5]. [280°]. Formed by reduction of the lactone of tri-phenyl-carbinol dicarboxylic acid by zinc-dust and NaOH (Hemilian, *B.* 16, 2375). Needles (from HOAc). Conc. H_2SO_4 forms a greenish-yellow solution, which on heating changes through green, blue, and violet to purple.—BaA″ 4aq.—Ag_2A'': pp.

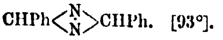
Tri-phenyl-methane dicarboxylic acid $CHPh_2.C_6H_3(CO_2H)_2$ [1:3:4]. [278°]. Formed by boiling di-phenyl-phthalide dicarboxylic acid with zinc-dust and NaOHAq (Hemilian, *B.* 19, 3068). Needles (from dilute alcohol). May be sublimed. Yields $CHPh_3$ when distilled with $Ba(OH)_2$. Re-oxidised by alkaline $KMnO_4$ to di-phenyl-phthalide dicarboxylic acid.—CaA″ 2aq: needles.—Ag_2A'': curdy pp.

Reference.—OXY-DI-PHENYL-METHANE CARBOXYLIC ACID.

DIPHENYL-METHANE DISULPHONIC ACID $C_{13}H_{10}(SO_3H)_2$. [59°]. Got by sulphonation (Doer, *B.* 5, 796). Deliquescent plates.—K_2A'' aq: prisms (from dilute alcohol).—BaA″.—CuA″: green plates.

Tri-phenyl-methane trisulphonic acid $C_{19}H_{13}(SO_3H)_3$. Formed by warming $CHPh_3$ with fuming H_2SO_4 (Kekulé a. Franchimont, *B.* 5, 908; Hemilian, *B.* 7, 1205).—$Ba_3A'''_2$ 8aq: needles, ppd. by adding alcohol to its aqueous solution.

DI-PHENYL-METHAZINE $C_{11}H_{12}O_2$ *i.e.*



$CHPh<\begin{matrix}N\\N\end{matrix}>CHPh$

[93°]. Formed by shaking a dilute solution of hydrazine with benzoic aldehyde (Curtius, *J. pr.* [2] 39, 44). Light-yellow prisms, v. sl. sol. hot water, v. sol. hot alcohol. Decomposed by boiling into CHPh:CHPh and nitrogen, and by boiling dilute acids into benzoic aldehyde and hydrazine. Reduced in alcoholic solution by sodium-amalgam to di-benzyl-hydrazine, and by excess of Na to benzylamine.

PHENYL-METHENYL-AMIDINE *v.* BENZAMIDINE.

Diphenyl-methenyl-diamine is described as DI-PHENYL-FORMAMIDINE.

PHENYL-METHENYL-AZIDINE $C_7H_9N_3$ *i.e.* $NH_2.CH:N_2HPh$. [225°]. Formed from phenyl-hydrazine and HCy (Fischer, *B.* 22, 1934). Insol. water, v. sol. hot alcohol. The nitrate and hydrochloride are crystalline.

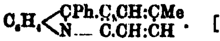
PHENYL METHENYL DI-ETHYL TRISULPHONE $C_6H_5.SO_2.CH(SO_2.C_2H_5)_2$. [166°]. S. 2 at 15°. Formed by oxidising $PhS.CH(SO_2Et)_2$ with alkaline $KMnO_4$ (Fromm, *A.* 253, 167; Laves, *B.* 25, 362). Snow-white needles, v. sol. alkalis.—KA′: prisms.—BaA'_2: tables.

TRI-PHENYL METHENYL TRIKETONE *v.* TRI-BENZOYL-METHANE.

TRI-PHENYL METHENYL TRISULPHONE $CH(SO_2Ph)_3$. [215°]. Formed by oxidising $PhS.CH(SO_2Ph)_2$ with alkaline $KMnO_4$ (Laves, *B.* 25, 348). Tables, v. sol. alcohol, insol. ether, m. sol. water.—KA′: tablets.—BaA'_2.—AgA′.

DI-PHENYL-DI-METHYL-ACETYLENE TETRAKETONE *v.* DI-BENZOYL-DI-ACETYL-ETHANE.

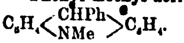
PHENYL-METHYL-ACRIDINE $C_{20}H_{15}N$ *i.e.*



$C_6H_4<\begin{matrix}\text{CPh.C.CH:CMe}\\ \text{N — C.CH:CH}\end{matrix}$

[136°]. Formed by heating phenyl-*p*-toluidine with benzoic acid and $ZnCl_2$ at 260° (Bonna, *A.* 289, 62). Needles, sl. sol. water. Its alcoholic solution shows greenish-blue fluorescence. Yields phenyl-acridine carboxylic acid [253°] on oxidation.—B′HCl: yellow needles.—B′HI.—$B'_2H_2SO_4$.—$B'C_6H_3N_3O_7$. Red needles.

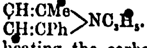
Phenyl-methyl-acridine dihydride



$C_6H_4<\begin{matrix}CHPh\\NMe\end{matrix}>C_6H_4$

[104°]. Formed by the action of MeI on phenyl-acridine dihydride; or by reduction of the methylo-chloride of phenyl-acridine with zinc-dust (Bernthsen a. Bender, *B.* 16, 1816). White needles or prisms. On oxidation with nitrous acid it gives the methylo-hydroxide of phenyl-acridine.

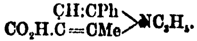
PHENYL-METHYL-ALLYL-PYRROLE



$\begin{matrix}\text{CH:CMe}\\ \text{CH:CPh}\end{matrix}>NC_3H_5$

[52°]. (278°). Formed by heating the carboxylic acid [158°] (Lederer a. Paal, *B.* 18, 2595). Large colourless plates. Blue fluorescence. Extremely sol. all ordinary solvents.

PHENYL-METHYL-ALLYL-PYRROLE CARBOXYLIC ACID



$\begin{matrix}\text{CH:CPh}\\ \text{CO}_2\text{H.C}=\text{CMe}\end{matrix}>NC_3H_5$

[158°]. Obtained by saponification of its ether, which is formed by the action of allylamine upon acetophenone-acetoacetic ether (Lederer a. Paal, *B.* 18, 2594). Short glistening prisms. V. sol. alcohol, ether, benzene, and acetic acid.

PHENYL-METHYL-AMIDO-ACETIC ACID $C_9H_{11}NO_2$ *i.e.* $CH_2(NPhMe).CO_2H$. *Phenyl-methyl-glycocoll.* Formed by heating chloro-acetic ether with dimethylaniline and saponifying the product by boiling HClAq (Silberstein, *B.* 17, 2661). Liquid.—HA′HCl: prisms.

Amide. $CH_2(NPhMe).CO.NH_2$. [168°]. Formed by heating $CH_2Cl.CONH_2$ with $NPhMe_2$ or NPhMeH. Crystals, sol. hot water. Its hydrochloride forms easily soluble prisms.

Methylo-chloride $CH_2(NPhMe_2Cl).CO_2H$. Formed by warming chloro-acetic acid with $NPhMe_2$ in ether (Zimmermann, *B.* 12, 2206). Needles. Moist Ag_2O forms an hydroxide.

Amide of the methylo-chloride $CH_2(NPhMe_2Cl).CO.NH_2$. Formed by heating chloro-acetamide with dimethylaniline in alcohol (S.). Crystals, decomposed by heat into MeCl and $CH_2(NPhMe).CO.NH_2$.

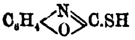
PHENYL-METHYL-ω-AMIDO-ACETOPHENONE $C_6H_5.CO.CH_2.NPhMe$. *Phenacyl-methyl-aniline.* [120°]. Formed by the action of NPhMeH or $NPhMe_2$ on ω-bromo-acetophenone (Staedel a. Siepermann, *B.* 18, 842; 14, 983; 21, 2196). Prisms (from alcohol). A solution of its hydrochloride gives a red pp. with dilute HNO_3 (Weller, *B.* 16, 27). $ZnCl_2$ forms $C_{15}H_{13}N$ [102°].—$B'_2H_2PtCl_6$: tables.—B′MeI. Crystals.—B′MeOH. Strongly alkaline.

PHENYL-METHYL-AMIDO-BENZENE PHOSPHINIC ACID $NPhMe.C_6H_4.P(OH)_2$. [150·5°]. Formed by the action of NaOHAq on the oily chloride $NPhMe.C_6H_4.PCl_2$, which is formed by the action of $AlCl_3$ on a mixture of NPh_2Me and PCl_3 (Michaelis, *A.* 260, 37). Small needles (from water) or plates (from alcohol).—NaHA″ 2aq. [265°]. Plates, v. e. sol. water.

PHENYL-METHYL-AMIDO-BENZOIC ACID $C_{14}H_{13}NO_2$ *i.e.* $C_6H_4(NPhMe).CO_2H$. [184°]. Formed from NPh_2Me and $COCl_2$ (Michler a. Sarauw, *B.* 14, 2180). Plates.—BaA'_2: pearly plates.—AgA': white pp.

PHENYL-METHYL-AMIDO-ETHANE SULPHONIC ACID $NPhMe.C_2H_4.SO_3H$. Formed from $CH_2Cl.CH_2.SO_3H$ and methylaniline at 160° (James, *J. pr.* [2] 31, 417). Silky crystals (from alcohol).

PHENYL - METHYL - AMIDO - ETHYL - PHTHALIMIDE $C_8H_4O_2:N.C_2H_4.NPhMe$. [105°]. Formed from bromo-ethyl-phthalimide and methyl-aniline at 165° (Newman, *B.* 24, 2199). Greenish-yellow four-sided tables, v. c. sol. C_6H_6.

PHENYL - METHYL - AMIDO-METHENYL-AMIDO-PHENOL $C_{14}H_{12}N_2O$ *i.e.* $C_6H_4{<}\substack{N\\O}{>}C.NPhMe$. (above 360°). Formed from  $C_6H_4{<}\substack{N\\O}{>}C.SH$ and methyl-aniline (Kalckhoff, *B.* 16, 1825). Syrup, with blue fluorescence.—$B'_2H_2PtCl_6$: prisms.

PHENYL - METHYL - AMIDO-DI-METHYL-PYRROLE $C_{13}H_{16}N_2$ *i.e.* $NPhMe.N{<}\substack{CMe:CH\\CMe:CH}$. [41°]. (310°). Formed by heating its dicarboxylic acid at 231° (Knorr, *A.* 236, 310). Crystalline mass, v. sol. alcohol. Volatile with steam.

Phenyl-methyl-amido-di-methyl-pyrrole dicarboxylic acid $C_{15}H_{16}N_2O_4$. Formed by saponification of its oily ether, which is formed from diacetyl-succinic ether and phenyl-methyl-hydrazine (K.). Prisms, decomposing at 231°.—AgA': flocculent pp.

PHENYL - METHYL - *p* - AMIDO - PHENOL. *Methyl derivative* $NPhMe.C_6H_4.OMe$. (313°). Formed from phenyl-*p*-amido-phenol, KOH, and MeI (Philip a. Calm, *B.* 17, 2433). Oil, insol. NaOHAq.

PHENYL - TETRA - METHYL - TRI - AMIDO-DI-PHENYL-NAPHTHYL-CARBINOL $C_{33}H_{33}N_3O$ *i.e.* $NPhH.C_{10}H_6.C(OH)(C_6H_4.NMe_2)_2$. [95°]. *Base of Victoria Blue B.* Formed by heating tetra-methyl-di-amido-benzophenone (10 pts.) with phenyl-(*a*)-naphthylamine (9 pts.), and $POCl_3$ (7 pts.) at 110° (Nathansohn a. Müller, *B.* 22, 1890). The base is set free by NaOHAq. Brick-red powder, v. sol. alcohol and benzene.—$(C_{33}H_{32}N_3Cl)_2PtCl_4$: violet needles.—$C_{33}H_{31}N_3C_6H_2(NO_2)_3OH$: dark-blue pp.

Phenyl - penta - methyl-tri-amido-di-phenyl-naphthyl-carbinol $C_{34}H_{35}N_3O$ *i.e.* $NPhMe.C_{10}H_6.C(OH)(C_6H_4.NMe_2)_2$. [77°]. The chloride $C_{34}H_{34}N_3Cl$, '*Victoria Blue* 4 *R*,' formed by the action of methyl-phenyl-(*a*)-naphthylamine on $CO(C_6H_4NMe_2)_2$ in presence of $POCl_3$ is v. sol. hot water (Nathansohn a. Müller, *B.* 22, 1892). The carbinol is a brick-red pp., v. sol. alcohol. It forms $(C_{34}H_{34}N_3Cl)_2PtCl_4$ and $C_{34}H_{33}N_3C_6H_2(NO_2)_3OH$ crystallising in very small dark-blue needles.

PHENYL - TETRA - METHYL - TRI-AMIDO-DI-PHENYL-NAPHTHYL-METHANE $C_{33}H_{33}N_3$ *i.e.* $NHPh.C_{10}H_6.CH(C_6H_4.NMe_2)_2$. [125°]. Formed by reducing the carbinol (*v. supra*) (Nathansohn a. Müller, *B.* 22, 1891). Flocculent pp., v. sol. hot alcohol. Yields $B'''_2H_2PtCl_6$ and $B'''C_6H_3N_3O_7$, both being crystalline.

Phenyl-penta-methyl-tri-amido-di-phenyl-naphthyl-methane $C_{34}H_{35}N_3$ *i.e.* $NPhMe.C_{10}H_6.CH(C_6H_4NMe_2)_2$. [87°]. Formed by reducing the carbinol (N. a. M.). Amorphous. Yields crystalline $B'''_2H_2PtCl_6$ and $B'''C_6H_3N_3O_7$.

PHENYL DI - METHYL - AMIDO - TOLYL KETONE $C_6H_5.CO.C_6H_3Me.NMe_2$. [67°]. (350°-360°). Formed from benzoic acid, di-methyl-*o*-toluidine, and P_2O_5 (O. Fischer, *A.* 206, 91).

PHENYL-TETRA - METHYL-DI-AMIDO-DI-TOLYL-METHANE $C_{23}H_{30}N_2$ *i.e.* $CHPh(C_6H_3Me.NMe_2)_2$. [109°]. Formed by heating di-methyl-*m*-toluidine with benzoic aldehyde and $ZnCl_2$ (Fischer, *B.* 13, 807). Prisms.—$B''H_2PtCl_6$ 2aq: small yellow crystals.

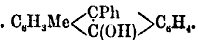
PHENYL-METHYL-AMINE *v.* METHYL-ANILINE.

Phenyl-di-methyl-amine *v.* DI-METHYL-ANILINE.

Di-phenyl-methyl-amine *v.* METHYL-DI-PHENYL-AMINE.

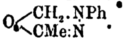
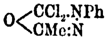
Tri-phenyl-methyl-amine *v.* TRI-PHENYL CARBINYLAMINE.

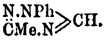
PHENYL-METHYL-ANTHRACENE $C_{21}H_{16}$ *i.e.* $C_6H_3Me{<}\substack{CPh\\CH}{>}C_6H_4$. [119°]. Obtained by distilling phenyl-methyl-anthranol with zinc dust (Hemilian, *B.* 16, 2367). Yellow pointed crystals. Dissolves in alcohol and ether, with a strong greenish-blue fluorescence. By CrO_3 in acetic acid it is oxidised to phenyl-methyl-oxanthranol.

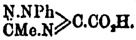
PHENYL-METHYL-ANTHRANOL $C_{21}H_{16}O$ *i.e.*  $C_6H_3Me{<}\substack{CPh\\C(OH)}{>}C_6H_4$. [157°]. Obtained by heating di-phenyl-tolyl-methane carboxylic acid with H_2SO_4 (Hemilian, *B.* 16, 2365). Yellow glistening tables. Sol. ether, boiling alcohol and acetic acid, insol. cold alkalis, but dissolves on boiling to a yellow solution. On oxidation it gives phenyl-methyl-oxanthranol.

PHENYL-DI-METHYL-ARSINE *v.* vol. i. p. 320.

DI - PHENYL - DI - METHYL - AZIMETHYLENE $N_2(CMePh)_2$. [121°]. Formed by the action of acetophenone on hydrazine hydrate or on $CPhMe:N.NH_2$ (Curtius, *J. pr.* [2] 44, 542).

PHENYL-METHYL-BIAZOLE DIHYDRIDE  $O{<}\substack{CH_2.NPh\\CMe:N}$. [140°]. Formed by the action of tin and HCl on  $O{<}\substack{CCl_2.NPh\\CMe:N}$ [122°], which is made by the action of $COCl_2$ on acetyl-phenyl-hydrazine (Freund a. Kuh, *B.* 23, 2838). Yellowish plates.

PHENYL-METHYL-TRIAZOLE $C_9H_9N_3$ *i.e.*  $\substack{N.NPh\\CMe.N}{>}CH$. Formed by heating its carboxylic acid to 180° (Bladin, *B.* 19, 2602). Oil. $B'_2H_2PtCl_6$ aq. [124°]. Lemon-yellow tables.

PHENYL-METHYL-TRIAZOLE CARBOXYLIC ACID  $\substack{N.NPh\\CMe.N}{>}C.CO_2H$. [177°]. Formed by saponifying its nitrile, which is got by the action of Ac_2O on phenyl-hydrazine dicyanide and also by gently warming phenyl-hydrazine dicyanide with an alcoholic solution of pyruvic acid (Bladin, *B.* 18, 1544; 19, 2598; 22, 1749; 25, 185).

Salts. — CuA'_2 1½aq. — PbA'_2 2½aq. — AgA' 1½aq.—$HA'HCl$: tables (from HClAq).

Ethyl ether EtA'. Oil.

Nitrile. [109°]. Prisms.

Amide $C_2N_3PhMe.CO.NH_2$. [170°]. Prisms, m. sol. water and alcohol.

Amidoxim $C_2N_3PhMe.C(NH_2):NOH$. [210°]. Formed from the nitrile and hydroxylamine in alcohol. Plates (from alcohol), v. sl. sol. water. $FeCl_3$ colours its alcoholic solution deep red. Yields B'HCl and $B'_2H_2PtCl_6$ [201°]. Ac_2O forms $C_2N_3PhMe.C(NH_2):NOAc$ [148°] and $C_2N_3PhMe.C{<}\begin{matrix}N.O\\N\end{matrix}{>}CMe$ [105·5°]. BzCl forms $C_2N_3PhMe.C(NH_2):NOBz$ [18[illegible]5°] converted by heat into $C_2N_3PhMe.C{<}\begin{matrix}N.O\\N\end{matrix}{>}CPh$ [167°].

DI-PHENYL-DI-METHYL-TETRAZONE NPhMe.N:N.NPhMe. [137°]. Formed by oxidising phenyl-methyl-hydrazine (Fischer, *A.* 190, 152; Tafel, *B.* 18, 1744). Monoclinic plates. With I in $CHCl_3$ it forms $C_{14}H_{16}N_4I_4$, a black crystalline pp.

DI-PHENYL-DI-METHYL-DI-TRIAZYL $\begin{matrix}N.NPh\\CMe.N\end{matrix}{>}C.C{<}\begin{matrix}NPh.N\\N-CMe\end{matrix}$ [223°]. Formed by heating the cyanide of phenyl-hydrazine with Ac_2O (Bladin, *B.* 21, 3063). Prisms (from alcohol).—$B''H_2Cl_2$.—$B''H_2PtCl_6$ ½aq. Plates.

DI-PHENYL-METHYL-BENZAMIDINE $C_6H_5.C(NMe).NPh_2$. Formed by heating di-phenyl-benzamidine with MeI at 130° (Bernthsen, *A.* 192, 17). Syrup.—$B'_2H_2PtCl_6$: yellow pp.

PHENYL *p*-METHYL-BENZYL KETONE $C_6H_5.CO.CH_2.C_6H_4Me$. [94°]. Formed from *p*-tolyl-acetic chloride, benzene, and $AlCl_3$ (Strassmann, *B.* 22, 1231). Yields an oxim [109°].

PHENYL-METHYL-BENZYL-UREA $NHPh.CO.NH.CH_2C_6H_4Me$. [131°]. Formed from *m*-methyl-benzylamine and phenyl cyanate (Brömme, *B.* 21, 2700).

TRI-PHENYL-METHYL-BROMIDE *v.* Bromo-tri-phenyl-methane.

PHENYL-METHYL-CARBAMIC ACID.

Ethyl ether NPhMe.CO.OEt. (244°). Formed from methylaniline and $Cl.CO_2Et$ (Gebhardt, *B.* 17, 3042). Yellow oil.

Chloride NPhMe.COCl. [88°]. (280°). Got by passing $COCl_2$ into a solution of methylaniline in benzene (Michler a. Zimmermann, *B.* 12, 1165). Tables (from alcohol), insol. water. Reacts with toluene and aluminium chloride, forming $NPhMe.CO.C_6H_4Me$ [70°] while $AlCl_3$ and *o*-, *m*-, and *p*- xylene give rise to the compounds $NPhMe.CO.C_6H_3Me_2$ melting at 78°, 54°, and 74° respectively (Lellmann, *B.* 24, 2114).

Phenyl ether $NPhMe.CO.OC_6H_5$. [58°]. Formed from the chloride and KOPh in alcohol (Lellmann a. Benz, *A.* 24, 2108). Large crystals.

Nitro-phenyl ethers $C_6H_4(NO_2)A'$. The *o*-, *m*-, and *p*- nitro-phenyl ethers melt at 110°, 105°, and 70° respectively. They yield on reduction the corresponding amido-phenyl ethers melting at 103°, 94°, and 104° respectively.

p-Tolyl ether C_6H_4MeA'. [62°].

PHENYL-METHYL-SEMI-CARBAZIDE $NPhMe.NH.CO.NH_2$. [133°]. Formed from phenyl-methyl-hydrazine hydrochloride and potassium cyanate (Fischer, *A.* 190, 164). Crystalline mass, m. sol. hot water. Yields a nitrosamine $NPhMe.N(NO).CO.NH_2$ [77°].

Phenyl-di-methyl-semi-carbazide $NMe_2.NH.CO.NHPh$. [108°]. Formed from phenyl-cyanate and di-methyl-hydrazine (Renouf, *B.* 18, 2172). Pyramids. Decomposed by HCl into the parent substances.

Di-phenyl-di-methyl-carbazide $CS(NH.NPhMe)_2$. [c. 168°]. Got by heating phenyl-methyl-hydrazine with CS_2 (Stahel, *A.* 258, 250).

PHENYL-METHYL-CYANIDE *v. Nitrile* of Phenyl-acetic acid.

Di-phenyl-methyl-cyanide *v. Nitrile* of Di-phenyl-acetic acid.

Di-phenyl-methyl dicyanide $C_{16}H_{13}N_3$ *i.e.* $N{<}\begin{matrix}CMe.N\\CPh:N\end{matrix}{>}CPh$. [110°]. (227° at 15 mm.). Formed from benzonitrile, AcCl, and $AlCl_3$ (Krafft a. Hansen, *B.* 22, 803; 23, 2382). Needles, sol. alcohol and ligroïn. Decomposed by diluted H_2SO_4 into benzoic acid, acetic acid, and NH_3. Oxidised by alkaline $KMnO_4$ to $C_3N_3Ph_2.CO_2H$ [c. 192°] which on heating yields $C_3N_3Ph_2H$ [75°] (205° at 9 mm.).

Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$.

DI-PHENYL-METHYLENE-*p*-AMIDO-BENZOIC ACID $CPh_2:N.C_6H_4.CO_2H$. [240°]. Formed from Ph_2CCl_2 and *p*-amido-benzoic acid (Hantzsch a. Krafft, *B.* 24, 3522). Short prisms.

PHENYL-METHYLENE-AMINE $CH_2:NPh$ or $CH_2{<}\begin{matrix}NPh\\NPh\end{matrix}{>}CH_2$? [140°]. Formed by adding aniline to a solution of formic aldehyde (Wellington a. Tollens, *B.* 18, 3309). Formed also from trioxymethylene and aniline (Kolotoff, *J.* 1885, 777). Long slender needles. Decomposed by water at 100° into trioxymethylene and aniline.

Phenyl-trimethylene-diamine $NHPh.C_3H_6.NH_2$. (282° cor.). S.G. $\frac{0}{0}$ 1·0356. A product of the action of Na on an alcoholic solution of phenyl-pyrazole (Balbiano, *G.* 18, 354; 19, 688; *Rend. Accad. Linc.* [4] 4, ii. 44). Formed also by boiling phenyl-γ-amido-propyl-phthalimide with HClAq (Goldenring, *B.* 23, 1169). Oil. Sulphide of carbon forms $NHPh.C_3H_6.NH.CS.SNH_2Ph.C_3H_6NH_2$, crystallising from alcohol in white plates.—B''2HCl: tufts of needles, v. e. sol. water. When heated it gives off NH_3 and $NPh:C_3H_6$, which forms $(C_9H_{11}N)_2H_2PtCl_6$.—$C_9H_{11}N,2C_6H_3N_3O_7$. Greenish crystals, decomposing at 195°.—**Succinate** [100°].

Phenyl-di-trimethylene-triamine $NPh(CH_2.CH_2.CH_2.NH_2)_2$. Formed by heating its phthalyl derivative with HClAq at 240° (Goldenring, *B.* 23, 1170).—B'''3HCl.—$B'''_2 3H_2PtCl_6$.

Di-phthalyl derivative $NPh(CH_2.CH_2.CH_2.N:C_8H_4O_2)_2$ [145°]. Formed from γ-bromo-propyl-phthalimide and aniline.

Di-phenyl-methylene-amine $CPh_2:NH$. Formed by heating CPh_2Cl_2 with carbamic ether at 130° (Hantzsch a. Krafft, *B.* 24, 3517). Colourless liquid.—B'HCl: snow-white powder.

Di-phenyl-methylene-diamine $CH_2(NHPh)_2$. [49°]. Formed by mixing a large excess of an aqueous solution of aniline with formic aldehyde solution (Pratesi, *G.* 14, 351; *cf.* Lermontoff, *B.* 7, 1255). Four-sided tables, sol. alcohol. Its hydrochloride is unstable.—$B''H_2PtCl_6$.

Di-phenyl-trimethylene-diamine $CH_2(CH_2.NHPh)_2$. Formed from aniline and trimethylene bromide (Hanssen, *B.* 20, 781). Thick brown liquid.—$B''H_2SO_4$. [156°]. Needles.

Nitrosamine $CH_2(CH_2.NPh.NO)_2$. [87°].

DI-PHENYL-METHYLENE-ANILINE $NPh:CPh_2$. [109°]. (above 360°). Formed from CPh_2Cl_2 and aniline (Pauly, *A.* 187, 199). Yellow tables (from ether). Split up by HClAq into aniline and benzophenone.

TETRA-PHENYL-DI-METHYLENE-TETRAZONE $N_2(N:CPh_2)_2$. Formed by shaking a benzene solution of $NH_2.N:CPh_2$ with HgO (Curtius a. Rauterberg, *J. pr.* [2] 44, 200). Red needles. Decomposes readily into nitrogen and $CPh_2:N.N:CPh_2$. Gaseous HBr forms CPh_2HBr [88°].

DI-PHENYL-TRIMETHYLENE-DI-CARBAMIC ACID.

Ethyl ether $CH_2(CH_2.NPh.CO_2Et)_2$. [56°]. Formed from the chloride and NaOEt (Hanssen, *B.* 20, 783). Crystalline.

Chloride $CH_2(CH_2.NPh.COCl)_2$. [102°]. Formed from $CH_2(CH_2NPhH)_2$ and $COCl_2$ in benzene. Needles.

PHENYL-TRIMETHYLENE DICARBOXYLIC ACID $CHPh\Big<{CH.CO_2H \atop CH.CO_2H}$. [175°]. Got by saponifying its ether. Prisms, m. sol. water, v. sol. alcohol and ether (Buchner a. Dessauer, *B.* 21, 2646; 25, 1152). When heated *in vacuo* it yields an anhydride $C_{11}H_8O_3$ [134°].—NaHA″: needles.

Di-methyl ether Me_2A''. [63°].

Ethyl ether Et_2A'' (257° at 120 mm.). Formed by distilling $CO_2Et.CH\Big<{N.CHPh \atop N.CH.CO_2Et}$ *in vacuo*. Thick oil.

Phenyl-trimethylene-tri-carboxylic acid $C_3H_2Ph(CO_2H)_3$. [188°]. Got by saponifying its ether (B. a. D.). Crystals containing 4aq.

Methyl ether Me_3A'''. [47°]. (210° at 20 mm.). Formed from NaOMe, methyl malonate, and methyl di-bromo-phenyl-propionate.

PHENYL METHYLENE ETHYL DIKETONE $C_6H_5.CO.CH_2.CO.C_2H_5$. *Propionyl-acetophenone.* (277°). S.G. ^{15} 1·081. Formed from acetophenone, propionic ether, and NaOEt (Stylos, *B.* 20, 2181). Liquid.

DI-PHENYL-METHYLENE-HYDRAZINE $CPh_2:N.NH_2$. [98°]. (c. 227° at 55 mm.). *Hydrazide of benzophenone.* Formed by heating benzophenone (5 g.) with hydrazine hydrate (1·8 g.) and alcohol (1 g.) at 150° (Curtius a. Lauterberg, *J. pr.* [2] 44, 192). Prisms (from alcohol). Reduces alcoholic $AgNO_3$ forming a mirror. Reduces Fehling's solution on warming. Boiling dilute H_2SO_4 splits off hydrazine. Reacts readily with ketones.—B′HCl. [183°].

Acetyl derivative. [107°]. Prisms.

Benzoyl derivative. [116·5°]. Prisms.

Tetra-phenyl-di-methylene-hydrazine $CPh_2:N.N:CPh_2$. *Di-phenyl-ketazine.* [162°]. Formed by boiling $CPh_2:N.NH_2$ with iodine in alcohol. Yellow prisms, v. sl. sol. hot water, sol. alkalis. Decomposed by boiling dilute H_2SO_4 into benzophenone and $N_2H_4H_2SO_4$.

Phenyl-trimethylene-hydrazine $C_9H_{12}N_2$. [58°]. Got from phenyl-hydrazine and trimethylene bromide (Marckwald, *C. C.* 1888, 1410). Converted by trimethylene bromide on further heating into $(PhN_2)_2(C_3H_6)_3$ [226°].

DI-PHENYL METHYLENE DIKETONE $CH_2(CO.C_6H_5)_2$. *Benzoyl-acetophenone. Dibenzoyl-methane.* [81°]. (over 200°).

Formation.—1. By boiling di-benzoyl-acetic acid with water (Baeyer a. Perkin, jun.; *B.* 16, 2184; *C. J.* 47, 240).—2. By the action of malonyl chloride and $AlCl_3$ upon benzene (Auger, *A. Ch.* [6] 22, 348).

Preparation.—By adding dry sodium ethylate to a mixture of acetophenone and benzoic ether, the reaction taking place with spontaneous heating. The crystalline mass is extracted with cold water, finally with dilute NaOH, and from the solution of the sodium salt the ketone is precipitated by means of CO_2; the yield is c. 50 p.c. of the acetophenone used (Claisen, *B.* 20, 655).

Properties.—Trimetric plates, v. sol. alkalis. Yields products of substitution by treatment with NaOEt and alkyl iodides.

Reactions.—1. *Bromine* (1 mol.) in $CHCl_3$ forms Bz_2CHBr [93°], which on heating with HOAc and KOAc yields Bz_2CHOAc [94°], which on further bromination gives $Bz_2CBr.OAc$ [102°] which is split up by heat into Ph.CO.CO.CO.Ph and AcBr.—2. Excess of *bromine* (2 mols.) in $CHCl_3$ forms Bz_2CBr_2 [95°] whence HOAc and KOAc form di-phenyl triketone.—3. Amyl nitrite and alcoholic HCl give $Bz_2C:NOH$ [146°], converted by nitrous acid into the triketone (Neufville a. Pechmann, *B.* 22, 852; 23, 3376).—4. *Phenyl-hydrazine* forms tri-phenyl-pyrazole (Japp a. Klingemann, *B.* 22, 2886).

PHENYL METHYLENE METHYL DIKETONE *v.* BENZOYL-ACETONE.

PHENYL METHYLENE METHYL SULPHONE-KETONE $C_6H_5.SO_2.CH_2.CO.CH_3$. *Acetonyl phenyl sulphone.* [57°]. Formed by oxidising $PhS.CH_2Ac$ with $KMnO_4$ (Delisle, *A.* 260, 262). Formed also from chloro-acetone and $C_6H_5.SO_2Na$ (Otto, *B.* 19, 1642; 21, 1871; 23, 756; *J. pr.* [2] 36, 402). Plates, sol. water and alcohol. Yields a phenyl-hydrazide [129°] and an oxim [148°]. Ammonia yields the compound $NH:CMe.CH_2.SO_2Ph$ [111°]. Phenyl mercaptan yields $(PhS)_2CMe.CH_2SO_2Ph$ [104]. Potash yields phenyl methyl sulphone. Br forms a bromo-derivative [96°] and a di-bromo-derivative [114°].

PHENYL-METHYLENE-PHTHALIMIDINE $C_{15}H_{11}NO$ *i.e.* $C_6H_4\Big<{C(CH_2) \atop CO-\!-}\Big>NPh$. [100°]. Formed by heating acetophenone *o*-carboxylic anilide at 230° (Mertens, *B.* 19, 2372). Prisms, v. sol. alcohol. An isomeride [265°], got by treating acetophenone *o*-carboxylic anilide with conc. H_2SO_4, is sl. sol. alcohol.

DI-PHENYL METHYLENE DISULPHONE $CH_2(SO_2Ph)_2$. [119°]. Formed by oxidation of $CH_2(SPh)_2$ which is got by boiling CH_2Cl_2 with NaSPh (Fromm, *A.* 253, 161). Needles, v. sl. sol. boiling water.

DI-PHENYL-DI-METHYLENE DI-SULPHONE KETONE $C_{15}H_{14}S_2O_5$ *i.e.* $CO(CH_2SO_2Ph)_2$. [150°]. Got from $CHBr.CO.CH_2.SO_2Ph$ and $C_6H_5.SO_2Na$. Got also from $CO(CHCl_2)_2$ and $C_6H_5.SO_2Na$ (Otto, *B.* 19, 1542; 22, 1967). Small crystals (from HOAc). Yields an oxim [137°] and a phenyl-hydrazide [171°]. PhSH forms $(PhS)_2C(CH_2.SO_2Ph)_2$ [191°].

DI-PHENYL-METHYLENE-DI-THIO-GLYCOLLIC ACID $CPh_2(S.CH_2.CO_2H)_2$. [176°]. Formed by heating benzophenone with thioglycollic acid and $ZnCl_2$ (Bongartz, *B.* 21, 488). Needles (from dilute HOAc), insol. hot water.

PHENYL-TRIMETHYLENE-THIO-UREA $\mathrm{CS}<\begin{matrix}\mathrm{NH\ .CH_2}\\ \mathrm{NPh.CH_2}\end{matrix}>\mathrm{CH_2}$. [215°]. Formed by boiling $NHPh.C_3H_6.NH.CS.SNPhH_2.C_3H_6.NH_2$ with water (Goldenring, *B.* 23, 1172). White prisms.

Di-phenyl-methylene-ψ-thio-urea $C_{14}H_{12}N_2S$ *i.e.* $\mathrm{S}<\begin{matrix}\mathrm{C(NPh)}\\ \mathrm{CH_2}\text{——}\end{matrix}>\mathrm{NPh}$. [68°]. Formed from di-phenyl-thio-urea and CH_2I_2 (Foerster, *B.* 21, 1872). Thin needles, v. e. sol. alcohol.—$B'_2H_2PtCl_6$. Crystalline pp.

Di-phenyl-trimethylene-ψ-thio-urea $\mathrm{S}<\begin{matrix}\mathrm{C(NPh)-NPh}\\ \mathrm{CH_2.CH_2.CH_2}\end{matrix}$. [123°]. Formed from di-phenyl-thio-urea and trimethylene bromide (F.).

Di-phenyl-trimethylene-di-thio-di-urea $CH_2(CH_2.NH.CS.NPhH)_2$. Formed from phenyl-thiocarbimide, trimethylene-diamine, and alcohol (Lellmann a. Würthner, *A.* 228, 236). Plates [115°] or nodules [60°], v. sol. alcohol.

Tri-phenyl-trimethylene-di-thio-di-urea $NHPh.CS.NH.CH_2.CH_2.CH_2.NPh.CS.NHPh$. [145°]. Formed by heating phenyl-trimethylene-diamine (1 g.) with phenyl-thiocarbimide (2 g.) and alcohol (15 c.c.) (G.). Slender needles.

DIPHENYL-METHYLENE-*p*-TOLUIDINE $C_6H_4MeN{:}CPh_2$. (above 360°). Formed from Ph_2CCl_2 and *p*-toluidine (Pauly, *A.* 187, 214). Oil, split up by acids into *p*-toluidine and benzophenone.

PHENYL-TRIMETHYLENE-UREA $\mathrm{CO}<\begin{matrix}\mathrm{NPh.CH_2}\\ \mathrm{NH\ .CH_2}\end{matrix}>\mathrm{CH_2}$. [215°]. Formed by heating phenyl-amido-propyl-urea at 240° (Goldenring, *B.* 23, 1173). Yellowish plates, sl. sol. hot Aq.

Di-phenyl-trimethylene-urea $\mathrm{CO}<\begin{matrix}\mathrm{NPh.CH_2}\\ \mathrm{NPh.CH_2}\end{matrix}>\mathrm{CH_2}$. [156°]. Formed, together with $CH_2(CH_2.NPh.COCl)_2$ [102°], from di-phenyl-trimethylene-diamine and $COCl_2$ in benzene (Hanssen, *B.* 20, 782). Plates.

Tetra-phenyl-trimethylene-di-urea $CH_2(CH_2.NPh.CO.NHPh)_2$. [153°]. Formed from $CH_2(CH_2.NPh.COCl)_2$ and aniline (H.).

PHENYL TRIMETHYLENYL KETONE $\mathrm{C_6H_5.CO.CH}<\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}$ or $\begin{matrix}\mathrm{CH\ :CPh}\\ \mathrm{CH_2.CH_2}\end{matrix}>\mathrm{O}$. *Benzoyl-trimethylene. Phenyl-furfurane dihydride* (239°) at 720 mm. V.D. 5·27 (calc. 5·04). Formed by heating its carboxylic acid at 200° (Perkin, jun., *B.* 16, 2140; *C. J.* 47, 842). Oil with aromatic odour. Alcoholic hydroxylamine forms the oxim in the cold, but by heating the ketone with alcoholic hydroxylamine hydrochloride at 135° there are formed $C_{33}H_{27}N_3O_3$ (a red amorphous powder) and $C_{30}H_{28}N_2O_2$ (a black brittle mass which forms deep-blue $B''H_2Cl_2$ and $B''H_2PtCl_6$).

Oxim. [87°]. Colourless plates.

PHENYL TRIMETHYLENYL KETONE CARBOXYLIC ACID $\begin{matrix}\mathrm{CH_2}\\ \mathrm{CH_2}\end{matrix}>\mathrm{CBz.CO_2H}$. [149°]. Formed by saponification of the ether. Monoclinic prisms; $a{:}b{:}c = 2{\cdot}380{:}1{:}2{\cdot}132$; $\beta = 83°4'$. M. sol. ether, sl. sol. water. Decomposed by water at 110° into phenyl oxypropyl ketone $CH_2OH.CH_2.CH_2Bz$, which when extracted with ether and dried over K_2CO_3 is found to have split off water, the resulting anhydride being possibly phenyl trimethylenyl ketone (Perkin, *C. J.* 51, 837).—AgA′: flocculent pp.

Ethyl ether Et_2A''. (282°) at 720 mm. Formed from benzoyl-acetic ether, ethylene bromide, and NaOEt (Perkin, *B.* 16, 2138; *C. J.* 47, 841). Oil.

Reference.—NITRO - PHENYL - TRIMETHYLENYL KETONE CARBOXYLIC ACID.

PHENYL-METHYL-ETHYLENE-DIAMINE $NH_2.CH_2.CH_2.NPhMe$. (255°). Formed by the action of HCl on $C_6H_4{:}C_2O_2{:}N.C_2H_4.NPhMe$ (Newman, *B.* 24, 2200). Liquid, v. sol. water and alcohol.—$B'C_6H_2(NO_2)_3OH$. [173°]. Needles.

Di phenyl di-methyl-ethylene-diamine $C_2H_4(NPhMe)_2$. The methylo-bromide $B''Me_2Br_2$, got by heating di-methyl-aniline with ethylene bromide (Hübner, *A.* 224, 346), crystallises in deliquescent prisms and yields $B''Me_2(OH)_2$, $B''Me_2Cl_2$, $B''Me_2PtCl_6$, $B''Me_2Cl_2 3HgCl_2$ [174°], $B''Me_2I_2$, $B''Me_2Cr_2O_7$, and $B''Me_2(C_6H_2N_3O_7)_2$ [124°].

PHENYL-METHYL-ETHYLENE DIKETONE *v.* ACETOPHENONE-ACETONE. Its carboxylic acid is described as ACETOPHENONE-ACETO-ACETIC ACID.

DI-PHENYL-DI-METHYL-*v*-ETHYLENE-DI-PYRROLE-DI-CARBOXYLIC ACID $\begin{matrix}\mathrm{CO_2H.C{:}CMe}\\ \mathrm{HC{:}CPh}\end{matrix}>\mathrm{N.C_2H_4.N}<\begin{matrix}\mathrm{CMe{:}C.CO_2H}\\ \mathrm{CPh{:}CH}\end{matrix}$. [181°]. Obtained by saponification of its ether, which is formed by mixing acetophenone-aceto-acetic ether with ethylene-diamine (Paal a. Schneider, *B.* 19, 3158). Crystalline solid. Sl. sol. alcohol, acetic acid, and conc. HCl, insol. other ordinary solvents. On heating above 180° it evolves CO_2, giving the free base.

Di-ethyl-ether Et_2A'': [197°]; plates; distillable under ordinary pressure; sol. alcohol, benzene, chloroform, and acetic acid, insol. water and petroleum-spirit.

PHENYL-METHYL-ETHYL-OSOTRIAZOLE $\mathrm{NPh}<\begin{matrix}\mathrm{N{:}CMe}\\ \mathrm{N{:}CEt}\end{matrix}$. (270°). Formed by condensation of the oxim-phenyl-hydrazide of $CH_3.CO.CO.C_2H_5$ (Pechmann, *A.* 262, 312). Needles. Yields a di-nitro- derivative [113°]. Oxidised by alkaline $KMnO_4$ to phenyl-methyl-triazole carboxylic acid.

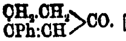
PHENYL-METHYL-ETHYL-PYRAZOLE $\mathrm{NPh}<\begin{matrix}\mathrm{N=CH}\\ \mathrm{CEt{:}CMe}\end{matrix}$. (283°). S.G. $\frac{15}{4}$ 1·0476. Got by the action of phenyl-hydrazine on $C_2H_5.CO.CHMe.CHO$ (Claisen, *B.* 22, 3276).

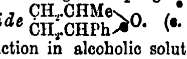
Reference.—OXY-PHENYL-METHYL-ETHYL-PYRAZOLE.

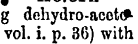
TRI-PHENYL-METHYL-ETHYL-THIO-BIURET $C_2S_2N_3Ph_3MeEt$. [157°]. Formed from di-phenyl-ethyl-thio-urea and NPhMe.CSCl (Billeter a. Strohl, *B.* 21, 108). An isomeride [156°] is formed from di-phenyl-methyl-urea and NPhEt.CSCl. Both bodies crystallise in needles, sl. sol. alcohol.

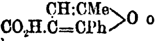
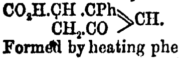
PHENYL-METHYL-ETHYL-THIO-UREA CS(NHMe).NPhEt. Got from methyl thiocarbimide and ethyl-aniline (Gebhardt, *B.* 17, 3037). Crystalline solid.

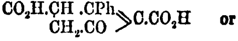
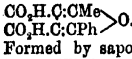
Di-phenyl-methyl-ethyl-thio-urea CS(NPhMe).NPhEt. [49·5°]. Formed from methyl-aniline and NPhEt.COCl (Billeter, *B.* 20, 1632). Monoclinic crystals.

PHENYL-METHYL-FURFURANE $C_{11}H_{10}O$, *i.e.* $\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH{:}CPh}\end{matrix}>\mathrm{O}$ or *Oxyphenyl-pentamethenyl* *hydride*  $\begin{matrix}CH_2.CH_2\\CPh{:}CH\end{matrix}\!>CO$. [40°]. (c. 238°). Formed by heating phenythronic acid, and prepared by warming acetophenone-acetone with fuming HClAq, the yield being 65 p.c. (Paal, *B.* 17, 2759; Fittig, *B.* 21, 2134; *A.* 250, 222). Needles or prisms, insol. water and alkalis, volatile with steam. Br forms $C_{11}H_9Br_5O$ [210°]. Phenyl-hydrazine forms a compound [165°-175°], crystallising from alcohol in golden spangles.

Tetrahydride  $\begin{matrix}CH_2.CHMe\\CH_2.CHPh\end{matrix}\!>O$. (c. 230°). Formed by reduction in alcoholic solution by Na. Oil, miscible with alcohol and ether.

PHENYL-METHYL-FURFURANE CARBOXYLIC ACID $C_{12}H_{10}O_3$ *i.e.*  $\begin{matrix}CO_2H.C{:}CMe\\HC{:}CPh\end{matrix}\!>O$. [181°]. Formed by boiling dehydro-acetophenone-acetoacetic ether (*cf.* vol. i. p. 36) with HClAq (Paal, *B.* 17, 2762). Needles. Boiling Ac_2O forms an acetyl derivative $C_{14}H_{12}O_4$ [83°], reconverted by NaOHAq into the parent acid.—KA'.—AgA': crystalline pp.

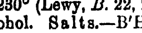
Phenyl-methyl-furfurane carboxylic acid $C_{12}H_{10}O_3$ *i.e.*  $\begin{matrix}CH{:}CMe\\CO_2H.C{=}CPh\end{matrix}\!>O$ or  $\begin{matrix}CO_2H.CH\ .CPh\\CH_2.CO\end{matrix}\!>CH$. *Phenuvic acid.* [145°]. Formed by heating phenythronic acid (Fittig, *B.* 21, 2134). Its ether is obtained from chloro-acetone and sodium benzoyl-acetic ether (Colefax, *C. J.* 59, 190). Long silky needles.—CaA'_2 2aq.—BaA_2'aq.—AgA': amorphous pp.

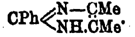
Phenyl-methyl-furfurane dicarboxylic acid $C_{13}H_{10}O_5$ *i.e.*  $\begin{matrix}CO_2H.CH\ .CPh\\CH_2.CO\end{matrix}\!>C.CO_2H$ or  $\begin{matrix}CO_2H.C{:}CMe\\CO_2H.C{:}CPh\end{matrix}\!>O$. *Phenythronic acid* [193°]. Formed by saponifying its ether with boiling baryta (Fittig, *A.* 250, 216). Silky needles, m. sol. hot water, v. sol. alcohol.—CaA'' 3aq. S. 5.—BaA'' aq.—Ag_2A'': crystalline pp.

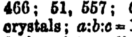
Mono-ethyl ether EtHA''. [112°]. Formed by the action of Ac_2O on a mixture of sodium succinate and benzoyl-acetic ether.—$Ca(EtA'')_2$: crystalline nodules (from alcohol).—$Ba(EtA'')_2$.—AgEtA'': white amorphous pp.

Di-ethyl ether Et_2A''. [44·5°].

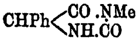
PHENYL-METHYL-GLYCOCOLL *v.* PHENYL-METHYL-AMIDO-ACETIC ACID.

PHENYL-METHYL-GLYOXALINE $C_{10}H_{10}N_2$ *i.e.*  $CMe\!<\!\begin{matrix}N-CH\\NH.CPh\end{matrix}$. [159°]. Formed by heating phenyl-methyl-oxazole with alcoholic NH_3 at 230° (Lewy, *B.* 22, 2195). Needles, v. sl. sol. alcohol. **Salts.**—B'HCl. [242°]. Needles.—$B'_2H_2PtCl_6$ 2aq. [212°]. Yellow prisms.

Phenyl-di-methyl-glyoxaline $C_{11}H_{12}N_2$ *i.e.*  $CPh\!<\!\begin{matrix}N-CMe\\NH.CMe\end{matrix}$. [230°-234°]. Formed by heating diacetyl with benzoic aldehyde and alcoholic NH_3 (Wadsworth, *C. J.* 57, 8). Needles (from benzene).—$B'_2H_2PtCl_6$: needles.

Di-phenyl-methyl-glyoxaline  $CMe\!<\!\begin{matrix}N-CPh\\NH.CPh\end{matrix}$. [235°]. Formed by the action of aldehyde and NH_3 on benzil (Japp, *C. J.* 49, 466; 51, 557; *C. J. Proc.* 3, 34). Trimetric crystals; $a{:}b{:}c = 1·207{:}1{:}1·920$. Crystallises with diphenylglyoxaline (1 mol.), the compound melting at 218°.

PHENYL-METHYL-HYDANTOIC ACID $C_6H_5.NH.CO.NH.CH(CH_3).CO_2H$ [170°]. Formed by the combination of phenyl cyanate with alanine and boiling the product with alcoholic KOH (Kühn, *B.* 17, 2884). Glistening scales.

PHENYL-METHYL-HYDANTOÏN  $CHPh\!<\!\begin{matrix}CO\ .NMe\\NH.CO\end{matrix}$ [162°]. Formed from phenyl-hydantoïn, KOMe, and MeI (Pinner, *B.* 21, 2325). Needles, sl. sol. cold alcohol.

***s*-PHENYL-METHYL-HYDRAZINE** $C_6H_5NH.NHMe$. *Hydrazo - phenyl - methyl.* Got by saponification of its dibenzoyl derivative, which is formed by heating NPhBz.NBzH with NaOMe and MeI (Tafel, *B.* 18, 1740). Obtained also by the action of alkalis on nitroso-antipyrin (Knorr, *A.* 238, 137). Oil, oxidised by HgO to PhN:NMe. Reduces Fehling's solution and ammoniacal $AgNO_3$ in the cold.—$B'_2H_2SO_4$. [180°].—**Oxalate:** white needles.

Di-benzoyl derivative PhNBz.NMeBz. [145°]. Crystals, v. sol. alcohol and ether.

u - **Phenyl - methyl - hydrazine** $NPhMe.NH_2$. (227° i.V.) at 745 mm. Formed by converting methyl-aniline into phenyl-methyl-nitrosamine, and reducing this body (5 pts.) by zinc-dust (20 pts.), HOAc (10 pts.), and water (35 pts.) at 0° (E. Fischer, *A.* 190, 152; 236, 199).

Properties.—Colourless oil, turning brown in air; m. sol. hot water, miscible with alcohol.

Reactions.—1. *Nitrous acid* yields NPhMe.NO, water, and N_2O.—2. *Diazobenzene nitrate* solution forms PhN_3 and methyl-aniline nitrate.—3. HgO added to its solution in chloroform produces NPhMe.N:N.NPhMe [137°].—4. Reacts with *aldehydes* and *ketones* in the same way as phenyl-hydrazine, forming products of condensation; thus benzoic aldehyde forms NPhMe.N:CHPh [104°] (Ebers, *A.* 227, 340), acetophenone forms NPhMe.N:CMePh [50°], acetone forms $C_{10}H_{14}N_2$ (216°) (Degen, A. 236, 152), propionic aldehyde yields $C_{10}H_{14}N_2$ (198° at 170 mm.), glucose yields $C_6H_{10}O_5{:}N.NPhMe$ [171°], while benzil yields $Ph.CO.CPh{:}N_2PhMe$ [56°] and $N_2PhMe{:}CPh.CPh{:}N_2PhMe$ [180°] (Kohlrausch, *A.* 253, 16; Fischer, *B.* 22, 87).—5. CS_2 at 100° forms $CS(NH.NPhMe)_2$ [c. 168°] (Stahel, *A.* 258, 250).—6. *Nitroso-aniline* forms $C_{13}H_{14}N_4O$ [151°], while *nitroso-dimethylaniline* gives $C_{15}H_{18}N_4O$ [141°] (O. Fischer, *B.* 22, 622).—7. With PhN:SO it forms PhNMe.N:SO [77°] crystallising from alcohol in yellow needles (Michaelis, *A.* 270, 120).

Salt.—$B'_2H_2SO_4$: plates, v. e. sol. water.

Acetyl derivative NPhMe.NHAc. [93°]. Prisms, m. sol. hot water. Converted by Na and MeI into NPhMe.NMeAc [68°], which is not decomposed by alkalis, but gives methylaniline when boiled with HClAq.

Benzoyl derivative NPhMe.NHBz. [153°]. Formed by heating NPhH.NHBz with NaOMe and MeI. Needles (Tafel, *B.* 18, 1743).

Sulphonic acid $SO_3H.C_6H_4NMe.NH_2$. Formed by heating with fuming H_2SO_4 (Pfülf, *A.* 239, 219). Plates.—NaA' aq: slender needles.

PHENYL-METHYL-IMESATIN *v.* *Anilide of Methyl* ISATIN.

DI-PHENYL METHYLIMIDO-DI-ETHYL DISULPHONE $NMe(C_2H_4.SO_2Ph)_2$. Formed by heating $NH(C_2H_4.SO_2Ph)$ with alcohol and MeI at 115° (Otto, *J. pr.* [2] 30, 335).—B'HCl [221°].

PHENYL-METHYL-INDOLE $C_{15}H_{13}N$ *i.e.* $C_6H_4{<}\substack{CH\\NMe}{>}CPh$. [101°]. Formed by heating the phenyl-hydrazide of acetophenone with $ZnCl_2$ at 130° (Fischer, *B.* 19, 1565; Degen, *A.* 236, 155). Formed also by heating $CH_2Bz.NMePh$ with $ZnCl_2$ at 180° (Staedel, *B.* 21, 2196; Culmann, *B.* 21, 2596), and by heating the isomeric $C_6H_4{<}\substack{CPh\\NMe}{>}CH$ with $ZnCl_2$ at 220° (Ince, *A.* 253, 40). Needles (from alcohol). Colours pine-wood, moistened with HCl, dark-red.

Acetyl derivative $C_6H_4{<}\substack{CAc\\NMe}{>}CPh$. [136°]. Formed by heating $CH_2Ac.CPh{:}N.NMePh$ with $ZnCl_2$ at 150°. Needles (from dilute HOAc).

Phenyl-methyl-indole $C_6H_4{<}\substack{CPh\\NMe}{>}CH$. [65°]. Formed from phenyl-acetic aldehyde and phenyl-methyl-hydrazine (Ince, *A.* 253, 38). Crystals, v. sol. benzene. Colours acidified pine-wood reddish-violet.—$B'C_6H_3N_3O_7$. [90].

Phenyl-methyl-indole $C_6H_4{<}\substack{CPh\\NH}{>}CMe$. [60°]. Formed by heating the phenyl-hydrazide of benzyl methyl ketone with $ZnCl_2$ (Trenkler, *A.* 248, 110). Prisms (from ligroïn).—**Picrate**: [142°]; v. sol. benzene.

PHENYL METHYL KETONE *v.* ACETOPHENONE.

Phenyl methyl diketone $C_6H_5.CO.CO.CH_3$. *Acetyl-benzoyl.* (217°). S.G. $\frac{14}{4}$ 1·1041. S. ·26 at 20°. Formed by distilling its oxim Bz.C(NOH)Me with dilute H_2SO_4 (Von Pechmann, *B.* 21, 2119; 22, 2129) or with isoamyl nitrite (Manasse, *B.* 21, 2177). Heavy oil, volatile with steam.

Oxim $C_6H_5.CO.C(NOH).CH_3$. *Nitroso-propiophenone.* [114°]. Formed by the action of isoamyl nitrite and HCl or NaOEt on the ketone (Claisen a. Manasse, *B.* 22, 529). Prepared by the action of nitrous acid on benzoyl-propionic ether (1 mol.) and KOHAq (3 mols.) (P.; Gudeman, *B.* 22, 562). Needles (from hot water), forming a deep-yellow solution in alkalis. $SnCl_2$ and HCl yield hydroxylamine and phenyl methyl diketone. Reduced by sodium-amalgam to a base which crystallises from alcohol in needles [108°].

Di-oxim Ph.C(NOH).C(NOH).Me. [236°]. Formed from the mono-oxim and hydroxylamine hydrochloride. Needles (from dilute alcohol).

Phenyl hydrazide $C_{15}H_{14}N_2O$. [145°]

Di-phenyl-di-hydrazide $CMe(N_2HPh).CPh(N_2HPh)$. [105°]. Yellow crystals, v. sol. ether.

Oxim-phenyl-hydrazide $CPh(N_2HPh).CMe{:}NOH$. [202°]. White needles.

Phenyl methyl triketone. *Mono-oxim* $C_6H_5.CO.C(NOH).CO.CH_3$. [124°]. Formed by the action of nitrous acid on phenyl methylene methyl diketone (Ceresole, *B.* 17, 814). Needles, v. sol. benzene, sol. alkalis.

Di-oxim $C_6H_5.C(NOH).C(NOH).CO.CH_3$. [178°]. Formed by heating the mono- oxim with hydroxylamine hydrochloride. Needles, insol. cold water, sol. alkalis.

PHENYL-METHYL-KETONE CARBOXYLIC ACID *v.* BENZOYL-ACETIC ACID and ACETOPHENONE CARBOXYLIC ACID.

PHENYL-METHYL-MALONIC ACID *v.* BENZYL-MALONIC ACID.

Tri-phenyl-methyl-malonic ether $CPh_3.CH(CO_2Et)_2$. [133·5°]. Formed from CPh_3Br and sodium malonic ether (Henderson, *B.* 20, 1014; *C. J. Proc.* 2, 251). Needles (from alcohol). Yields tri-phenyl-propionic acid when heated with alcoholic potash.—NaA′aq: needles.—BaA'_2aq.—AgA′: minute white crystals.

PHENYL - DI - METHYL - NAPHTHALENE TETRAHYDRIDE *v.* METHRONOL.

PHENYL - METHYL - (β)-NAPHTHOTRIAZINE DIHYDRIDE $C_{18}H_{15}N_3$ *i.e.* $C_{10}H_6{<}\substack{N.CHMe\\N.NPh}$. Formed by adding aldehyde to a mixture of benzene-azo-(β)-naphthylamine and alcohol (Goldschmidt a. Poltzer, *B.* 24, 1004). Plates, v. sol. hot alcohol.—B′HCl. [252°].—$B'_2H_2PtCl_6$. Yellow needles.—B′MeI. [244°].—$B'_2Me_2PtCl_6$. [260°]. Yellow needles.

PHENYL - METHYL - (β)-NAPHTHYL-THIO-UREA $C_{18}H_{16}N_2S$ *i.e.* $NPhMe.CS.NHC_{10}H_7$. [127°]. Formed from (β)-naphthyl thiocarbimide and methyl-aniline (Gebhardt, *B.* 17, 2091). Yellow needles.

PHENYL - METHYL - NITROSAMINE *v.* *Nitrosamine* of METHYL-ANILINE, vol. iii. p. 285.

PHENYL-METHYL-OSOTRIAZOLE $NPh{<}\substack{N{:}CH\\N{:}CMe}$. (242°). S.G. $\frac{17}{4}$ 1·1071. Formed by oxidising the diphenyl-hydrazide of pyruvic aldehyde and warming the resulting $\substack{NPh.N{:}CH\\NPh.N{:}CMe}$. Formed also by the action of NaOH on $CH_3.C(N_2HPh).CH{:}NOAc$ (Pechmann, *B.* 21, 2751; *A.* 262, 279). Oil. Yields a tri-nitro- derivative [138°], and a sulphonic acid, of which the Na salt crystallises in hexagonal plates.

Phenyl-di-methyl-osotriazole $NPh{<}\substack{N{:}CMe\\N{:}CMe}$. [35°]. (354°). Formed by heating the phenyl-hydrazide-oxim of diacetyl with Ac_2O (P.). Crystalline, insol. water, sol. conc. HClAq, but reppd. by water. Yields a di-nitro- derivative [139°] and a tri-nitro- derivative [227°].

PHENYL-METHYL-OSOTRIAZOLE CARBOXYLIC ACID $NPh{<}\substack{N{:}CMe\\N{:}C.CO_2H}$. [198°]. Formed by oxidising phenyl-di-methyl-osotriazole with $KMnO_4$ (Pechmann, *A.* 262, 308). Needles, v. sl. sol. water.—AgA′: white pp.

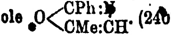
PHENYL-METHYL-OXAMIDE $C_9H_{10}N_2O_2$ *i.e.* $NHPh.C_2O_2.NHMe$. [180°]. Formed from $NHMe.C_2O_2.OEt$ and aniline (Wallach, *A.* 184, 70). Needles.

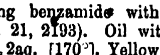
PHENYL-METHYL-OXANTHRANOL $C_{21}H_{16}O_2$ *i.e.* $C_6H_3Me{<}\substack{CPh(OH)\\CO}{>}C_6H_4$. [195°]. Formed by oxidation of phenyl-methyl-anthranol with $K_2Cr_2O_7$ and HOAc (Hemilian, *B.* 16, 2360). Trimetric tables, v. sol. hot alcohol, insol. alkalis. Conc. H_2SO_4 forms a purple solution.

Isomeride $\left[1{:}\substack{4\\5}\right]C_6H_3Me{<}\substack{CPh(OH)\\CO}{>}C_6H_4$. [213°]. Formed by oxidising di-phenyl-tolyl-methane *o*-carboxylic acid with K_2CrO_4 and conc. H_2SO_4 (Hemilian, *B.* 19, 3064). Prisms, insol. alkalis. Reduced by zinc-dust to a phenyl-methyl-anthranol.

PHENYL-METHYL-OXAZOLE $C_{10}H_9NO$ *i.e.*

$O<\begin{matrix}CPh:CH\\CMe:N\end{matrix}$. [45°]. (242°). Formed by heating acetamide with bromo-acetophenone at 125° (Blümlein, *B.* 17, 2579; Lewy, *B.* 20, 2576; 21, 924). Needles (from alcohol). Yields benzoic acid on oxidation. Na and alcohol form an oily tetrahydride $C_{10}H_{13}NO$ (251°), which yields crystalline $C_{10}H_{12}BzNO$ [140°]. HI and P give oily $C_{10}H_{18}$ (c. 275°). Conc. nitric acid forms $C_{10}H_8(NO_2)NO$ [157°], which may be reduced to $C_{10}H_8(NH_2)NO$ [115°]. Hydroxylamine, phenylhydrazine, and hot zinc-dust have no action.—$B'HCl$.—$B'_2H_2PtCl_6$ 2aq.—$B'C_6H_3N_3O_7$. [134°].

Phenyl-methyl-oxazole

$O<\begin{matrix}CPh:N\\CMe:CH\end{matrix}$. (240°). Formed by boiling benzamide with chloroacetone (Lewy, *B.* 21, 2193). Oil with fruity odour.—$B'_2H_2PtCl_6$ 2aq. [170°]. Yellow needles.

Dihydride

$O<\begin{matrix}CPh{=}N\\CHMe.CH_2\end{matrix}$. (244°). Formed by the action of KOH on bromo-propyl-benzamide in hot aqueous or alcoholic solution, the product being distilled with steam (Gabriel a. Heymann, *B.* 23, 2499). Liquid. Partly converted, by evaporation with excess of HClAq (or HBrAq), into β-chloro- (or bromo-) propyl-benzamide [78°] (or [73°]). Boiling with an equivalent of HClAq yields β-amido-propyl benzoate. —$B'_2H_2PtCl_6$.—$B'_2H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$.[167°].

PHENYL-TRI-METHYL-PHENYL-CARBINOL $C_{16}H_{18}O$ *i.e.* $CHPh(OH).C_6H_2Me_3$. *Phenyl-mesitylene carbinol.* [34°]. (330°). Formed by reducing benzoyl-mesitylene with sodium-amalgam (Louise, *Bl.* [2] 45, 231; *A. Ch.* [6] 6, 209). Prisms. Boiling diluted H_2SO_4 (1:1) converts it into $(C_{16}H_{17})_2O$ [137°].

Ethyl ether $C_{16}H_{17}EtO$. [32°]. Prisms.

Acetyl derivative $C_{16}H_{17}AcO$. [52°].

Benzoyl derivative. [94°]. Crystals.

DIPHENYL TRIMETHYLPHENYLENE DIKETONE $(C_6H_5.CO)_2C_6HMe_3$. [117°]. Formed by heating $C_6H_5.CO.C_6H_2Me_3$ with BzCl and $AlCl_3$ (Louise, *C. R.* 98, 151; *A. Ch.* [6] 6, 236). Prisms, sol. alcohol and ether.

Di-phenyl tetramethylphenylene diketone $C_6Me_4(CO.C_6H_5)_2$. [270°]. A product of the action of BzCl and $AlCl_3$ on durene (Friedel a. Crafts, *C. R.* 88, 880). Minute prisms, sol. benzene, almost insol. boiling alcohol.

PHENYL METHYLPHENYL KETONE *v.* PHENYL TOLYL KETONE.

Phenyl dimethylphenyl ketone *v.* PHENYL XYLYL KETONE.

Phenyl trimethylphenyl ketone $C_6H_5.CO.C_6H_2Me_3$[1:2:4:6]. *Benzoyl-mesitylene. Phenyl mesityl ketone.* [35°]. (319°). V.D. 8·18. Formed from BzCl, mesitylene, CS_2, and $AlCl_3$ (Elbs, *J. pr.* [2] 35, 485; *cf.* Louise, *A. Ch.* [6] 6, 200; *C. R.* 96, 499; Claus, *B.* 19, 2879). Prisms (from alcohol), sol. acetone and ligroïn. Does not react with hydroxylamine (Smith, *B.* 24, 4052).

Reactions.—1. Conc. H_2SO_4 or $H_2S_2O_7$ at 100° gives benzoic acid and mesitylene sulphonic acid.—2. Conc. H_2SO_4 at 50° forms phenyl-mesityl-ketone sulphonic acid $C_{16}H_{15}O.SO_3H$.—3. A mixture of fuming HNO_3 and $H_2S_2O_7$ forms two trinitro-derivatives [188°] and [145°]. 4. HNO_3 (S.G. 1·1) at 200° forms benzoyl-uvitic or phenyl-tolyl-ketone dicarboxylic acid.—5. *Potash-fusion* gives mesitylene and KOBz.—6. HI reduces it to benzyl-mesitylene.—7. *Sodium-amalgam* yields the carbinol.—8. *Chromic acid* oxidises it to $C_6H_5.CO.C_6H_2Me_2.CO_2H$.

Phenyl tetra-methyl-phenyl ketone $C_6H_5.CO.C_6HMe_4$. [119°]. (343°). Formed by heating durene with BzCl and $AlCl_3$ at 120° (Friedel, Crafts, a. Ador, *C. R.* 88, 980). Crystalline. Decomposed by potash-fusion into benzoic acid and durene. Reduced by HIAq and P at 240° to $CH_2Ph.C_6HMe_4$ [60·5°], (310°).

Isomeride $C_6H_5.CO.C_6HMe_4$. [63°]. (300°). *Formed from BzCl and isodurene (got from* toluene, MeCl, and $AlCl_3$). Crystals (Essner a. Gossin, *Bl.* [2] 42, 171).

PHENYL TRIMETHYLPHENYL KETONE *o*-CARBOXYLIC ACID $C_6H_2Me_3.CO.C_6H_4.CO_2H$. [212°]. Formed from phthalic anhydride, mesitylene, and $AlCl_3$ (F. Meyer a. Gresly, *B.* 15, 639; *A.* 234, 234). Needles (from alcohol).

Phenyl tetramethylphenyl ketone carboxylic acid *v.* TETRA-METHYL-BENZOYL-BENZOIC ACID.

PHENYL-TRIMETHYLPHENYL-THIO-UREA $NHPh.CS.NHC_6H_2Me_3$. [193°]. Formed by heating methyl-thiocarbimide with an alcoholic solution of aniline (Eisenberg, *B.* 15, 1014).

PHENYL-DI-METHYL-PHOSPHINE PMe_2Ph. (192° cor.). S.G. $\frac{11}{}$ ·977. Formed from PCl_2Ph and $ZnMe_2$ in benzene (Michaelis, *A.* 181, 359). Liquid, oxidised by air. Combines with CS_2 forming PMe_2PhCS_2 crystallising in red plates and yielding $B'_2H_2PtCl_6$ (Czimatis, *B.* 15, 2017).

Salts.—$B'HCl$: crystalline, sl. sol. ether, v. e. sol. alcohol.—$B'2HCl$. Liquid.—$B'_2H_2PtCl_6$.

Methylo-iodide PMe_3PhI. [205°].

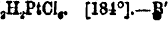
Bromo-ethylo-bromide $PMe_2Ph(C_2H_4Br)Br$. [173°]. Formed from PMe_2Ph and $C_2H_4Br_2$ (Gleichmann, *B.* 15, 199). Yields $(B'(C_2H_4Br)Br)_2PtCl_4$ and the unstable $B'C_2H_4Br_2$. An alcoholic solution of phenyl-di-methyl-phosphine forms $(PMe_2Ph)_2C_2H_4Br_2$ [above 300°], S. (alcohol) 2 at 21°, which gives unstable $(PMe_2Ph)_2C_2H_4Br_6$ [171°].

Di-phenyl-methyl-phosphine $PMePh_2$. (284°). S.G. $\frac{15}{}$ 1·08. Formed from $PClPh_2$ and $ZnMe_2$ (Michaelis a. Link, *A.* 207, 210). Liquid. Yields PMe_2Ph_2I [241°], $(PMe_2Ph_2)_2PtCl_6$ [218°], and $PMePh_2O$ [112°] (Michaelis a. La Coste, *B.* 18, 2116; *A.* 229, 316).

PHENYL-DI-METHYL-PHOSPHINE *p*-CARBOXYLIC ACID $C_6H_4(CO_2H).PMe_2$. The methylo-chloride $C_6H_4(CO_2H).PMe_3Cl$, formed by oxidation of the methylo-chloride of *p*-tolyl-di-methyl-phosphine, crystallises in prisms (Michaelis, *B.* 15, 2018). It yields the compounds $B'Me_2PtCl_6$, $C_6H_4(CO_2H).PMe_3OH$ 2aq, and $C_6H_4(CO_2H)PMe_3.SO_4H$.

Oxide $C_6H_4(CO_2H).POMe_2$. [243°]. Formed by oxidation of the ethyleno-bromide of tolyl-di-methyl-phosphine. Colourless prisms.

PHENYL METHYL PROPYLENE DIKETONE $C_6H_5.CO.CHEt.CO.CH_3$. (265°–270°). Formed from benzoyl-acetone, Na, and EtI (Claisen a. Lowman, *B.* 21, 1152). Liquid.

PHENYL-METHYL-PROPYLENE-ψ-THIO-UREA

$\begin{matrix}CHMe.S\\CH_2{-}N\end{matrix}{>}CNPhMe$. (c. 300°). Formed by heating methyl-aniline with allyl thiocarbimide and HClAq at 100° (Prager, *B.* 22, 2996). —$B'_2H_2PtCl_6$. [184°].—$B'C_6H_3N_3O_7$. [125°].

TRI-PHENYL-METHYL-PROPYL-DI-THIO-BIURET $C_2S_2N_3Ph_3MePr$. [110°]. Formed from NPhMeCSCl and di-phenyl-propyl-thio-urea (Billeter a. Strohl, *B.* 21, 109). Small yellow pyramids. An isomeride [111°] is formed from NPhPr.CSCl and di-phenyl-methyl-thio-urea.

DI-PHENYL-METHYL-PROPYL-THIO-UREA NPhMe.CS.NPhPr. [56°]. Formed from $CSCl_2$, propyl-aniline, and MeCl or from $CSCl_2$, methyl-aniline, and PrCl (Billeter a. Strohl, *B.* 21, 103). Colourless prisms.

DI-PHENYL-DI-METHYL-PYRAZINE $CMe<\begin{smallmatrix}N:CPh\\CPh.N\end{smallmatrix}>CMe$. [124°]. Formed when phenyl amido-ethyl ketone is allowed to stand with NH_3Aq (Schmidt, *B.* 22, 3253).—B'HCl: needles.—$B'_2H_2PtCl_6$.

Di-phenyl-methyl-pyrazine dihydride $N<\begin{smallmatrix}CPh.CPh\\CH_2.CHMe\end{smallmatrix}>N$. [112°]. Formed from benzil and propylene-diamine (Strache, *B.* 21, 2363). Needles, v. sol. benzene; m. sol. alcohol.

Di-phenyl-tetra-methyl-pyrazine dihydride $C_{20}H_{22}N_2$ *i.e.* $NPh<\begin{smallmatrix}CMe:CMe\\CMe:CMe\end{smallmatrix}>NPh$. [108°]. (281°). Formed by heating β-bromo-β-acetyl-propionic acid (1 pt.) with aniline (3 pts.) at 95°; the yield being 70 p.c. of the theoretical amount (Wolff, *B.* 20, 429). Satiny plates, v. sol. ether and conc. HClAq.

References.—NITRO- and OXY-DI-PHENYL-METHYL-PYRAZINE.

PHENYL-METHYL-PYRAZOLE $NPh<\begin{smallmatrix}N=CMe\\CH:CH\end{smallmatrix}$. [37°]. (255°). S.G. ^{15} 1·085.

Formation.—1. By heating oxy-phenyl-methyl-pyrazole $NPh<\begin{smallmatrix}N=CMe\\CO.CH_2\end{smallmatrix}$ with zinc-dust (Knorr, *A.* 238, 199).—2. From acetoacetic aldehyde, phenyl-hydrazine, and HOAc (Claisen, *B.* 21, 1147; 24, 1888).—3. By heating its carboxylic acid at 210° (Ach, *A.* 253, 55).—4. From oxy-phenyl-methyl-pyrazole dihydride and P_2S_5 (Knorr a. Duden, *B.* 25, 766).

Properties.—Needles, v. sol. alcohol and ether; volatile with steam. Oxidised by $KMnO_4$ to phenyl-pyrazole carboxylic acids [146°].

Salt.—$B'H_2PtCl_6$: orange needles.

Dihydride $NPh<\begin{smallmatrix}N=CMe\\CH_2.CH_2\end{smallmatrix}$. [75°]. Formed by reducing the base in alcoholic solution with Na. Flat needles, m. sol. alcohol.

Phenyl-methyl-pyrazole $NPh<\begin{smallmatrix}N - CH\\CMe:CH\end{smallmatrix}$. (262°). Formed by distilling its dicarboxylic acid (Knorr a. Laubmann, *B.* 22, 178). Got also from acetone, oxalic acid, and phenyl-hydrazine (Claisen a. Roosen, *B.* 24, 1890). Yields phenyl-pyrazole carboxylic acid [183°] on oxidation by $KMnO_4$.—$B'_2H_2PtCl_6$ 2aq. [147°].

Phenyl-di-methyl-pyrazole $NPh<\begin{smallmatrix}N=CMe\\CMe:CH\end{smallmatrix}$. (273° i.V.). Formed by heating its carboxylic acid (Knorr, *B.* 20, 1103) and by warming acetyl-acetone with phenyl-hydrazine (K.; Combes, *Bl.* [2] 50, 145). Oil, volatile with steam.—$B'_2H_2PtCl_6$ 4aq. Decomposes at 186°.

Methylo-iodide B'MeI. [190°]. Crystals, v. sol. water.—$B'_2Me_2PtCl_6$. Decomposes at 220°.

Dihydride $NPh<\begin{smallmatrix}N=CMe\\CHMe.CH_2\end{smallmatrix}$. (290° i.V.). Formed by adding Na to a boiling alcoholic solution of the base.

Phenyl-tri-methyl-pyrazole. *Dihydride* $NPh<\begin{smallmatrix}N=CMe\\CMe_2.CH_2\end{smallmatrix}$. Formed by heating mesityl oxide with phenyl-hydrazine (Fischer a. Knoevenagel, *A.* 239, 203). Oil, v. e. sol. ether and alcohol, sl. sol. water. Its solution in dilute HCl gives a violet colour with $K_2Cr_2O_7$.—$B'_2H_2PtCl_6$: crystalline pp.

Di-phenyl-methyl-pyrazole $C_{16}H_{14}N_2$ *i.e.* $NPh<\begin{smallmatrix}N - CPh\\CMe:CH\end{smallmatrix}$. [63°]. (335° or 355°). Formed by heating its carboxylic acid at 250°, and also by warming benzoyl-acetone with phenyl-hydrazine (Knorr, *B.* 18, 314; Fischer, *B.* 18, 2185). Insol. water, v. sol. alcohol. Weak base. Yields $C_{16}H_{13}BrO_2$ [75°]. — $B'_2H_2PtCl_6$ aq. — B'MeI. [187°].—$B'_2Me_2PtCl_6$. [241°]. Orange-red needles.

Dihydride $C_{16}H_{16}N_2$. [109°]. Long prisms (from ether). Its acid solution is coloured intensely red by nitrous acid.

Di-phenyl-methyl-pyrazole $C_{16}H_{14}N_2$ *i.e.* $NPh<\begin{smallmatrix}N\ CH\\CPh:CMe\end{smallmatrix}$. [47°]. (365°). Formed by heating its carboxylic acid, and also, together with its dihydride, by distilling the phenyl-hydrazide of benzylidene-acetone (Knorr, *B.* 18, 931; 20, 1100). Weak base.—$B'_2H_2PtCl_6$: red prisms.—B'MeI. [192°].—$B'_2Me_2PtCl_6$. [229°].

Dihydride $C_{16}H_{16}N_2$. [114°]. (c. 350°). Prisms. Its solutions fluoresce blue and give a blue colour with nitrous acid.

Tri-phenyl-methyl-pyrazole. *Tetrahydride* $NPh<\begin{smallmatrix}NMe\ .CHPh\\CHPh.CH_2\end{smallmatrix}$. [110°]. Formed by the action of Na and boiling alcohol on tri-phenyl-pyrazole methylo-iodide (Knorr a. Laubmann, *B.* 21, 1205). Insol. water, v. sol. alcohol. Resinified by conc. HNO_3.

References.—OXY-AMIDO- and OXY-PHENYL-METHYL-PYRAZOLE.

PHENYL-METHYL-PYRAZOLE CARBOXYLIC ACID $NPh<\begin{smallmatrix}N=C.CO_2H\\CMe:CH\end{smallmatrix}$. [106°]. Formed from acetone, oxalic acid, and phenyl hydrazine (Claisen a. Roosen, *B.* 24, 1891).

Methyl ether MeA'. (256° at 109 mm.).

Amide. [146°].

Phenyl-methyl-pyrazole carboxylic acid $NPh<\begin{smallmatrix}N=CMe\\C(CO_2H):CH\end{smallmatrix}$. [166°]. Formed by heating $NPh<\begin{smallmatrix}N\ :CMe\\CO.C(OH)\end{smallmatrix}>CH$ with HClAq at 170° (Ach, *A.* 253, 54). Needles, sol. hot alcohol.

Phenyl-methyl-pyrazole dicarboxylic acid $C_{12}H_{10}N_2O_4$ *i.e.* $NPh<\begin{smallmatrix}N - C.CO_2H\\CMe:C.CO_2H\end{smallmatrix}$. [198°]. Formed by oxidising phenyl-di-methyl-pyrazole carboxylic acid with alkaline $KMnO_4$ (Knorr a. Laubmann, *B.* 22, 177). Needles (from water).

Phenyl-di-methyl-pyrazole carboxylic acid $NPh<\begin{smallmatrix}N=CMe\\CMe:C.CO_2H\end{smallmatrix}$. [197°]. Got by saponifying its ether, which is obtained from ethylidene-acetoacetic ether and phenyl-hydrazine (Knorr, *B.* 20, 1102). Needles, v. sl. sol. water.—KA'.

Ethyl ether EtA'. [68°]. (286° at 260 mm.).

Di-phenyl-methyl-pyrazole carboxylic acid $C_{17}H_{14}N_2O_2$ *i.e.* $NPh<\begin{matrix}N\text{—}CPh\\CMe:C.CO_2H\end{matrix}$ [205°]. Got from its ether, which is obtained by the action of phenyl-hydrazine on benzoyl-aceto-acetic ether (Knorr a. Blank, *B.* 18, 311). Sol. alkalis and conc. HClAq, insol. water.

Ethyl ether EtA'. [122°].

Di-phenyl-methyl-pyrazole carboxylic acid $NPh<\begin{matrix}N{=}C.CO_2H\\CPh:CMe\end{matrix}$. [194°]. Formed from its ether, which is got by mixing benzylidene-aceto-acetic ether with phenyl-hydrazine (Knorr a. Blank, *B.* 18, 931). Crystalline, v. sol. alkalis and acids.

Ethyl ether EtA'. [110°].

References.—Nitro- and Oxy-phenyl-methyl-pyrazole carboxylic acid.

PHENYL-DI-METHYL-PYRIDAZINE. *Dihydride* $NPh<\begin{matrix}NH\ .CMe\\CMe:CH\end{matrix}>CH$. [82°]. (176° at 730 mm.). Formed by heating the dicarboxylic acid at 220° (Knorr, *B.* 18, 304, 1568). Volatile with steam. Insol. water and alkalis, sol. conc. HClAq. Colours pinewood, dipped in HClAq, red. H_2SO_4 added to its solution in HOAc containing phenanthraquinone gives a deep-red colour.

Dicarboxylic acid of the dihydride $C_{14}H_{14}N_2O_4$. Obtained from its ether, which is formed by mixing acetic acid solutions of di-acetyl-succinic ether and phenyl-hydrazine. Needles (from HOAc).—BaA''.

Ethyl ether Et_2A''. [127°]. Prisms.

Reference.—Oxy-phenyl-methyl-pyridazine.

PHENYL-DI-METHYL-PYRIDINE $N\lessdot\begin{matrix}CMe:CH\\CMe.CH\end{matrix}\gtrdot CPh$. [55°]. (287°) at 731 mm. Formed by distilling its dicarboxylic acid with lime (Bally, *B.* 20, 2591). Prisms (from ether). —B'HCl 3aq : needles.—$B'_2H_2PtCl_6$ 4aq : needles. — $B'HNO_3$. [177°]. Needles. — $B'H_2Cr_2O_7$. Needles.—$B'C_6H_3N_3O_7$. [222°]. Needles.

Methylo-iodide B'MeI. Granules, sl. sol. water.—$B'_2Me_2PtCl_6$. [250°].

Hexahydride $C_5NH_8Me_2Ph$. (274°) at 731 mm. Got by adding Na to an alcoholic solution of phenyl-di-methyl-pyridine. Liquid. Does not give a pp. with picric acid.—B'HCl.—$B'HNO_3$. [210°].—$B'_2H_2PtCl_6$. [237°]. Plates.

References.—Nitro- and Oxy-phenyl-di-methyl-pyridine.

PHENYL-METHYL-PYRIDINE DICARBOXYLIC ACID $C_{14}H_{11}NO_4$ *i.e.* $CO_2H.C_6H_4.C\lessdot\begin{matrix}CH.CH\ :CMe\\C(CO_2H):N\end{matrix}$. [201°]. Formed by oxidising methyl-(β)-naphthoquinoline by $KMnO_4$ in acid solution (F. Seitz, *B.* 22, 257). Needles (containing aq) or anhydrous prisms. $FeSO_4$ colours its aqueous solution lemon-yellow. — Na_2A'' 2aq. — ZnA'' 1½aq. — CuA'' 1½aq : minute bluish-green plates.

Phenyl-di-methyl-pyridine carboxylic acid $N\lessdot\begin{matrix}CMe:C(CO_2H)\\CMe\text{——}CH\end{matrix}\gtrdot CPh$. [190°]. Got from its ether, which is formed by heating the mono-ethyl ether of the dicarboxylic acid (Hantzsch, *B.* 17, 2911). Small prisms (containing 2aq), v. sol. hot water.—CuA'_2.—$(HA')_2H_2PtCl_6$ aq.

Ethyl ether EtA'. (316°-320°). Thick liquid. Yields $(EtA')_2H_2PtCl_6$ [196°] and also EtA'MeI [c. 206°], which is converted by alcoholic potash into $C_{15}H_{15}NO_2$ [161°], split up by HClAq at 180° into acetic acid and oxy-phenyl-di-methyl-pyridine [112°].

Phenyl-di-methyl-pyridine dicarboxylic acid $N\lessdot\begin{matrix}CMe:C(CO_2H)\\CMe.C(CO_2H)\end{matrix}\gtrdot CPh$.

Mono-ethyl ether HEtA''. [180°]. Formed by boiling the di-ethyl ether with alcoholic KOH (1 mol.) (H.). Cubes (from alcohol).

Di-ethyl ether Et_2A''. [67°]. Formed by oxidising its dihydride with nitrous acid.

Dihydride of the di-ethyl ether $N\lessdot\begin{matrix}CHMe.CH(CO_2Et)\\CMe\text{——}C(CO_2Et)\end{matrix}\gtrdot CPh$. [157°]. Formed by heating a mixture of benzoic aldehyde, aceto-acetic ether, and alcoholic NH_3 (Schiff a. Puliti, *B.* 16, 1607; Bally, *B.* 20, 2591). Formed also by mixing benzylidene-acetoacetic ether with β-imido-butyric ether (Beyer, *B.* 24, 1666). Colourless crystals, sol. alcohol.

(β)-Phenyl-di-methyl-pyridine dicarboxylic acid $[1:2]CO_2H.C_6H_4.C\lessdot\begin{matrix}CMe\ :\ CH\\C(CO_2H).N\end{matrix}\gtrdot CMe$. Formed by oxidising di-methyl-(β)-naphthoquinoline with $KMnO_4$ (Reed, *J. pr.* [2] 35, 311). Syrup.—AgA'.

Reference.—Oxy-phenyl-di-methyl-pyridine carboxylic acid.

PHENYLTRI-METHYL-PYRIDYL KETONE CARBOXYLIC ETHER $N\lessdot\begin{matrix}CMe.C(CO_2Et)\\CMe:C(CO.Ph)\end{matrix}\gtrdot CMe$. Formed by the action of nitrous acid on its dihydride.—$B'HNO_3$: white plates.—B'HCl. [192°]. Prisms.—$B'_2H_2PtCl_6$: needles.

Dihydride $NH<\begin{matrix}CMe:C(CO_2Et)\\CMe:C(CO.Ph)\end{matrix}>CHMe$. [187°]. Formed from ethylidene-acetoacetic ether and $C_6H_5.CO.CH_2.C(NH).CH_3$ (Beyer, *B.* 24, 1667). Yellowish plates.

Methyl derivative of the dihydride $NMe<\begin{matrix}CMe:C(CO_2Et)\\CMe:C(CO.Ph)\end{matrix}>CHMe$. [87°]. Formed, in like manner, by the action of the methylimide of benzoyl-acetone on ethylidene-acetoacetic ether (B.). Yellowish-white needles.

PHENYL-METHYL-PYRIMIDINE $C_{11}H_{10}N_2$ *i.e.* $CPh\lessdot\begin{matrix}N.CMe\\N:CH\end{matrix}>CH$. [74°-78°]. Formed by distilling the oxy-derivative (from benzamidine and acetoacetic ether) with zinc-dust (Pinner, *B.* 18, 2850). Colourless needles.—$B'_2H_2Cl_2PtCl_4$. [190°].

References.—Oxy- and Oxy-amido-phenyl-methyl pyrimidine.

PHENYL-METHYL-PYRROLE $C_{11}H_{11}N$ *i.e.* $NH<\begin{matrix}CMe:CH\\CPh:CH\end{matrix}$. [101°]. Got by heating acetophenone-acetone $CH_2Bz.CH_2Ac$ with alcoholic NH_3 at 150°; the yield being 70 p.c. of the theoretical (Paal, *B.* 18, 367). Plates, v. sol. alcohol. May be sublimed. Gives a purple-red colour with isatin and H_2SO_4.

Phenyl-di-methyl-pyrrole $C_{12}H_{13}N$ *i.e.* $NPh<\begin{matrix}CMe:CH\\CMe.CH\end{matrix}$. [52°]. (252°). Formed by distilling its dicarboxylic acid at 244° (Knorr, *A.* 236, 306).

DI-PHENYL-METHYL-PYRROLE $C_{17}H_{15}N$ i.e. $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CPh:CH}\\ \mathrm{CMe:CH}\end{array}$. [84°]. Formed by heating the carboxylic acid [226°] to above its melting-point (Lederer a. Paal, *B.* 18, 2596). Large tables.

Tetra-phenyl-methyl-pyrrole $\mathrm{NMe}{<}\begin{array}{l}\mathrm{CPh:CPh}\\ \mathrm{CPh:CPh}\end{array}$. [214°]. Formed by heating bidesyl $C_{28}H_{22}O_2$ [255°] with aqueous methylamine at 150° (Fehrlin, *B.* 22, 554). Groups of minute needles, sol. hot alcohol and ether.

Reference.—Oxy - tri - phenyl - methyl - pyrrole.

PHENYL-METHYL-PYRROLE CARBOXYLIC ACID $\mathrm{NH}{<}\begin{array}{l}\mathrm{CMe:C.CO_2H}\\ \mathrm{CPh:CH}\end{array}$. [c. 190°]. Got by saponification of its ether, which is formed by allowing acetophenone-acetoacetic ether to stand with excess of NH_3Aq (Lederer a. Paal, *B.* 18, 2593). Flat needles (from HOAc).

Ethyl ether EtA'. [120°]. Needles.

Phenyl-di-methyl-pyrrole carboxylic ether $C_{15}H_{17}NO_2$ *i.e.* $\mathrm{NMe}{<}\begin{array}{l}\mathrm{CMe:C.CO_2Et}\\ \mathrm{CPh:CH}\end{array}$. [112°]. Formed from acetophenone acetoacetic ether and $NMeH_2Aq$ (L. a. P.). Plates (from alcohol-ether), v. e. sol. alcohol.

Phenyl-di-methyl-pyrrole ***m*****-carboxylic acid** $\mathrm{CO_2H.C_6H_4.N}{<}\begin{array}{l}\mathrm{CMe:CH}\\ \mathrm{CMe:CH}\end{array}$. [135°]. Formed by heating acetonyl-acetone with *m*-amido-benzoic acid and alcohol (Paal, *B.* 19, 558). Flat crystals, sl. sol. water, v. sol. alcohol.

Phenyl-di-methyl-pyrrole di-carboxylic acid $\mathrm{CO_2H.CH_2.N}{<}\begin{array}{l}\mathrm{CMe:C.CO_2H}\\ \mathrm{CPh:CH}\end{array}$. [152°]. Got by saponifying its ether. Small needles (from alcohol), sl. sol. water.

Ethyl ether Et_2A''. [131°]. Got by allowing acetophenone-acetoacetic ether to stand with glycocoll and HOAc (Paal a. Schneider, *B.* 19, 3160). Needles (from HOAc), sl. sol. water.

Phenyl-di-methyl-pyrrole dicarboxylic acid $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CMe:C.CO_2H}\\ \mathrm{CMe:C.CO_2H}\end{array}$. Got from its ether. Powder, decomposing at 224° into CO_2 and phenyl-di-methyl-pyrrole.—CaA''.—$CaH_2A''_2$: prisms.

Ethyl ether Et_2A''. [38°]. (280°) at 500 mm. Formed by warming di-acetyl-succinic ether with aniline and HOAc (Knorr, *A.* 236, 305). Crystals.

Di-phenyl-methyl-pyrrole carboxylic acid $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CPh:CH}\\ \mathrm{CMe:C.CO_2H}\end{array}$. [226°]. Obtained by saponification of its ether, which is formed by boiling acetophenone-aceto-acetic ether with an acetic acid solution of aniline (Lederer a. Paal, *B.* 18. 2595). Small needles (from acetic acid).

Ethyl ether A'Et: [100°]; prisms.

Di-phenyl-methyl-pyrrole di-*o*-carboxylic acid $\mathrm{NMe}{<}\begin{array}{l}\mathrm{C(C_6H_4.CO_2H):CH}\\ \mathrm{C(C_6H_4.CO_2H):CH}\end{array}$. [231°]. Formed from $C_2H_4(CO.C_6H_4.CO_2H)_2$ and methylamine in alcohol at 100° (Baumann, *B.* 20, 1489). Deep-yellow plates, insol. water, sl. sol. ether.

Di-phenyl-methyl-pyrrole dicarboxylic acid $\mathrm{CO_2H.C_6H_4.N}{<}\begin{array}{l}\mathrm{CMe:C.CO_2H}\\ \mathrm{CPh:CH}\end{array}$. [210°]. Formed by saponifying its ether, which is got from acetophenone-acetoacetic ether, *m*-amido-benzoic acid, and HOAc (Paal a. Schneider, *B.* 19, 3162). Needles (from dilute alcohol).

Ethyl ether EtA'. [160°]. Needles.

Reference.—Oxy - phenyl - methyl - pyrrole carboxylic acid.

PHENYL-METHYL-QUINAZOLINE DIHYDRIDE $C_{15}H_{14}N_2$ *i.e.* $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{N\,-CMe}\\ \mathrm{CH_2.NPh}\end{array}$. [60°]. Formed by reduction of the acetyl derivative of *o*-nitro-benzyl-aniline with tin and HClAq (Paal a. Krecke, *B.* 23, 2638). Rosettes of white needles, insol. water, m. sol. ligroïn. The tin double chloride melts at 122°.—B'HCl 2aq. [257°].—$B'_2H_2PtCl_6$. Flat orange needles. Decomposes at 223°.

Reference.—Oxy - phenyl - methyl - quinazoline.

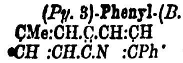
(*Py.* 1,3) - PHENYL-METHYL-QUINOLINE $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{CPh:CH}\\ \mathrm{N{=\!=}CMe}\end{array}$. [100°]. Formed by boiling an alcoholic solution of *o*-amido-benzophenone with acetone and KOHAq (Geigy a. Königs, *B.* 18, 2406; 19, 2428). Obtained also from paraldehyde, acetophenone, HCl, and aniline, and by heating benzoyl-acetone-anilide $C_{16}H_{15}NO$ with H_2SO_4 on the water-bath (Beyer, *J. pr.* [2] 33, 420; *B.* 20, 1771). Tables (from ether).—$B'H_2SO_4$. [236°].—$B'_2H_2PtCl_6$ 2aq. [225°]. Its acid solutions fluoresce blue. By heating with phthalic anhydride and $ZnCl_2$ at 150° it is converted into the phthalone $C_{21}H_{15}NO_2$ [270°], which crystallises from alcohol or HOAc in sparingly-soluble orange-red crystals.

(*Py.* 3,1)-Phenyl-methyl-quinoline $C_{16}H_{13}N$ *i.e.* $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{CMe:CH}\\ \mathrm{N{=\!=}CPh}\end{array}$. *Flavoline.* [65°]. (374°). V.D. 7·7 (calc. 7·6). Formed by distilling flavenol with zinc-dust. Prepared by adding a little dilute (10 p.c.) NaOHAq to a solution of equimolecular quantities of *o*-amido-acetophenone and acetophenone, and then heating on the water-bath (Fischer, *B.* 15, 1503; 16, 68; 19, 1037). Thick tables. Yields flavaniline on nitration and reduction. Salts.—B'HCl 2aq.—$B'_2H_2PtCl_6$: reddish-yellow needles.—B'MeI. [185°] (Bernthsen a. Hess, *B.* 18, 34). Converted by KOHAq into a strongly alkaline solid 'methyl-flavolinium hydrate.'—$B'_2Me_2PtCl_6$.

(*Py.* 3,2)-Phenyl-methyl-quinoline $\mathrm{C_6H_4}{<}\begin{array}{l}\mathrm{CH:CMe}\\ \mathrm{N{=}CPh}\end{array}$. [53°]. (above 300°). Formed by heating a mixture of CHPh:CMe.CHO, aniline, and conc. HClAq at 200° (Miller a. Kinkelin, *B.* 19, 527). Trimetric prisms, v. sol. alcohol and ether.—$B'_2H_2PtCl_6$: orange plates.—$B'C_6H_3N_3O_7$. [202°]. Large yellow plates.

(*B.* 2)-Phenyl-(*Py.* 4)-methyl-quinoline tetrahydride $C_{16}H_{17}N$ *i.e.* $\begin{array}{l}\mathrm{CPh:CH.C.CH_2\,.CH_2}\\ \mathrm{CH\;:CH.C.NMe.CH_2}\end{array}$. Formed by reducing (*B.* 2)-phenyl-quinoline methylo-chloride with tin and HClAq (La Coste a. Sorger, *A.* 230, 24). Amorphous powder, insol. cold water.—B'HCl.—B'HI.—$B'C_6H_3N_3O_7$. [147°].—B'MeI aq. [195°]. Yellow plates.

(*Py.* 3)-Phenyl-(*B.* 4)-methyl-quinoline $\begin{array}{l}\mathrm{CH:CH\;\,.C.CH:CH}\\ \mathrm{CH:CMe.C.N{=}CPh}\end{array}$. [50°]. Formed by distilling its (*Py.* 1)-carboxylic acid with soda-lime (Doebner a. Giesecke, *A.* 242, 299). Plates (from alcohol).—$B'_2H_2PtCl_6$. Brick-red needles.

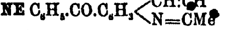
(*Py.* 3)-Phenyl-(*B.* 2)-methyl-quinoline  $\begin{array}{l}\text{CMe:CH.C.CH:CH}\\ \text{CH :CH.C.N :CPh}\end{array}$ [68°]. (above 360°). Got by distilling its carboxylic acid with soda-lime (D. a. G.). Small yellow needles (from dilute alcohol).—$B'_2H_2PtCl_6$: golden needles.

References.—NITRO- and OXY-PHENYL-METHYL-QUINOLINE.

(*Py.* 3)-PHENYL-(*B.* 4)-METHYL-QUINOLINE (*Py.* 1)-CARBOXYLIC ACID $C_{17}H_{13}NO_2$. [245°]. Formed by heating equi-molecular proportions of *o*-toluidine, benzoic aldehyde, and pyruvic acid in alcoholic solution on the water-bath (Doebner a. Giesecke, *A.* 242, 298). Small yellow crystals (from alcohol), v. sl. sol. hot water.—CuA'_2aq.—AgA'aq: needles (from Aq).

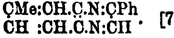
(*Py.* 3)-Phenyl-(*B.* 2)-methyl-quinoline (*Py.* 1)-carboxylic acid. [228°]. Formed in like manner from *p*-toluidine (D. a. G.). Yellow needles (from alcohol).—CuA'_2.—PbA'_2.—AgA'.—$H_2A'_2H_2PtCl_6$: golden needles, v. sl. sol. hot Aq.

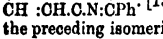
Reference.—OXY-PHENYL-METHYL-QUINOLINE CARBOXYLIC ACID.

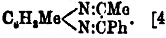
PHENYL (*Py.* 3)-METHYL-(*B.* 2)-QUINOLYL KETONE  $C_6H_5.CO.C_6H_3<\begin{array}{l}\text{CH:CH}\\ \text{N=CMe}\end{array}$ [68°]. (above 300°). Formed from amido-benzophenone, paraldehyde, and HClAq at 100° (Hinz, *A.* 242, 323). Needles (from water) or plates (from alcohol).—$B'_2H_2PtCl_6$2aq.—$B'_2H_2Cr_2O_7$.—B'MeI. [220°]. Small dark-green needles; v. sol. water.

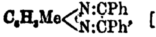
Phenyl (*Py.* 3)-methyl-(*B.* 4)-quinolyl ketone. [108°]. Formed by boiling *o*-amido-benzophenone with dilute H_2SO_4 and paraldehyde (Geigy a. Königs, *B.* 18, 2406). Matted needles (from dilute alcohol).

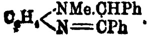
PHENYL-DI-METHYL-QUINOLYL-THIO-UREA $NHPh.CS.NH.C_{11}H_{10}N$. [159°]. Formed by heating phenyl-thiocarbimide with amido-di-methyl-quinoline (Marckwald, *B.* 23, 1025). Prisms, v. sol. hot alcohol.—$B'_2H_2PtCl_6$: pp.

PHENYL-METHYL-QUINOXALINE  $\begin{array}{l}\text{CMe:CH.C.N:CPh}\\ \text{CH :CH.C.N:CH}\end{array}$ [79°]. Formed by reducing $C_6H_3Me(NO_2).NH.CH_2Bz$ with $SnCl_2$ and HCl (Lellmann a. Donner, *B.* 23, 171). Needles, v. sol. alcohol.—$B'HgCl_2$. [223°]. White needles.

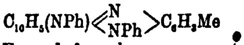
Phenyl-methyl-quinoxaline  $\begin{array}{l}\text{CMe:CH.C.N:CH}\\ \text{CH :CH.C.N:CPh}\end{array}$ [135°]. Formed, together with the preceding isomeride, by the action of chloro-acetophenone on tolylene-*o*-diamine (Hinsberg, *A.* 237, 370). Formed also by warming phenyl-glyoxylic aldehyde $C_6H_5.CO.CHO$ with tolylene-*o*-diamine sulphate and NaOAc (Pechmann, *B.* 20, 2905). Needles, v. sol. hot alcohol and ether.

Phenyl-di-methyl-quinoxaline  $C_6H_3Me<\begin{array}{l}\text{N:CMe}\\ \text{N:CPh}\end{array}$ [48°]. Formed by boiling phenyl methyl diketone with tolylene-*o*-diamine in ether (Müller a. Pechmann, *B.* 22, 2130). V. sol. most solvents.

Di-phenyl-methyl-quinoxaline $C_{21}H_{16}N_2$ *i.e.*  $C_6H_3Me<\begin{array}{l}\text{N:CPh}\\ \text{N:CPh}\end{array}$ [111°]. Formed by heating benzil with tolylene-*o*-diamine in alcoholic solution (Hinsberg, *B.* 17, 322). Silvery plates. May be distilled. Weak base. Nearly insol. Aq.

Di-phenyl-*v*-methyl-quinoxaline dihydride  $C_6H_4<\begin{array}{l}\text{NMe.CHPh}\\ \text{N=CPh}\end{array}$ [133°]. Formed by heating phenylene-methyl-*o*-diamine with benzoïn at 165° (Fischer a. Busch, *B.* 24, 2682). Yellow needles, m. sol. alcohol. Its solutions fluoresce greenish-yellow.

Reference.—OXY-PHENYL-METHYL-QUINOXALINE.

PHENYL-METHYL-ROSINDULINE  $C_{10}H_5(NPh)<\begin{array}{l}\text{N}\\ \text{NPh}\end{array}>C_6H_3Me\ \left[\begin{array}{l}1\\ 2\end{array}4\right]$. [232°]. Formed from benzene-azo-*p*-tolyl-(α)-naphthylamine (Fischer a. Hepp, *A.* 256, 243). Reddish-brown bronzed plates. Split up by conc. HClAq at 200° into aniline and methyl-rosindone.

PHENYL-METHYL-SUCCINIC ACID PHENYL-PYROTARTARIC ACID.

Phenyl-tri-methyl-succinic acid $C_{13}H_{16}O_4$ *i.e.* $CH_2Ph.CH(CO_2H).CMe_2.CO_2H$. [140°]. Formed from bromo-isobutyric ether and sodium benzyl-malonic ether, the resulting ether (200°–220°) being saponified (Bischoff, *B.* 24, 1060). Short needles (from water), v. sol. alcohol and ether.

Di-phenyl-di-methyl-succinic acid. *Nitrile* CPhMe(CN).CPhMe.CN. [227°]. Formed from CHPhMe.CN by treatment with NaOEt and I (Chalanay a. Knoevenagel, *B.* 25, 289). Insol. benzene, sl. sol. alcohol.

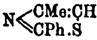
PHENYL-METHYL-SULPHAMIC ACID $NPhMe.SO_3H$. Formed from $ClSO_3H$ and methyl-aniline in chloroform (Traube, *B.* 24, 362).—NH_4A'. Turns violet in air. Decomposed by boiling HClAq into methyl-aniline and H_2SO_4. The potassium salt is a crystalline powder, sl. sol. alcohol, v. sol. water.

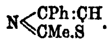
PHENYL-DI-METHYL SULPHAMIDE $SO_2(NMe_2)(NHPh)$. [85°]. Formed from $NMe_2.SO_2Cl$ and aniline (Behrend, *A.* 222, 128). Needles (from ether). Yields $SO_2(NMe_2)(NPhNa)$, crystallising in needles, v. sol. water and alcohol.

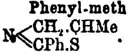
PHENYL METHYL SULPHIDE PhSMe. (188°). Formed from $Pb(SPh)_2$ and MeI at 100° (Obermeyer, *B.* 20, 2926). Liquid.

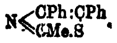
PHENYL METHYL SULPHONE $C_7H_8SO_2$ *i.e.* $C_6H_5.SO_2.CH_3$. [89°]. Formed from benzene sulphinic acid, NaOEt, and MeI at 100°, and also by boiling $C_6H_5.SO_2.CH_2.CO_2H$ with alcoholic potash (Michael a. Palmer, *Am.* 6, 254; 7, 65; Otto a. Rössing, *B.* 18, 156; 21, 652; 22, 1449, 1452; 23, 755). Plates (from hot water), v. e. sol. alcohol and ether.

PHENYL METHYL SULPHONE ω-CARBOXYLIC ACID *v.* PHENYL-SULPHONO-ACETIC ACID.

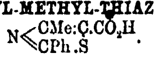
PHENYL-METHYL-THIAZOLE $C_{10}H_9NS$ *i.e.*  $N\ll\begin{array}{l}\text{CMe:CH}\\ \text{CPh.S}\end{array}$. (279° cor.). Formed from thiobenzamide and chloro-acetone in alcohol (Hubacher, *A.* 259, 236). Oil.

Phenyl-methyl-thiazole  $N\ll\begin{array}{l}\text{CPh:CH}\\ \text{CMe.S}\end{array}$. [68·5°]. (284° cor.). Formed from thioacetamide and ω-bromo-acetophenone (Hantzsch, *B.* 21, 913; *A.* 250, 269). Weak base. Not attacked in boiling alcoholic solution by sodium (Schatzmann, *A.* 261, 7).—B'HCl: sl. sol. Aq.

Phenyl-methyl-thiazole. *Dihydride*  $N\ll\begin{array}{l}\text{CH}_2\text{.CHMe}\\ \text{CPh.S}\end{array}$. Formed by boiling propylene bromide with thiobenzamide (Gabriel a. Heymann, *B.* 24, 785). Yellowish liquid.—*Picrate* $B'C_6H_3N_3O_7$: crystalline.

Di-phenyl-methyl-thiazole  $N\ll\begin{array}{l}\text{CPh:CPh}\\ \text{CMe.S}\end{array}$.

°]. Formed from thioacetamide and bromo-oxybenzoïn in alcohol (Hubacher, *A.* 259, 4). Stellate groups of needles, insol. water. Hydrochloride: [97°]; white crystals from dilute HClAq).

PHENYL-METHYL-THIAZOLE CARBOXYLIC ACID  $N<\begin{smallmatrix}CMe:C.CO_2H\\CPh.S\end{smallmatrix}$. [203°]. Formed by saponifying its ether. Needles, sl. sol. ether.

Ethyl ether EtA′. [43°]. Formed from thiobenzamide and chloro-acetic ether (Hubacher, *A.* 259, 237).

PHENYL (α)-METHYL-THIENYL KETONE $C_6H_5.CO.C_4H_2MeS$. [124°]. Formed by heating $C_4H_2Me(HgCl)S$ with BzCl at 100° (Volhard, *A.* 267, 181; *cf.* Ernst, *B.* 19, 3280). Needles (from ligroïn).

TRI-PHENYL-DI-METHYL-DI-THIO-BIURET $C_{22}H_{21}N_3S_2$ *i.e.* $NPh(CS.NPhMe)_2$ or CS(NPhMe).S.C(NPh)(NPhMe). [202°]. Formed from Cl.CS.NPhMe and aniline (Billeter a. Strohl, *B.* 21, 108). Needles, v. sl. sol. cold alcohol.

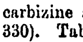
PHENYL-METHYL-DI-THIO-CARBAMIC ACID NPhMe.CS.SMe. [88°]. Formed by heating NPhMe.C(NMe).SMe. or NPhMe.C(NH).SMe with CS_2 at 160° (Bertram, *B.* 25, 51). Plates.

PHENYL-METHYL-THIOCARBAMIC CHLORIDE NPhMe.CS.Cl. [35°]. Formed from methyl-aniline and $CSCl_2$ (Billeter, *B.* 20, 1631). Yellowish crystals. Converted by alcohol into $(NPhMe.CS)_2O$ [116·5°].

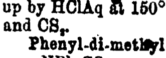
PHENYL-METHYL-THIO-SEMI-CARBAZIDE NHPh.NH.CS.NHMe. [89°]. Formed from methyl-thiocarbimide and phenyl-hydrazine (Dixon, *C. J.* 57, 262). Trimetric prisms, v. sl. sol. cold water. H_2SO_4 forms an azure-blue solution. $CuSO_4$ gives a deep-blue colour, and $FeCl_3$ a greenish-blue.

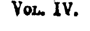
Phenyl-methyl-thio-semi-carbazide NHPh.CS.NH.NHMe. [143°]. Formed from methyl-hydrazine and phenyl-thiocarbimide (Brüning, *A.* 253, 11). Prisms (from alcohol).

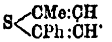
Di-phenyl-methyl-thio-semi-carbazide NPhMe.NH.CS.NHPh. [154°]. Formed from phenyl-methyl-hydrazine and phenyl-thiocarbimide (Fischer, *A.* 190, 166). V. sol. hot alcohol.

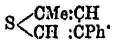
PHENYL-METHYL-THIOCARBIZINE  $CS<\begin{smallmatrix}NPh\\NMe\end{smallmatrix}$. [123°]. Formed from phenyl-thiocarbizine and MeI at 100° (Fischer, *A.* 212, 330). Tables (from water). Not attacked by nitrous acid.

PHENYL-METHYL-THIOHYDANTOÏC ACID $NHPh.CS.NH.CHMe.CO_2H$. Formed from alanine and phenyl-thiocarbimide in alcohol (Marckwald, *B.* 24, 3280; *cf.* Aschan, *B.* 17, 421).—KA′: minute needles.

PHENYL-METHYL-THIOHYDANTOÏN  $CS<\begin{smallmatrix}NPh.CO\\NH-CHMe\end{smallmatrix}$. [184°]. Formed by treating phenyl-methyl-thiohydantoïc acid (*v. supra*) with HCl. Small prisms (from alcohol). Split up by HClAq at 150° into aniline, alanine, CO_2, and CS_2.

Phenyl-di-methyl-thiohydantoïn  $CS<\begin{smallmatrix}NPh.CO\\NH.CMe_2\end{smallmatrix}$. [67°]. Formed from phenyl-thiocarbimide and α-amido-isobutyric acid (Marckwald, *B.* 24, 3282). Crystals, sl. sol. Aq.

PHENYL-METHYL-THIOPHENE $C_{11}H_{10}S$ *i.e.*  $S<\begin{smallmatrix}CMe:CH\\CPh:CH\end{smallmatrix}$. [51°]. (271° uncor.). Got by heating acetophenone-acetone with P_2S_3 at 125°, the yield being 70 p.c. of the theoretical amount (Paal, *B.* 18, 367). Needles, volatile with steam. Gives the indophenine reaction.

Phenyl-methyl-thiophene  $S<\begin{smallmatrix}CMe:CH\\CH:CPh\end{smallmatrix}$. [73°]. Formed by heating $CH_2Ac.CHPh.CO_2Na$ with P_2S_3 or P_2S_5 (Paal a. Püschel, *B.* 20, 2558). Plates, v. sol. hot alcohol. Gives the indophenine reaction on warming. Br forms $C_{11}H_6Br_4S$ [137°].

***s*-PHENYL-METHYL-THIO-UREA** $C_8H_{10}N_2S$ *i.e.* CS(NHPh)(NHMe). [1[illegible]3°]. Formed from methyl-thiocarbimide and aniline (Gebhardt, *B.* 17, 3038). Six-sided tables. Yields NH_2Me and $CS(NHPh)_2$ on boiling with aniline.

***u*-Phenyl-methyl-thio-urea** $CS(NH_2)(NPhMe)$. [107°]. Formed from methyl-aniline hydrochloride and potassium sulphocyanide (Gebhardt, *B.* 17, 2094). Tables (from alcohol) or prisms (from hot water).

Phenyl-methyl-ψ-thio-urea MeS.C(NH)(NHPh). [71°]. Formed by warming phenyl-thio-urea with MeI and alcohol (Bertram, *B.* 25, 49). Colourless crystals, sl. sol. hot water. Converted by dilute H_2SO_4 at 160° into MeS.CO.NHPh.—B′HI. [147°].—$B'H_2SO_4$. [171°].—$B'_2H_2SO_4$. [171°].—$B'HNO_3$. [113°].—B′HOAc. [115°].—$B'_2H_2PtCl_6$. [184°].—$B'C_6H_2(NO_2)_3OH$. [175°]. Yellow plates.

Phenyl-di-methyl-thio-urea CS(NHMe)(NPhMe). [114°]. Formed from methyl-thiocarbimide and methyl-aniline (G.).

Phenyl-di-methyl-ψ-thio-urea MeS.C(NH)(NPhMe). Formed from phenyl-methyl-ψ-thio-urea and methyl iodide (B.). Oil. Converted by dilute H_2SO_4 at 160° into MeS.CO.NPhMe [54°].—B′HI. [184°].—$B'C_6H_3N_3O_7$. Small prisms.

Phenyl-tri-methyl-ψ-thio-urea $C_{10}H_{14}N_2S$ *i.e.* MeS.C(NMe)(NPhMe). *Methyl-imido-methyl-phenyl-carbamic thiic methyl ether.* Formed by methylation of phenyl-di-methyl-ψ-thio-urea (B.).—B′HI. [c. 184°].—$B'_2H_2PtCl_6$. [c. 174°].—$B'C_6H_3N_3O_7$. [126°]. Lemon-yellow crystals.

Di-phenyl-methyl-thio-urea CS(NHPh)(NPhMe). [87°]. (205°). Formed from phenyl-thiocarbimide and methyl-aniline (G.). Prisms, v. sol. hot alcohol. Decomposed into the parent substances by distillation with steam. Boiling aniline yields $CS(NHPh)_2$ and methyl-aniline.

Di-phenyl-methyl-ψ-thio-urea MeS.C(NPh)(NHPh). [110°]. Formed from $CS(NHPh)_2$ and MeI. Conc. HClAq at 150° yields aniline and methyl-mercaptan.—B′HI.

Di-phenyl-di-methyl-thio-urea $CS(NPhMe)_2$. [72·5°]. Formed from NPhMe.CS.Cl and methyl-aniline (Billeter, *B.* 20, 1631). Prisms (from ligroïn).

Di-phenyl-di-methyl-ψ-thio-urea MeS.C(NPh)(NPhMe). (above 300°). Formed from CS(NHPh)(NPhMe) and MeI (Bertram, *B.* 25, 57). CS_2 at 160° forms $NPhMe.CS_2Me$.—B′HI. Crystalline meal, sl. sol. hot water.

Reference.—OXY-DI-PHENYL-METHYL-ψ-THIO-UREA.

PHENYL-METHYL-UREA $C_8H_{10}N_2O$ *i.e.* $CO(NH_2)(NPhMe)$. [82°]. Formed from methyl-aniline hydrochloride and potassium cyanate (Gebhardt, *B.* 17, 2095). Thin crystals.

Phenyl-di-methyl-urea $CO(NMe_2)(NPhMe)$. Formed from $NMe_2.COCl$ and aniline (Michler a. Escherich, *B.* 12, 1163). Crystals (from alcohol).

Di-phenyl-methyl-urea $CO(NPhMe)(NHPh)$. [104°]. (204°). Formed from phenyl cyanate and methyl-aniline (G.). Small needles.

Di-phenyl-di-methyl-urea $CO(NPhMe)_2$. [121°]. (c. 350°). Formed from $NPhMe.COCl$ and methyl-aniline (Michler a. Zimmermann, *B.* 12, 1165). Tables (from alcohol).

PHENYL-(β)-NAPHTHACRIDINE

$C_{10}H_6<\begin{matrix}CPh\\N\end{matrix}>C_{10}H_6$. [297°]. **S.** (alcohol) ·04 at 15°; **S.** (benzene) ·29 at 18°. Formed by heating a mixture of di-(β)-naphthylamine with BzCl or with benzoic acid and P_2O_5 or $ZnCl_2$ (Claus a. Richter, *B.* 17, 1595; Ris, *B.* 17, 2029; Klopsch, *B.* 18, 1586). Needles, v. sol. hot benzene.—B'HCl.—$B'_2H_2PtCl_6$: yellow needles.

Dihydride $C_{10}H_6<\begin{matrix}CHPh\\NH\end{matrix}>C_{10}H_6$. Got from benzoic aldehyde (1 mol.) and (β)-naphthylamine (2 mols.) in presence of condensing agents (Claisen, *A.* 237, 273). Oxidised to phenyl-naphthacridine.

(β)-**PHENYL-NAPHTHALENE** $C_{16}H_{12}$ *i.e.* $C_{10}H_7.C_6H_5$. [102°]. V.D. 7·12 (calc. 7·05). Formed by passing a mixture of naphthalene and bromo-benzene through a red-hot tube (Watson Smith, *B.* 12, 2049; *C. J.* 39, 546; *C. J. Proc.* 5, 70). Formed also by the action of H_2SO_4 (80 g.) diluted with water (44 g.) on $CHPh(OH).CH_2OH$ (Zincke a. Breuer, *A.* 226, 23; 240, 137). Fluorescent plates. May be sublimed. Gives rise on oxidation to a quinone $C_{16}H_{10}O_2$ [110°].

A **hydrocarbon** $C_{16}H_{12}$ [104°] got by distilling chrysoquinone with soda-lime is perhaps identical with the above (Graebe, *B.* 6, 66; 7, 792; Schmidt, ***J. pr.*** [2] 9, 285).

(α)-**Phenyl-naphthalene dihydride** *v.* ATRONENE.

Reference.—OXY-AMIDO-PHENYL-NAPHTHALENE.

DI-PHENYL-NAPHTHAMIDINE $C_{23}H_{18}N_2$ *i.e.* $C_{10}H_7.C(NPh).NHPh$. [183·5°]. Formed from (α)-naphthoic acid, aniline, and PCl_3 (Bössneck, *B.* 16, 642). Needles (from alcohol).

PHENYL-(β)-NAPHTHINDOLE $C_{18}H_{13}N$ *i.e.* $C_{10}H_6<\begin{matrix}CH\\NH\end{matrix}>CPh$. [130°]. Formed by heating the (β)-naphthyl-hydrazide of acetophenone with $ZnCl_2$ at 170° (Ince, *A.* 253, 42). Crystals, v. sol. alcohol and ether. Colours pinewood green.—$B'C_6H_3N_3O_7$. [166°]. Brown needles.

Phenyl-(β)-naphthindole $C_{10}H_6<\begin{matrix}CPh\\NH\end{matrix}>CH$. [211°]. Formed by the action of alcoholic HCl on the (β)-naphthyl-hydrazide of phenyl-acetic aldehyde (I.). Needles, suddenly decomposed on fusion. Colours pinewood green. $ZnCl_2$ at 170° converts it into the preceding isomeride.—$B'C_6H_3N_3O_7$. [120°]. Reddish-brown needles.

PHENYL-NAPHTHOTRIAZINE. *Dihydride* $C_{17}H_{13}N_3$ *i.e.* $C_{10}H_6<\begin{matrix}N.CH_2\\N.NPh\end{matrix}$. [184°]. Formed by heating benzene-azo-(β)-naphthylamine with formic paraldehyde at 140° (Goldschmidt a. Poltzer, *B.* 24, 1002). Plates (containing $\frac{2}{3}$ aq).—B'HCl. [254°].—$B'_2H_2PtCl_6$.

Di-phenyl-(αβ)-naphthotriazine $C_{23}H_{17}N_3$ *i.e.* $C_{10}H_6<\begin{matrix}N.CHPh\\N.NPh\end{matrix}$? [194°]. Got by heating a solution of $CHPh{:}N.C_{10}H_6.N_2Ph$ in HOAc (Meldola, *C. J.* 57, 330). White flattened needles.

PHENYL-NAPHTHOPHENANTHRAZINE

$\begin{matrix}C_6H_4.CH.N\\C_6H_4.CH.N\end{matrix}>C_{10}H_6$. The *phenylo-nitrate* $B'PhNO_3$, formed by boiling phenanthraquinone with phenyl-naphthylene-diamine in HOAc and then adding HNO_3 crystallises in dichroic needles or prisms (Witt, *B.* 20, 1185).

(*Py.* 3)-**PHENYL-(α)-NAPHTHOQUINOLINE** $C_{19}H_{13}N$ *i.e.* $C_{10}H_6<\begin{matrix}CH{:}CH\\N{=}CPh\end{matrix}$. [68°]. Formed by heating its (*Py.* 1)-carboxylic acid with soda-lime (Döbner, *A.* 249, 114). Yellow needles (from alcohol-ether). Yields a syrupy tetrahydride. *Salts.*—$B'_2H_2PtCl_6$ 2aq.—$B'H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$. [167°]. Thin needles (from alcohol).

(*Py.* 3)-**Phenyl-(β)-naphthoquinoline.** [188°]. Formed by heating its carboxylic acid with soda-lime (D.). Needles or plates, insol. water, v. sol. alcohol.—$B'_2H_2PtCl_6$ aq.—$B'C_6H_3N_3O_7$. [250°]. Yellow plates, sl. sol. ether.—$B'_2H_2Cr_2O_7$.

Ethylo-iodide. [233°]. Plates, insol. ether.

(*Py.* 3)-**PHENYL-(α)-NAPHTHOQUINOLINE** (*Py.* 1)-**CARBOXYLIC ACID** $C_{20}H_{13}NO_2$ *i.e.* $C_{10}H_6<\begin{matrix}C(CO_2H){:}CH\\N{=\!=\!=}CPh\end{matrix}$. [300°]. Formed by heating (α)-naphthylamine with pyruvic acid and benzoic aldehyde in alcoholic solution (D.). Yellow needles (from alcohol-acetone). May be reduced to a tetrahydride. Produces, on oxidation, di-phenyl-pyridine tri-carboxylic acid and $CO_2H.C_5NHPh<\begin{matrix}C_6H_4\\CO\end{matrix}$.—NaA' $\frac{1}{2}$aq.—CaA'_2 4aq.—ZnA'_2.—PbA'_2.—AgA': insoluble powder.

Ethyl ether EtA'. [103°]. Needles.

(*Py.* 3)-**Phenyl-(β)-naphthoquinoline** (*Py.* 1)-**carboxylic acid** $C_{20}H_{13}NO_2$. [296°]. Formed in like manner from (β)-naphthylamine (D.). Needles, v. sl. sol. alcohol.—KA' 5aq.—NaA' 5aq.—CaA'_2 6aq.—ZnA'_2 2aq.—$Cu_2A'_3$ aq (?).—AgA'.

PHENYL-NAPHTHOQUINOXALINE

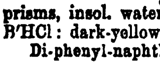
$C_{10}H_6<\begin{matrix}N{:}CH\\N{:}CPh\end{matrix}$. The *phenylo-bromide* B'PhBr, formed from phenyl-naphthylene-diamine and bromo-acetophenone, crystallises in yellow plates, and is converted by NaOH into B'PhOH [148°], which crystallises in prisms, and yields $B'PhNO_3$ (Fischer a. Busch, *B.* 24, 1873).

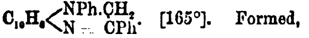
Di-phenyl-naphthoquinoxaline

$C_{10}H_6<\begin{matrix}N{:}CPh\\N{:}CPh\end{matrix}$. [147°]. Formed by heating naphthylene-(1,2)-diamine hydrochloride with benzil in alcohol (Lawson, *B.* 18, 2426). Light-brown plates, v. sol. alcohol and ether.

Phenylo-hydroxide

$C_{10}H_6<\begin{matrix}N{=\!=\!=\!=}CPh\\NPh(OH){:}CPh\end{matrix}$. [167°]. Formed by oxidation of $C_{10}H_6<\begin{matrix}N{=\!=}CPh\\NPh.CHPh\end{matrix}$ [164°], which is got by heating phenyl-naphthylene-*o*-diamine with benzoïn at 200° (Fischer, *B.* 24, 722, 1871). Formed also from naphthylene-phenyl-diamine and benzil (Fischer, *B.* 24, 2679). Yellow prisms, insol. water, v. sol. ether.—$B'HNO_3$.—$B'HCl$: dark-yellow needles, v. sol. alcohol.

Di-phenyl-naphthoquinoxaline dihydride  $C_{10}H_6<\begin{matrix}NPh.CH_2\\ N \text{ — } CPh\end{matrix}$. [165°]. Formed, together with a compound melting at 195°, from naphthylene-phenyl-diamine and benzoyl-carbinol at 155° (Fischer a. Busch, *B.* 24, 2680). Orange needles, v. sol. benzene, v. sl. sol. alcohol.

PHENYL-NAPHTHOROSINDULINE  $C_6H_4<\begin{matrix}\text{————}C{:}N\text{—}C{:}CH\\ C(NPh).CH{:}C.NPh.C{:}CH\end{matrix}>C_6H_4$. [2[illegible]°]. Formed, together with naphthyl-rosinduline, from benzene-azo-di-(α)-naphthylamine, hydrochloride, aniline, and alcohol at 165° (Fischer a. Hepp, *A.* 256, 247). Deep-red bronzed plates. Conc. HClAq forms aniline and naphthorosindone [295°].

DI-PHENYL-(α)-NAPHTHYL-ACETAMIDINE $C_{10}H_7.CH_2.C(NPh).NHPh$. [130°]. Formed from (α)-naphthyl-acetic acid (3 mols.), aniline (6 mols.), and PCl_3 (Boessneck, *B.* 16, 642). Needles, sol. ether and benzene.

PHENYL-(α)-NAPHTHYL-AMINE $C_{16}H_{13}N$ *i.e.* $C_6H_5.NH.C_{10}H_7$. [60°]. Forms by heating (α)-naphthylamine hydrochloride with aniline at 250° (Girard a. Vogt, *Bl.* [2] 18, 67; Streiff, *B.* 13, 1852). Prepared by heating a mixture of (α)-naphthol (15 pts.), aniline (19·4 pts.) and $CaCl_2$ (11·6 pts.) under pressure for 9 hours at 280°; the yield being 26 p.c. of the theoretical (Friedländer, *B.* 16, 2077). White plates or prisms, v. sol. alcohol. Its solutions show blue fluorescence. Yields a tri-bromo- derivative [137°] and a di-nitro- derivative [77°]. H_2SO_4 at 100° forms a tetra-sulphonic acid.—$B'HCl$: prisms, decomposed by water.—$B'C_6H_3N_3O_7$.

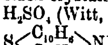
Acetyl derivative $C_{18}H_{15}NO$. [115°].

Benzoyl derivative. [152°].

Nitrosamine. $C_{10}H_7.NPh.NO$. [92°]. Reddish-yellow crystals (Fischer a. Hepp, *B.* 20, 1247).

Phenyl-(β)-naphthylamine $C_{16}H_{13}N$. [108°]. (395°). Formed by heating (β)-naphthol with aniline and $ZnCl_2$ at 190° (Merz a. Weith, *B.* 13, 1300), or with aniline hydrochloride (Merz a. Weith, *B.* 13, 1850).

Preparation.—A mixture of (β)-naphthol (15 pts.), aniline (19·4 pts.), and $CaCl_2$ (11·6 pts.) is heated under pressure at 280° for 9 hours; the yield is 98 p.c. of the theoretical (Friedländer, *B.* 16, 2075).

Properties.—White needles, sol. MeOH. Yields a tetra-bromo- derivative [198°] and a nitro- derivative [87°]. With nitroso-di-methyl-aniline hydrochloride and HOAc it yields lustrous black crystals, which form a violet solution in H_2SO_4 (Witt, *B.* 21, 723). Sulphur at 240° forms  $S<\begin{matrix}C_{10}H_6\\ C_6H_4\end{matrix}>NH$ [178°] (Kym, *B.* 23, 2466). H_2SO_4 at 100° forms a trisulphonic acid

Salts.—$B'HCl$: unstable crystalline powder. —$B'C_6H_3N_3O_7$. Brownish needles, v. sol. $CHCl_3$.

Acetyl derivative. [93°]. Crystals.

Benzoyl derivative. [136°] (Streiff, *A.* 209, 151); [148°] (Claus a. Richter, *B.* 17, 1591).

Nitrosamine $C_{10}H_7.NPh.NO$. [93°].

Di-phenyl-naphthylamine $C_{10}H_7NPh_2$. [142°]. (335°–340° at 85 mm.). Formed by adding α-bromo-naphthalene (20 g.) to a boiling solution of potassium (3·3 g.) in diphenylamine (20 g.) mixed with aniline (15 c.c.) (Herz, *B.* 23, 2541). Silky needles (from dilute alcohol), insol. water.

References.—Nitro-amido-, Di-nitro-, and Nitroso- Phenyl-naphthyl-amine.

PHENYL-(α)-NAPHTHYLAMINE BLUE *v.* Tri-naphthyl-tri-amido-tri-phenyl-carbinyl chloride.

PHENYL-(β)-NAPHTHYL-CARBAMIC ACID.

Ethyl ether $C_{10}H_7NPh.CO_2Et$. [93°]. Formed by the action of NaOEt on the chloride (Paschkowezky, *B.* 24, 2919). Satiny needles.

Phenyl ether $C_{10}H_7NPh.CO_2Ph$. [149°]. S. (96 p.c. alcohol) ·36 at 17°; S. (benzene) 2·3 at 17°. Formed from the chloride and NaOPh. Needles, v. sl. sol. cold alcohol.

Chloride $C_{10}H_7NPh.COCl$. [102°]. Formed from phenyl-(β)-naphthylamine and $COCl_2$ in toluene (Kym, *B.* 23, 425). White plates.

PHENYL-(α)-NAPHTHYL CARBINOL $Ph.CH(OH).C_{10}H_7$. [86·5°]. (above 360°). Formed from the ketone, zinc-dust, and KOH (Elbs, *J. pr.* [2] 35, 504; *cf.* Lehne, *B.* 13, 359; Beckmann, *B.* 22, 915). Crystals, v. sol. alcohol. Gives a violet colour with H_2SO_4.

Phenyl-di-(α)-naphthyl carbinol $C_{27}H_{20}O$ *i.e.* $Ph.C(C_{10}H_7)_2OH$. [160°–170°]. Formed, together with benzoic aldehyde, by boiling phenyl-(α)-naphthyl-(β)-pinacolin $(C_{10}H_7)_2CPhBz$ (got by reducing phenyl (α)-naphthyl ketone with zinc and alcoholic HCl) with alcoholic KOH (Elbs, *J. pr.* [2] 35, 507). Grey crystalline crusts (from ether-alcohol), m. sol. alcohol, v. sol. ether.

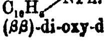
PHENYL-(β)-NAPHTHYL-CARBINYL-THIO-UREA. *Tetrahydride* $C_{18}H_{20}N_2S$ *i.e.* $NHPh.CS.NH.CH_2C_{10}H_{11}$. [140°]. Formed from $C_{10}H_{11}.CH_2NH_2$ and phenyl thiocarbimide (Bamberger a. Helwig, *B.* 22, 1913). Vitreous rosettes.

PHENYL-NAPHTHYL-CARBINYL-UREA. *Tetrahydride* $NHPh.CO.NH.CH_2C_{10}H_{11}$. Formed from naphthyl-carbinylamine and phenyl cyanate (Bamberger, *B.* 22, 1913). The (α)-compound melts at 126·5°, the (β)-isomeride at 141°. Both crystallise in needles.

PHENYL-(α)-NAPHTHYLENE-DIAMINE $C_{16}H_{14}N_2$ *i.e.* $C_{10}H_6(NH_2)(NHPh)$ [1:4]. [148°]. Formed by reducing nitroso-phenyl-(α)-naphthylamine (Wacker, *A.* 243, 305). Needles (from alcohol) or plates (from benzene).

Phenyl-*o*-naphthylene-diamine $C_{10}H_6(NH_2)(NHC_6H_5)$ [1:2]. *Amido-(β)-naphthyl-phenyl-amine.* [140°]. Formed, together with aniline, by reduction of benzene-azo-(β) naphthyl-phenyl-amine with $SnCl_2$ (Zincke a. Lawson, *B.* 20, 1170; Witt, *B.* 20, 1184). Broad needles or plates. Nitrous acid passed into HOAc (11 pts.) containing the hydrochloride in suspension forms $C_{16}H_8N_4O_2$ or $C_{16}H_{10}N_4O_2$ [208°], whence $SnCl_2$ forms $C_{16}H_{12}N_4$ [194°], which yields $B'HCl$, $C_{16}H_{11}AcN_4$ [261°] and $C_{16}H_{10}Ac_2N_4$ [177°], and gives with benzoic aldehyde a compound $C_{23}H_{16}N_4$ [15[illegible]°] (Zincke a. Campbell, *A.* 255, 349).

Salts.—$B'HCl$: long colourless glistening needles, v. sl. sol. water, more readily in alcohol. —$^{\times}B'H_2SO_4$: needles, similar solubility.

Phenyl-dinaphthylene-amine $C_{26}H_{17}N$ *i.e.*  $\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}>NPh$. [c. 144°]. Formed by heating (ββ)-di-oxy-dinaphthyl with aniline-zinc-chloride.

at 300° (Walder, *B.* 15, 2175). Prisms or needles, sol. alcohol.—$B'2C_6H_3N_3O_7$. [169°].

Di-phenyl-naphthylene-diamine [2:2′] $C_{10}H_6(NHPh)_2$. [168°]. Formed, together with $C_{10}H_6(OH)(NHPh)$ [163°], by heating dioxy-naphthalene with aniline and $CaCl_2$ (Annaheim, *B.* 20, 1372; Clausius, *B.* 23, 528). Silvery plates (from hot benzene).

Acetyl derivative $C_{26}H_{22}N_2O_3$. [198°].

Di-phenyl-naphthylene-*p*-diamine [1:4] $C_{10}H_6(NHPh)_2$. [144°]. Formed by reducing the di-anilide of (*α*)-naphthoquinone with zinc, HOAc, and alcohol (Fischer a. Hepp, *A.* 256, 255). Colourless prisms.

DI-PHENYL-NAPHTHYLENE-DI-THIO-UREA $C_{10}H_6(NH.CS.NHPh)_2$. [355°–360°]. Formed from naphthylene (1,2)-diamine and phenyl-thio-carbimide (Bamberger a. Schieffelin, *B.* 22, 1376). Needles.

DI-PHENYL-NAPHTHYLENE-UREA $C_{10}H_6(NH.CO.NHPh)_2$. [335°]. Formed from naphthylene (1,2)-diamine and phenyl cyanate (Bamberger a. Schieffelin, *B.* 22, 1376). Crystalline granules, v. sl. sol. benzene.

PHENYL-NAPHTHYL-ETHANE $C_{18}H_{16}$ *i.e.* $C_{10}H_7.CH_2.CH_2Ph$. Formed by heating naphthyl benzyl ketone with HI and P at 155° (Graebe a. Bungener, *B.* 12, 1078). Yields chrysene on passing through a red-hot tube.

***s*-PHENYL-(*β*)-NAPHTHYL-ETHYLENE** $C_6H_5.C_2H_2.C_{10}H_7$. [145°]. Formed by distilling (*β*)-naphthyl cinnamate, CO_2 being split off (Anschütz, *B.* 18, 1946). Silvery plates.

Di-bromide. [192°].

PHENYL-NAPHTHYL-ETHYLENE-*ψ*-THIO-UREA $NPh:C<\begin{matrix}N(C_{10}H_7)\\S.CH_2\end{matrix}>CH_2$. [185°]. Formed from phenyl-(*α*)-naphthyl-urea and ethylene bromide (Foerster, *B.* 21, 1870).

DI-PHENYL-NAPHTHYL-GUANIDINE $C_{23}H_{19}N_3$ i.e. $CN_3H_2Ph_2(C_{10}H_7)$. [155°]. Formed by heating di-phenyl-thio-urea with (*α*)-naphthylamine, alcohol, and PbO (Tiemann, *B.* 3, 6; *Z.* [2] 6, 309). Crystalline, sol. alcohol.

PHENYL-(*β*)-NAPHTHYL-GUANIDINE CARBOXYLIC ACID $C_{10}H_7NH.C(NH).NH.C_6H_4.CO_2H$. Formed by heating cyan-carbimidamido-benzoic acid with (*β*)-naphthylamine (Griess, *B.* 16, 338). Crystals sl. sol. hot alcohol.—B′HCl. Six-sided plates.

PHENYL (*α*)-NAPHTHYL-KETONE $C_{17}H_{12}O$ *i.e.* $C_6H_5.CO.C_{10}H_7$. Mol. w. 232. [75·5°]. (385°) (Schweizer, *A.* 261, 196). V.D. 119 (calc. 116). S. (alcohol) 2·5 at 12°.

Formation. — 1. Together with the (*β*)-isomeride, by heating naphthalene with HOBz and P_2O_5 at 210° (Merz, *B.* 6, 541, 966, 1238).—2. By heating (*α*)-naphthoic acid with benzene and P_2O_5 (M.).—3. Together with a smaller quantity of the (*β*)- isomeride, by the action of $AlCl_3$ on a mixture of naphthalene, CS_2, and BzCl. The two ketones are separated by crystallisation from alcohol-ether (Elbs, *J. pr.* [2] 35, 503; *B.* 19, 1965; Rospendowski, *C. R.* 102, 872).—4. By heating naphthalene with BzCl and $ZnCl_2$, or Zn (Roux, *A. Ch.* [6] 12, 338; Kegel, *A.* 247, 178).

Properties.—Trimetric prisms, very slightly volatile with steam.

Reactions.—1. Br forms $C_{17}H_{11}BrO$ [98°] (E.); [100·5°] (Rospendowski), whence HNO_3 gives $C_{17}H_9Br(NO_2)_2O$ decomposing at 90°.—2. Conc. H_2SO_4 with a few drops of water forms at 100°–150° benzoic acid and naphthalene (*β*)-sulphonic acid.—3. *Soda-lime* at 350° forms naphthalene and NaOBz.—4. *Chromic acid mixture* forms $C_6H_5.CO.C_6H_3(CO_2H)_2$[1:2:3]. [155°].—5. *Sodium* acting on its ethereal solution forms a greenish-yellow compound $(C_{10}H_7.CPh)_2O_2Na_2$, whence water produces $CPh(C_{10}H_7)_2.CO.C_6H_5$ and other bodies, while CO_2 acting on the Na compound forms a yellow powder, split up by water into ketone and $C_6H_5.C(C_{10}H_7)(OH).CO_2H$ [148°] (Beckmann a. Paul, *A.* 266, 10).

Oxim $C_6H_5.C(NOH).C_{10}H_7$. [142°]. Groups of white needles (from dilute alcohol) (Kegel, *A.* 247, 181). Oxidised by CrO_3 in HOAc to $C_6H_5.CO.C_6H_3<\begin{matrix}CO.CH\\CO.CH\end{matrix}$ [152°], which yields an anilide $C_6H_3Bz<\begin{matrix}CO.C.NHPh\\CO.CH\end{matrix}$ [200°] and a *p*-toluide [197°] both converted by boiling NaOHAq into $C_6H_3Bz<\begin{matrix}CO.C.OH\\CO.CH\end{matrix}$ [222°].

Phenyl (*β*)-naphthyl ketone [82°]. S. 2 at 12°. Formed, at the same time as the (*α*)- isomeride, from naphthalene (*v. supra*). Formed also by heating (*β*)-naphthoic acid with benzene and P_2O_5 (Merz). Needles, v. sol. hot alcohol.

Oxim. [176°]. Needles. Oxidised by CrO_3 in HOAc to yellow $C_6H_3Bz<\begin{matrix}CO.CH\\CO.CH\end{matrix}$ [132°], which is converted by heating with aniline into dark-red plates of $C_6H_3Bz<\begin{matrix}CO.C.NHPh\\CO.CH\end{matrix}$ [210°].

Reference. — DI-OXY-PHENYL-NAPHTHYL-KETONE.

PHENYL NAPHTHYL KETONE *o*-CARBOXYLIC ACID $C_{10}H_7.CO.C_6H_4.CO_2H$. [174°]. The chloride is formed from naphthalene, phthalic anhydride, and $AlCl_3$ (Ador a. Crafts, *Bl.* [2] 31, 531). Prisms (from dilute alcohol).

PHENYL-NAPHTHYL-METHANE *v.* BENZYL-NAPHTHALENE.

Phenyl-di-(*α*)-naphthyl-methane $C_{27}H_{20}$ *i.e.* $C_6H_5CH(C_{10}H_7)_2$. [c. 180°]. Formed from phenyl-(*α*) naphthyl-(*β*)-pinacolin by distilling with zinc-dust. Got also by heating phenyl-di-(*α*)-naphthyl-carbinol with zinc-dust (Elbs, *J. pr.* [2] 35, 508). Grey powder; cakes together at 100°.

Di-phenyl-naphthyl-methane $C_{10}H_7.CHPh_2$. [134° and 149°]. Formed by heating di-phenyl-carbinol with naphthalene and P_2O_5 at 140° (Lehne, *B.* 13, 358; Hemilian, *Bl.* [2] 34, 326). Needles, sol. benzene and ether, sl. sol. alcohol.

PHENYL-(*α*)-NAPHTHYL-METHYL-PYRROLE $\begin{matrix}CH:CPh\\CH:CMe\end{matrix}>NC_{10}H_7$. [74°]. (above 360°). Formed by heating the carboxylic acid [244°] (Lederer a. Paal, *B.* 18, 2598). Plates. V. e. sol. alcohol, benzene, and ligroin.

Phenyl-(*β*)-naphthyl-methyl-pyrrole $\begin{matrix}CH:CPh\\CH:CMe\end{matrix}>NC_{10}H_7$. [52°]. Formed by heating the carboxylic acid [249°] (L. a. P.). Small white concentric needles. V. sol. alcohol.

PHENYL-(*α*)-NAPHTHYL-METHYL-PYRROLE CARBOXYLIC ACID $\begin{matrix}CH:CPh\\CO_2H.C{=}CMe\end{matrix}>NC_{10}H_7$. [244°]. Formed by

heating acetophenoneacetoacetic ether with (α)-naphthylamine at 130°, and saponification of the product (Lederer a. Paal, *B.* 18, 2598). Needles. V. sol. alcohol, benzene, and acetic acid.

Phenyl-β-naphthyl-methyl-pyrrole carboxylic acid. [249°]. Formed in like manner, using (β)-naphthylamine (L. a. P.). Small white needles, sol. alcohol and HOAc.

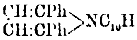
Ethyl ether EtA′. [115°]. Plates.

PHENYL-(β)-NAPHTHYL-METHYL-THIO-UREA $C_{10}H_7NH.CS.NPhMe$. [127°]. Got from (β)-naphthyl-thiocarbimide and methyl-aniline (Gebhardt, *B.* 17, 2091). Long yellow needles.

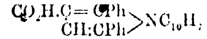
Phenyl-(α)-naphthyl-methyl-ψ-thio-urea $C_{10}H_7N{:}C(SMe).NHPh$. [96°]. Formed from phenyl (α)-naphthyl-thio-urea and MeI (Foerster, *B.* 21, 1870). Small white needles. Yields (α)-naphthyl-thiocarbimide on heating with CS_2.

PHENYL-(α)-NAPHTHYL-(β)-PINACOLIN $C_6H_5.C(C_{10}H_7)_2.CO.C_6H_5$. [c. 130°]. From phenyl-(α)-naphthyl ketone by boiling with zinc and HCl (Elbs, *J. pr.* [2] 35, 505). Pale greenish-yellow crystalline crusts, v. sol. ether, sl. sol. alcohol, insol. water. Cakes together at 100°–110°. Boiling alcoholic KOH forms benzoic aldehyde and phenyl-di-naphthyl-carbinol.

PHENYL-(α)-NAPHTHYL-PINACONE $C_{10}H_7CPh(OH).CPh(OH).C_{10}H_7$. [61°]. A product of the action of sodium-amalgam on an alcoholic solution of phenyl-(α)-naphthyl ketone (Lehne, *B.* 13, 1360). Needles (from ether).

DI-PHENYL-(α)-NAPHTHYL-PYRROLE  $\begin{matrix}CH{:}CPh\\CH{:}CPh\end{matrix}{>}NC_{10}H_7$. [149°]. Formed by heating its carboxylic acid with lime (Paal a. Braikoff, *B.* 22, 3092). Needles, v. sol. hot alcohol.

Di-phenyl-(β)-naphthyl-pyrrole. [208°]. Formed in like manner (P. a. B.). Needles.

DI-PHENYL-(α)-NAPHTHYL-PYRROLE CARBOXYLIC ACID  $\begin{matrix}CO_2H.C{=}CPh\\CH{:}CPh\end{matrix}{>}NC_{10}H_7$. [272°]. Got by saponifying its ether, which is obtained from phenacyl-benzoyl-acetic ether and (α)-naphthylamine (Paal a. Braikoff, *B.* 22, 3091). Small white plates, sl. sol. hot alcohol.—KA′. Sl. sol. hot water.

Ethyl ether EtA′. [182°]. Needles.

Di-phenyl-(β)-naphthyl-pyrrole carboxylic acid. [above 350°]. Got in like manner, using (β)-naphthylamine. Plates.—KA′. Sl. sol. water.

Ethyl ether EtA′. [182°]. Needles.

PHENYL-(α)-NAPHTHYL SULPHIDE $C_{10}H_7.SPh$. [42°] (K. a. B.); [49°]. (c. 215° at 15 mm.). Formed from $Pb(SPh)_2$ and $C_{10}H_7Br$ (Krafft a. Bourgeois, *B.* 23, 3047). Formed also from (α)-diazonaphthalene chloride and NaSPh (Ziegler, *B.* 23, 2471). Prisms (from dil. alcohol).

Phenyl (β)-naphthyl sulphide. [52°]. (c. 221° at 14 mm.). Formed in like manner. Needles.

PHENYL (α)-NAPHTHYL SULPHONE $C_6H_5.SO_2.C_{10}H_7$. [100°]. Formed by oxidising phenyl (α)-naphthyl sulphide with CrO_3 and HOAc (Krafft a. Bourgeois, *B.* 23, 3047). Formed also, together with the (β)-isomeride, by heating benzene sulphonic acid with naphthalene and P_2O_5 at 175° (Michael a. Adair, *B.* 10, 585). Crystals (from alcohol).

Phenyl (β)-naphthyl sulphone. [116°]. Formed in like manner, and also by heating naphthalene (β)-sulphonic acid with benzene and P_2O_5 (M. a. A.), and by the action of zinc-dust or $AlCl_3$ on a mixture of naphthalene and benzene sulphonic chloride (Crustschoff, *B.* 7, 1167; Otto a. Beckurts, *B.* 11, 2069). Needles.

PHENYL-(α)-NAPHTHYL-THIO-SEMICARBAZIDE $NHPh.CS.NH.NHC_{10}H_7$. [135°]. Formed from (α)-naphthyl-hydrazine and phenyl-thio-carbimide (Freund, *B.* 24, 4191). Needles.

Phenyl-(β)-naphthyl-thio-semicarbazide. [202°]. Formed in like manner from (β)-naphthyl-hydrazine (F.). White plates.

PHENYL-(α)-NAPHTHYL-THIO-UREA $NHPh.CS.NHC_{10}H_7$. [163°]. Formed from (α)-naphthylamine and phenyl-thiocarbimide (Hofmann, *Pr.* 9, 274), and also from aniline and (α)-naphthyl-thiocarbimide (Mainzer, *B.* 15, 1414). Plates, v. sl. sol. alcohol. With ethylene bromide it gives two bases [185°] and [130°].

Tetrahydride $NHPh.CS.NHC_{10}H_{11}$. [153°]. Formed from phenyl-thiocarbimide and (α)-naphthylamine tetrahydride (Bamberger, *B.* 21, 1794). Prisms, v. sol. benzene-alcohol.

Phenyl-(β)-naphthyl-thio-urea $NHPh.CS.NHC_{10}H_7$. [165°]. Formed from (β)-naphthylamine and phenyl thiocarbimide (M.; Freund a. Wolf, *B.* 25, 1468). Plates. Split up by HClAq at 150° into aniline, (β)-naphthylamine, and phenyl and (β)-naphthyl thiocarbimides. $COCl_2$ in toluene forms $NPh{:}C{<}\begin{matrix}NC_{10}H_6\\S\end{matrix}{>}CO$ [117°].

Tetrahydride $NHPh.CS.NHC_{10}H_{11}$. [161°]. Formed from phenyl thiocarbimide and (β)-naphthylamine tetrahydride (Bamberger a. Müller, *B.* 21, 858). Prisms (from alcohol).

PHENYL-(α)-NAPHTHYL-UREA. *Tetrahydride* $NHPh.CO.NHC_{10}H_{11}$. [193°]. Formed from (α)-naphthylamine tetrahydride and phenyl cyanate (Bamberger, *B.* 21, 1794). Needles.

u-Phenyl-(β)-naphthyl-urea $NH_2.CO.NPh.C_{10}H_7$. [190°]. Formed by heating $NPh(C_{10}H_7).COCl$ and alcoholic NH_3 at 130° (Kym, *B.* 23, 426). Needles, sl. sol. cold alcohol.

Phenyl-(β)-naphthyl-urea $NHPh.CO.NHC_{10}H_7$. [221°]. Formed from phenyl cyanate and (β)-naphthylamine (Goldschmidt, *B.* 21, 2567). Prisms (from alcohol).

Tetrahydride $NHPh.CO.NHC_{10}H_{11}$. [166°]. Formed from phenyl cyanate and the tetrahydride of (β)-naphthylamine (Bamberger a. Müller, *B.* 21, 859). Needles, v. e. sol. alcohol.

Phenyl-di-(β)-naphthyl-urea $C_{27}H_{20}N_2O$ *i.e.* $NHPh.CO.N(C_{10}H_7)_2$. [182°]. Formed from phenyl cyanate and di-(β)-naphthylamine (Gebhardt, *B.* 17, 3039). Formed also by heating $N(C_{10}H_7)_2.COCl$ with aniline in $CHCl_3$ at 130° (Kym, *B.* 23, 429; Kühn a. Landau, *B.* 23, 811). Needles (from alcohol). By heating with aniline it is converted into $CO(NHPh)_2$ and di-(β)-naphthylamine.

Phenyl-tri-(β)-naphthyl-urea $CO(NPhC_{10}H_7).N(C_{10}H_7)_2$. [168°]. S. (alcohol) ·9 at 16°; S. (benzene) 4·54 at 16°. Formed from $(C_{10}H_7)_2N.COCl$ and phenyl-(β)-naphthylamine at 260° (Paschkowezky, *B.* 24, 2924). Granular crystals, sl. sol. cold alcohol.

Di-phenyl-(β)-naphthyl-urea $NHPh.CO.NPhC_{10}H_7$. [133°]. Formed from $NPh(C_{10}H_7).COCl$ and aniline (Kym, *B.* 23, 426). White plates, sl. sol. cold alcohol.

u-Di-phenyl-di-(β)-naphthyl-urea $NPh_2.CO.N(C_{10}H_7)_2$. [104°]. Formed by heating $NPh_2.COCl$ with $(C_{10}H_7)_2NH$ at 220° or by heating $(C_{10}H_7)_2N.COCl$ with NPh_2H at 260° (Paschkowezky, *B.* 24, 2923). Crystalline powder, m. sol. cold alcohol.

s-Di-phenyl-di-(β)-naphthyl-urea $CO(NPh.C_{10}H_7)_2$. [186°]. S. (alcohol) 1 at 18·5°. S. (benzene) 59 at 18·5°. Formed by heating $C_{10}H_7NPh.COCl$ with $C_{10}H_7NPh.COCl$ at 250° (P.). Polyhedral granules. Converted by HClAq at 250° into aniline, (β)-naphthol, and CO_2.

Tri-phenyl-(β)-naphthyl-urea $NPh_2.CO.NPh.(C_{10}H_7)$. [128°]. Formed from $C_{10}H_7NPh.COCl$ and NPh_2H at 240° (P.). Crystalline powder, v. sol. alcohol.

PHENYL *o*-NITRO-BENZYL KETONE $C_6H_5.CO.CH_2.C_6H_4NO_2$. *Nitro-deoxybenzoïn.* Formed, together with the *p*-isomeride, by nitrating phenyl benzyl ketone (Ney, *B.* 21, 2448). Sol. ether (difference from *p*-isomeride). The *p*-isomeride yields a crystalline oxim [107°].

PHENYL *p*-NITRO-BENZYL OXIDE $C_6H_5.O.CH_2.C_6H_4NO_2$. [91°]. Formed from *p*-nitro-benzyl chloride and KOPh (Kumpf, *B.* 17, 1076). Plates (from alcohol).

Reference.—NITRO-PHENYL-NITRO-BENZYL OXIDE.

PHENYL NITRODIPHENYLETHYL KETONE $C_6H_5.CO.CHPh.CH_2.C_6H_4NO_2$. Formed from nitro-benzyl chloride, deoxybenzoïn, and NaOEt (Buddeberg, *B.* 23, 2071). The *o*-compound melts at 102° and yields diphenylquinoline [96°] (420°) on reduction. The *p*-isomeride melts at 112° and yields an amido-compound [141°] on reduction.

DI-PHENYL-DINITROSACYL. So-called. $C_{16}H_{10}N_2O_4$. [87°]. The chief product of the action of HNO_3 (S. G. 1·4) on acetophenone (Hollemann, *B.* 21, 860, 2835). It is accompanied by an isomeride [179°]. Crystals (from ether). Converted by acids and alkalis into benzoic and oxalic acids, NH_3, and hydroxylamine. Ac_2O yields $C_{16}H_{10}Ac_2N_2O_5$ [149°]. Aniline and benzanilide form compounds melting at 205° and 160° respectively.

DI-PHENYL-NITROSAMINE *v. Nitrosamine* of DI-PHENYL-AMINE.

PHENYL-NITRO-TOLYL-THIO-UREA *v.* NITRO-PHENYL-TOLYL-THIO-UREA.

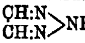
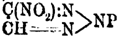
DI-PHENYL-NITRO-*p*-TOLYL-UREA $NPh_2.CO.NHC_6H_3Me(NO_2)$ [1:4:3]. [139·5°]. Formed from nitro-*p*-toluidine and $NPh_2.COCl$ at 125° (Lellmann a. Bonhöffer, *B.* 20, 2121). Yellow needles, v. sol. chloroform and benzene.

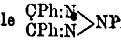
PHENYL-OCTINOIC ACID $C_{14}H_{16}O_2$ *i.e.* $PhC(C_2H_3)(C_2H_2Et).CO_2H$ (310°–320°). This appears to be one of the products of the action of CO at 170° on a mixture of NaOEt and $PhCH_2.CO_2Na$ (M. Schroeder, *A.* 221, 46).

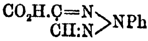
PHENYL-OCTOIC ACID. *Nitrile.* $C_6H_{13}.CHPh.CN$. (287°). Formed from phenyl-acetonitrile, hexyl iodide, and NaOH (Rossolymo, *B.* 22, 1237). Oil.

DI-PHENYL-*n*-OCTYL TRICYANIDE $C_8H_{17}.C_3N_3Ph_2$. [43°]. (285° at 15 mm.). Formed from $C_8H_{17}.COCl$, benzonitrile, and $AlCl_3$ (Krafft a. Koenig, *B.* 23, 2384).

PHENYL-OCTYL-THIO-UREA $C_{15}H_{24}N_2S$ *i.e.* $C_8H_{17}NH.CS.NHPh$. [53°]. Formed from aniline and *sec*-octyl-thiocarbimide (Jahn, *B.* 8, 804).

ν-PHENYL-OSOTRIAZOLE $C_8H_7N_3$ *i.e.*  $\left.\begin{array}{l}CH{:}N\\CH{:}N\end{array}\right>NPh$. [224°]. Formed by warming the osotetrazone of glyoxal with $FeCl_3$ and HClAq (Pechmann, *A.* 262, 291). Sl. sol. water, v. sol. alcohol. HNO_3 yields  $\left.\begin{array}{l}C(NO_2){:}N\\CH{=\!=}N\end{array}\right>NPh$ [184°].

Tri-phenyl-osotriazole  $\left.\begin{array}{l}CPh{:}N\\CPh{:}N\end{array}\right>NPh$. [122°]. Formed by heating the diphenyl-dihydrazide of benzil with alcohol at 210° (Auwers a. V. Meyer, *B.* 21, 2806). White plates.

PHENYL-OSOTRIAZOLE CARBOXYLIC ACID  $\left.\begin{array}{r}CO_2H.C{=}N\\CH{:}N\end{array}\right>NPh$. [192°]. Formed by oxidising phenyl-methyl-osotriazole with $KMnO_4$ (Von Pechmann, *B.* 21, 2760). Formed also by boiling the phenyl-hydrazide of di-nitroso-acetone with NaOHAq (Pechmann, *A.* 262, 283). White needles, sol. alcohol, not volatile with steam. Yields a nitro-compound [236°] which may be reduced to an amido-compound [252°].

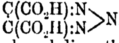
Salts.—KA' aq.—BaA'_2 4aq.—CdA'_2 4aq.

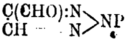
Methyl ether MeA'. [90°]. (286°).

Ethyl ether EtA'. [59°]. (306°).

Amide $C_2N_3HPh.CONH_2$. [143·5°]. Formed by boiling the phenyl-hydrazide of acetyl-di-nitroso-acetone with Na_2CO_3Aq (P.). Needles.

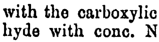
Nitrile $C_2HN_3Ph.CN$. [94·5°]. (191° at 60 mm.). Formed by the action of NaOH on the phenyl-hydrazide of di-nitroso-acetone (Pechmann, *A.* 262, 297). Plates, v. sol. ether. H_2S and alcoholic NH_3 convert it into the thio-amide $C_2HN_3Ph.CS.NH_2$ [132°].

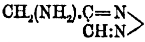
Phenyl-osotriazole dicarboxylic acid  $\left.\begin{array}{l}C(CO_2H){:}N\\C(CO_2H){:}N\end{array}\right>NPh$. [256°]. Formed by oxidising phenyl-di-methyl-osotriazole with $KMnO_4$ (Pechmann, *A.* 262, 311). Crystalline powder. After fusion it melts at 184°.—CaA'': needles.—Ag_2A''.

PHENYL-OSOTRIAZOLE CARBOXYLIC ALDEHYDE  $\left.\begin{array}{l}C(CHO){:}N\\CH\;-\;-\;N\end{array}\right>NPh$. [70°]. Formed by boiling its oxim with dilute H_2SO_4 (Pechmann, *A.* 262, 294). Insol. cold water.

Oxim $C_2HPhN_3.CH{:}NOH$. [115°]. A product of the action of alkalis on the compound $CH(NOH).C(N_2HPh).CH(NOAc)$.

Phenyl-hydrazide $C_2HPhN_3.CH{:}N_2HPh$. [118°–140°]. Plates, v. sol. alcohol.

PHENYL-OSOTRIAZYL ALCOHOL  $\left.\begin{array}{r}CH_2(OH).C{=}N\\CH{:}N\end{array}\right>NPh$. [67°]. Formed, together with the carboxylic acid, by warming the aldehyde with conc. NaOHAq (Pechmann, *A.* 262, 296). Prisms, v. e. sol. alcohol, sl. sol. cold Aq.

PHENYL-OSOTRIAZYL-AMINE $C_9H_{10}N_4$ *i.e.*  $\left.\begin{array}{r}CH_2(NH_2).C{=}N\\CH{:}N\end{array}\right>NPh$. (233° at 100 mm.). Formed from $C_2HPhN_3.CS.NH_2$ by treatment in alcoholic solution with Zn and HCl (Pechmann, *A.* 262, 300).—$B'HCl$. [229°]. Tables.—$B'_2H_2PtCl_6$. Prisms.—**Di-thio-carbamate.** [123°]. Tables.

PHENYL-OXALACETIC ETHER $C_{14}H_{16}O_5$ *i.e.* $CO_2Et.CO.CHPh.CO_2Et$. Formed by the action of Na on a mixture of oxalic ether and phenyl-acetic ether (Wislicenus, *B.* 20, 591; *A.* 246, 339). Oil, decomposed by distillation, v. sol. alkalis. $FeCl_3$ colours its alcoholic solution red. Boiling dilute H_2SO_4 gives CO_2 and phenyl-pyruvic acid [155°].

Phenyl-hydrazide $CO_2Et.C(N_2HPh).CHPh.CO_2Et$. [70°]. Needles (from dilute alcohol), v. sol. ether.

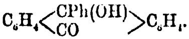
Ethyl ether of the semi-nitrile $CN.CHPh.CO.CO_2Et$. [130°]. Formed from phenylacetonitrile, oxalic ether, and Na or NaOEt (Erlenmeyer, jun., *B.* 22, 1483). Plates. $FeCl_3$ colours its alcoholic solution green.

PHENYL-OXAMIC ACID *v.* Oxalic acid.

PHENYL-OXAMIDE *v.* Oxalic acid.

PHENYL-OXAMIDE CARBOXYLIC ACID *v.* Oxalic acid.

PHENYL-OXANTHRANOL $C_{20}H_{14}O_2$ *i.e.*

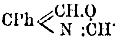


$C_6H_4\left<\begin{matrix}CPh(OH)\\CO\end{matrix}\right>C_6H_4$. [208°]. Formed by oxidation of phenyl-anthranol with $K_2Cr_2O_7$ and HOAc (Baeyer, *A.* 202, 58). Colourless tables, insol. water, sol. alcohol. Conc. H_2SO_4 forms a purple solution. Reduced by zinc-dust and HOAc to phenyl-anthranol. Benzene and H_2SO_4 form crystalline $C_{26}H_{18}O$.

Acetyl derivative $C_{20}H_{13}AcO_2$. [196°].

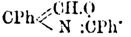
Reference.—Di-chloro- and Oxy-phenyl-oxanthranol.

PHENYL-OXAZOLE C_9H_7NO *i.e.*



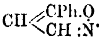
$CPh\left<\begin{matrix}CH.O\\N:CH\end{matrix}\right.$ [6°]. (221°). Formed by heating bromo-acetophenone with formamide at 140° (Lewy, *B.* 20, 2578; Blümlein, *B.* 17, 2580).—B'HCl. [80°].—$B'_2H_2PtCl_6$ 2aq: yellow needles.

Di-phenyl-oxazole



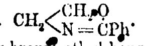
$CPh\left<\begin{matrix}CH.O\\N:CPh\end{matrix}\right.$ [103°]. (339°). Formed by heating ω-bromo-acetophenone with benzamide at 145° (B.; L.). Plates (from alcohol).—B'HCl. Needles.

Phenyl-iso-oxazole



$CH\left<\begin{matrix}CPh.O\\CH:N\end{matrix}\right.$ [23°]. Formed from the oxim of benzoyl-acetic aldehyde and AcCl (Claisen a. Stock, *B.* 24, 134).

PHENYL-OXAZOLE DIHYDRIDE C_9H_9NO *i.e.*



$CH_2\left<\begin{matrix}CH_2.O\\N=CPh\end{matrix}\right.$ (243°). Formed by warming bromo-ethyl-benzamide with alkalis (Gabriel a. Heymann, *B.* 23, 2495). Liquid, smelling like phenyl-thiazole dihydride. Miscible with alcohol and ether, sl. sol. water. HBrAq forms bromo-ethyl-benzamide and $CH_2(OBz).CH_2NH_2$.—$B'_2H_2PtCl_6$.—$B'_2H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$. [177°].

DI-PHENYL OXIDE $C_{12}H_{10}O$ *i.e.* Ph_2O. Mol. w. 170. [28°]. (253°). $\mu_A = 1{\cdot}5675$ at 25°.

Formation.—1. By distilling cupric benzoate (List a. Limpricht, *A.* 90, 190).—2. By warming diazobenzene sulphate or chloride with phenol (Hofmeister, *B.* 3, 747; *A.* 159, 204; Hirsch, *B.* 23, 3709).—3. By heating phenol with $ZnCl_2$ at 350°, the yield being 6 p.c. (Merz a. Weith, *B.* 14, 187).—4. By heating phenol with $AlCl_3$ (M. a. W.).—5. Together with diphenylene ketone oxide and a body melting at 111°, by distilling sodium salicylate with phenyl phosphate (R. Richter, *J. pr.* [2] 28, 273).

Preparation.—By distilling $Al(OPh)_3$ (Gladstone a. Tribe, *C. J.* 41, 6).

Properties.—Prisms (from cold alcohol), smelling like geraniums, almost insol. water and KOHAq. Conc. H_2SO_4 forms $O(C_6H_4.SO_3H)_2$, which forms $Na_2A''x$aq, BaA'', and Ag_2A''.

References.—Di-amido-, Di-bromo-, and Di-nitro- and Di-oxy- Di-phenyl oxide.

PHENYL-OXY-ACETAMIDINE *v.* Mandel-amidine.

PHENYL-OXY-ACETIC ACID *v.* Mandelic acid.

DI-PHENYL-OXY-ANGELIC ACID *v.* *Di-hydro*-corniculario acid.

PHENYL *p*-OXY-BENZYL KETONE $C_6H_5.CO.CH_2.C_6H_4OH$. [129°]. Formed from $CH_2Bz.C_6H_4NH_2$ by the diazo- reaction (Ney, *B.* 21, 2449). White spangles (from water).

Acetyl derivative. [87°]. Plates.

Isomeride *v.* Benzoïn.

PHENYL-OXY-BENZYL-UREA $C_{14}H_{14}N_2O_2$ *i.e.* [1:2] $C_6H_4(OH).CH_2.NH.CO.NHPh$. Formed by warming $C_6H_4(OH).CH_2NH_2$ with phenyl cyanate and benzene. Needles, sol. alcohol and ether.

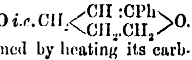
Methyl derivative [1:2] $C_6H_4(OMe).CH_2.NH.CO.NHPh$. [145°]. Formed from $C_6H_4(OMe).CH_2NH_2$ and phenyl cyanate (Goldschmidt a. Ernst, *B.* 23, 2743).

PHENYL-OXY-BROMO-PROPIONIC ACID *v.* Bromo-oxy-phenyl-propionic acid.

PHENYL OXYBUTYL KETONE $C_{11}H_{14}O_2$ *i.e.* $C_6H_5.CO.CH_2.CH_2.CH_2.CH_2OH$. [41°]. Formed by boiling the anhydride of its carboxylic acid with water (Perkin, jun., *C. J.* 51, 733; 57, 310). Iridescent plates, v. sol. alcohol. If left to stand over H_2SO_4 it is converted into the anhydride.

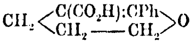
Oxim $C_6H_5.C(NOH).C_4H_8OH$. [57°]. Minute plates, sl. sol. ligroin.

Anhydride $C_{11}H_{12}O$ *i.e.*



$CH_2\left<\begin{matrix}CH:CPh\\CH_2.CH_2\end{matrix}\right>O$. (250° at 720 mm.). Formed by heating its carboxylic acid at 200° (Perkin, *B.* 16, 1792; 19, 2559; *C. J.* 51, 730). Oil. Converted by HBrAq into phenyl bromo-butyl ketone.

PHENYL OXY-BUTYL KETONE CARBOXYLIC ACID. *Anhydride* $C_{12}H_{12}O_3$ *i.e.*



$CH_2\left<\begin{matrix}C(CO_2H):CPh\\CH_2\text{——}CH_2\end{matrix}\right>O$. *Benzoyl-tetramethylene carboxylic acid. Phenyl dehydrohexone carboxylic acid.* [144°]. Formed by saponification of its ether, which is made by the action of trimethylene bromide on sodium benzoyl-acetic ether (Perkin, jun., *C. J.* 51, 726; *B.* 19, 2557). Monoclinic crystals, $a:b:c = 2{\cdot}638:1:3{\cdot}398$; $\beta = 74°41'$. V. sol. alcohol and ether. Converted by conc. HBrAq in the cold into $C_6H_5.CO.C_4H_8Br$.—CaA''.—PbA'': white pp.—AgA': white pp.

Ethyl ether EtA'. [60°]. Monoclinic prisms; $a:b:c = 1{\cdot}002:1:{\cdot}591$; $\beta = 68°\,34'$.

Reference.—Nitro-phenyl oxy-butyl ketone anhydride carboxylic acid.

PHENYL-OXY-BUTYRIC ACID *v.* Oxy-phenyl-butyric acid.

PHENYL OXY-ψ-CUMYL KETONE $C_6H_5.CO.C_6HMe_3OH$. [187°]. Formed by the action of nitrous acid on phenyl amido-ψ-cumyl ketone (Fröhlich, *B.* 17, 1806). Plates, v. sol. alcohol, sol. alkalis.

PHENYL OXYETHYL SULPHONE $C_6H_5.SO_2.C_2H_4OH$. Formed by heating glycollic chlorhydrin with sodium-benzene sulphinate and a little water at 120° (Otto, *J. pr.* [2] 30, 186). Prepared by boiling $C_2H_4(SO_2C_6H_5)_2$ with KOHAq. Liquid, sl. sol. water, miscible with alcohol and ether. *Reactions.* — 1. Conc. H_2SO_4 forms $C_6H_5.SO_2.C_2H_4.O.SO_3H$, which yields $3\frac{1}{2}BaA'_2$ aq, crystallising from water in needles.—2. *Sodium-amalgam* reduces it to alcohol and $Ph.SO_2H$ or PhSH.—3. PCl_5 forms $PhSO_2.C_2H_4Cl$, crystallising from benzene in six-sided tablets [56°].—4. PCl_3 forms the sparingly soluble **anhydride** $(Ph.SO_2.C_2H_4)_2O$ [70°].—5. Aqueous NH_3 at 120° forms $(Ph.SO_2.C_2H_4)_2NH$.—6. *Chromic acid* oxidises it to $Ph.SO_2.CH_2.CO_2H$

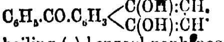
Acetyl derivative $C_{10}H_{12}SO_4$. Oil.

Benzoyl derivative $Ph.SO_2.C_2H_4.OBz$ [125°].

PHENYL OXY-METHYL KETONE *v.* BENZOYL-CARBINOL.

PHENYL-OXY-NAPHTHYL KETONE. *Ethyl derivative* $C_{10}H_6(OEt).CO.C_6H_5$. [75°]. Formed from $C_{10}H_7.OEt$, BzCl, and $AlCl_3$ (Gattermann, *B.* 23, 1209). Needles.

Phenyl-di-oxy-naphthyl ketone


$C_6H_5.CO.C_6H_3<\begin{matrix}C(OH):CH\\C(OH):CH\end{matrix}$ [191°]. Formed by boiling (a)-benzoyl-naphthoquinone with $SnCl_2$ and alcohol (Kegel, *A.* 247, 183). White plates.

Acetyl derivative. [155°]. Plates.

Isomeride *v.* DI-OXY-PHENYL-NAPHTHYL-KETONE.

PHENYL-OXYPHENYLBIAZYL-HYDRAZINE

$\begin{matrix}NPh.N\\CO\ .O\end{matrix}>C.NH.NHPh.$ [181°]. Formed by heating di-phenyl-carbazide with $COCl_2$ at 100° (Freund a. Kuh, *B.* 23, 2831). White crystals, insol. benzene. Oxidised by $FeCl_3$ to $C_2N_2PhO_2.N:NPh$ [200°].

PHENYL-OXY-PHENYLTHIOBIAZYL-HYDRAZINE

$\begin{matrix}NPh.N\\CO-S\end{matrix}>C.NH.NHPh.$ [124°]. Formed by the action of $COCl_2$ on di-phenyl-thiocarbazide, the resulting $C_2N_2PhSO.N:NPh$ [140°] being reduced by alcoholic ammonium sulphide (Freund a. Kuh, *B.* 23, 2827). Needles.

DI-PHENYL-DIOXYPHENYLENE DI-KETONE *v.* DIOXYPHENYLENE DIPHENYL DI-KETONE.

PHENYL-OXY-PIVALIC ACID *v.* β-OXY-PHENYL-VALERIC ACID.

PHENYL-OXY-PROPIONIC ACID *v.* OXY-PHENYL-PROPIONIC ACID.

DI-PHENYL OXYPROPYLENE DISULPHONE $CH(OH)(CH_2.SO_2.C_6H_5)_2$. Formed by oxidation of the product of the action of NaSPh on dichlorhydrin (Otto a. Rössing, *B.* 23, 758). Oil, v. sol. alcohol.

Benzoyl derivative. [150°]. Needles.

DI-PHENYL OXY-PROPYL SULPHONE. *Anhydride* $(C_6H_5.SO_2.CH_2.CH_2.CH_2)_2O$. [85°]. Formed by heating di-phenyl trimethylene di-sulphone with alcoholic potash at 120° (Otto, *B.* 24, 1833). Hexagonal tables, insol. water.

PHENYL OXYTOLYL KETONE. *Methyl derivative.* $C_6H_5.CO.C_6H_3Me.OMe$. [80°]. Formed from $C_6H_4Me(OMe)$, BzCl, and $AlCl_3$ (Koenigs a. Carl, *B.* 24, 3897). Crystals.

PHENYL-OXY-VALERIC ACID *v.* OXY-PHENYL-VALERIC ACID.

Di-phenyl-oxy-valeric acid *v.* *Tetrahydro-*CORNICULARIC ACID.

PHENYL-PARABAMIC ACID *v.* PARABAMIC ACID.

PHENYL-PARACONIC ACID *v.* *Anhydride* of OXY-BENZYL-SUCCINIC ACID and NITRO-PHENYL-PARACONIC ACID.

DI-PHENYL-PENTADECYL TRICYANIDE $C_3N_3Ph_2(CH_2)_{14}CH_3$. [64°]. (328° at 13 mm.). Formed by heating benzonitrile with palmityl chloride and $AlCl_3$ from 40° to 100° (Krafft a. Hansen, *B.* 22, 809). Globular groups of needles (from isobutyl alcohol), v. sol. ether.

PHENYL PENTADECYL KETONE $C_6H_5.CO.C_{15}H_{31}$. [59°]. (251° at 15 mm.). Formed from palmityl chloride, benzene, and $AlCl_3$ (Krafft, *B.* 19, 2982; 21, 2266). Plates (from alcohol), sol. ether. Yields benzoic and pentadecoic acids on oxidation.

Reference.—OXY-PHENYL PENTADECYL KETONE.

PHENYL-PENTANE *v.* AMYL-BENZENE.

PHENYL-PENTANE DICARBOXYLIC ACID $CO_2H.C_6H_4.CEt_2.CO_2H$. [198°]. Formed by the action of KOHAq upon its **anhydride**

$C_6H_4<\begin{matrix}CEt_2.CO\\CO\ \ .O\end{matrix}$ [53°], which is got by the action of alcoholic potash and EtI on di-oxy-ethyl-isoquinoline (Pulvermacher, *B.* 20, 2494). Crystalline.—BaA″.—Ag_2A''; yellow powder.

Phenyl-pentane tricarboxylic ether $CHEt(CO_2Et).C(CH_2Ph)(CO_2Et)_2$. (336° cor.). S.G. $\frac{20}{4}$ 1·0899. μ_D = 1·4867 at 20°. Formed from sodium butane tricarboxylic ether and benzyl chloride (Bischoff a. Mintz, *B.* 23, 654). Yields, on saponification, two benzyl-ethyl-succinic acids [157·5°] and [123·5°].

Phenyl-pentane tricarboxylic acid $CMe_2(CO_2H).C(CH_2Ph)(CO_2H)_2$. [178°]. *Ethyl ether* Et_3A'''. (337° cor.). S.G. $\frac{20}{4}$ 1·0950. μ_D = 1·4831 at 20°. Formed in like manner from isobutane tricarboxylic ether (B. a. M.). Yields, on saponification, the acid and also benzyl-di-methyl-succinic acid [155°].

Phenyl-pentane tri-carboxylic acid $CHMe(CO_2H).CH_2.C(CH_2Ph)(CO_2H)_2$. [130°]. One of the acids got by saponifying the product of the action of benzyl chloride on sodium isobutane tricarboxylic ether (Bischoff, *B.* 23, 1947). Plates (from water).

Di-phenyl-pentane tetra-carboxylic ether $CH_2(C(CO_2Et)_2.CH_2Ph)_2$. (c. 280° at 20 mm.). Formed from disodium propane tetra-carboxylic ether and benzyl chloride (Dressel, *A.* 256, 191). Thick oil.

PHENYL-PENTENOIC ACID $C_{11}H_{12}O_2$ *i.e.* $C_6H_5.C_4H_6.CO_2H$. *Hydrocinnamenylacrylic acid.* [31°]. Formed by reduction of phenyl-pentinoic acid by sodium-amalgam (Baeyer a. Jackson, *B.* 13, 122). Plates. Yields di-oxy-phenyl-valeric acid on oxidation by alkaline $KMnO_4$ (Fittig a. Mayer, *A.* 268, 51).

Dibromide. [109°]. Prisms.

PHENYL-PENTINOIC ACID $C_{11}H_{10}O_2$ *i.e.* $C_6H_5.CH:CH.CH:CH.CO_2H$. *Styryl-acrylic acid.* [166°]. Formed from cinnamic aldehyde, Ac_2O, and NaOAc (Perkin, *C. J.* 31, 403; Fittig, *A.* 268, 50). Prisms (from water). On oxidation by alkaline $KMnO_4$ it yields benzoic aldehyde and racemic and oxalic acids (Doebner, *B.* 23, 2374).—SrA'_2 2aq.—Ag_2A''.

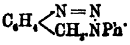
Chloride $C_{12}H_{13}OCl$. [25°].

Amide. [186°]. Tables (from alcohol).

Di-phenyl-pentinoic acid $C_6H_5CH:CH.CH:CPh.CN$. [119°]. Formed from cinnamic aldehyde, phenyl-acetonitrile, and NaOEt (Freund a. Immerwahr, *B.* 23, 2856). Needles, v. sol. alcohol and ether.

Reference.—NITRO- and OXY-PHENYL PENTINOIC ACID.

PHENYL-PHENTRIAZINE. *Dihydride.*


$C_6H_4<\begin{matrix}N=N\\CH_2.NPh\end{matrix}$ [128°]. Formed by adding

$NaNO_2$ to a solution of *o*-amido-benzyl-phenyl-hydrazine or *o*-amido-benzyl-aniline in HClAq at 0° (Busch, *B.* 25, 448). Plates, v. sol. alcohol. Salts.—$B'HCl$.—$B'_2H_2PtCl_6$. [130°].—$B'C_6H_3N_3O_7$. [111°]. Orange-red needles.

PHENYL-PHENTRIAZOLE $C_{12}H_9N_3$ *i.e.* $C_6H_4\lessdot\substack{N\\N}>NPh$. [109°]. Occurs as a by-product in the manufacture of amido-azo-benzene (Gattermann, *B.* 21, 1633). Formed by the action of phenyl-hydrazine on bromo-di-nitro-benzene, the resulting nitro-phenyl-phentriazole $[1:4:5]C_6H_3(NO_2):N_3Ph$ being reduced to amido-phenyl-phentriazole [183°] and NH_2 then eliminated (Kehrmann a. Messinger, *B.* 25, 899).

Isomeride $C_6H_4<\substack{NPh\\N}>N$. *Phenyl-phenylene-azimide.* [90°]. Formed from *o*-amido-diphenylamine and nitrous acid (Schöpff, *B.* 23, 1843). Needles, sol. alcohol.

PHENYL-PHEN-(β)-NAPHTHACRIDINE $C_6H_4<\substack{N\\CPh}>C_{10}H_6$. [198° uncor.]. Formed by heating a mixture of phenyl-(β)-naphthylamine and benzoic acid with P_2O_5 or $ZnCl_2$ (Claus a. Richter, *B.* 17, 1595). Sublimes in white needles.—$B'_2H_2PtCl_6$: glittering yellow needles.

DI-PHENYL PHENYL-ACETYLENE DI-KETONE *v.* DEHYDRO-ACETOPHENONE-BENZIL, vol. i. p. 37.

Di-phenyl-diphenylacetylene diketone *v.* OXYLEPIDEN, vol. iii. p. 137.

PHENYL-PHENYL-AMIDO-ACETIC ACID $C_6H_4Ph.NH.CH_2.CO_2H$. Formed from *p*-amido-diphenyl and chloro-acetic acid (Zimmermann, *B.* 13, 1966). Plates (from hot water).—EtA'. [95°]. Needles (from dilute alcohol).

PHENYL PHENYL-AMIDO-ETHYL KETONE $C_6H_5.CO.C_2H_4NHPh$. [38°]. Formed from $C_6H_5.CO.C_2H_4Br$ and aniline (Pampel a. Schmidt, *B.* 19, 2896). Yellow crystals.

Acetyl derivative. [103°]. Needles.

PHENYL PHENYL-AMYL KETONE $C_{18}H_{20}O$ *i.e.* $C_6H_5.CO.CHPh.CH_2Pr$. [78°]. (330° cor.). Formed from phenyl benzyl ketone, NaOEt, and isobutyl bromide (V. Meyer a. Oelkers, *B.* 21, 1295). Needles. Yields an oxim [118°] crystallising in prisms.

PHENYL-PHENYL-BENZAMIDINE $C_{19}H_{14}N_2$ *i.e.* $CPh\lessdot\substack{NH\\N}>C_6H_3Ph$. [198°]. Formed from $C_6H_3Ph(NO_2).NHBz$, tin, and HOAc (Hübner, *A.* 209, 347). Plates (from alcohol).—$B'HCl$.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$: needles, sl. sol. water.

PHENYL-PHENYL BENZYL KETONE $C_{20}H_{16}O$ *i.e.* $C_6H_4Ph.CO.CH_2Ph$. [150°]. (above 360°). Formed from diphenyl, phenyl-acetic chloride, and $AlCl_3$ (Päpcke, *B.* 21, 1339). Plates (from alcohol). Converted by NaOEt and $CSCl_2$ into $C_6H_4Ph.CO.CPh:CS$ [above 320°].

PHENYL PHENYL-BUTYL KETONE $C_6H_5.CO.CHPhPr$. [33°]. (330°). Formed from sodium deoxybenzoïn and *n*-propyl bromide (Bischoff, *B.* 22, 346). Thread-like needles (from alcohol). Yields an **oxim** [100°].

Phenyl phenyl-isobutyl ketone $C_6H_5.CO.CHPhPr$. [48°]. (325°). Yields an **oxim** [70°] and a phenyl-hydrazide [72°].

DI-PHENYL-DI-PHENYL-CARBINOL $(C_6H_4Ph)_2CH.OH$. [151°]. S. (alcohol) 1·25; (ether) 9; (ligroïn) ·5 at 15°. Got by reducing the corresponding ketone with sodium-amalgam (Adam, *A. Ch.* [6] 15, 260; *cf.* Weiler, *B.* 7, 1189). Plates.

PHENYL-DI-PHENYL-CARBINYLAMINE $C_6H_5.C_6H_4.CHPh.NH_2$. [77°]. Got by reducing the oxim $C_6H_5.C_6H_4.C(NOH).C_6H_5$ by sodium amalgam (Koller, *M.* 12, 508). Needles (from ether), insol. water. Conc. H_2SO_4 forms a deep-violet colour, becoming claret-red on warming.—$B'HOAc$. [161°]. White needles (from water).—$B'HCl$. [252°]. White needles.—$B'HNO_3$. [211°].—$B'_2H_2PtCl_6$4aq. [191°]. Yellow needles.

Phenyl-triphenylcarbinyl-amine $NHPh.CPh_3$. [146°]. Formed from aniline and CPh_3Br (Elbs, *B.* 17, 703; Hemilian a. Silberstein, *B.* 17, 746). Hexagonal prisms, v. sol. CS_2. Yields a nitrosamine [c. 156°] and a tetra-sulphonic acid $C_{25}H_{17}(SO_3H)_4N$ which yields easily soluble Ba_2A^{iv} and Cu_2A^{iv}.

PHENYL TRI-PHENYL-CARBINYL KETONE *v.* (β)-BENZPINACOLIN.

DI-PHENYL-DIPHENYLENE-DI-UREA. $NHPh.CO.NH.C_6H_4.C_6H_4.NH.CO.NHPh$. [above 300°]. Concentric needles (from aniline). Formed by adding phenyl cyanate (2 mols.) to an ethereal solution of benzidine (Kuhn, *B.* 18, 1478).

PHENYL PHENYL-ENNYL KETONE $C_6H_5.CO.CHPh.C_8H_{17}$. [61°]. (350°-355°). Formed from deoxybenzoïn (E. Bischoff, *B.* 22, 348). Yields an oxim [101°] crystallising in long needles.

PHENYLPHENYL-ETHYL ALCOHOL $[1:3]C_6H_4Ph.CHMe.OH$. [86°]. Formed by reducing $C_6H_4Ph.CO.CH_3$ with sodium-amalgam (Adam, *A. Ch.* [6] 15, 257). Crystalline mass. Cannot be distilled.

DI-PHENYL DIPHENYLETHYLENE DI-KETONE $CHPhBz.CHPhBz$. *Bidesyl. Hydro-oxylepiden.* [255°]. Formed as described in vol. iii. p. 139. Needles (from benzene), insol alcohol. On boiling for two hours with alcohol it changes to an isomeride [261°], sol. alcohol (Fehrlin, *B.* 22, 553).

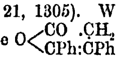
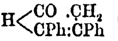
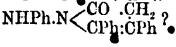
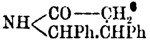
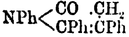
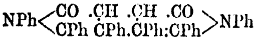
Isomeride. [161°]. *Isobidesyl.* Accompanies bidesyl when prepared from deoxybenzoïn, NaOEt, and I, or from BzCHBrPh, NaOEt, and deoxybenzoïn (Knövenagel, *B.* 21, 1356). Prisms (from alcohol). Reacts with hydroxylamine forming $C_{56}H_{47}N_3O_4$ [110°-120°]. Conc. H_2SO_4 forms with bidesyl and isobidesyl a green solution, turning brown. NH_3 forms tetra-phenyl-pyrrole.

PHENYL PHENYL-ETHYL KETONE $C_6H_5.CO.CHMe.C_6H_5$. [53°]. (318° cor.). Formed from $C_6H_5.CO.CHNa.C_6H_5$ and MeI (V. Meyer a. Oelkers, *B.* 21, 1297). Needles (from alcohol). Forms an oxim [120°].

Phenyl phenyl-ethyl ketone $C_6H_5.CO.CH_2.CH_2.C_6H_5$. [73°]. (above 360°). Formed by reducing phenyl styryl ketone with zinc-dust and HOAc (Schneidewind, *B.* 21, 1325). Plates (from alcohol). Yields an oxim [87°]. Isoamyl nitrite and NaOEt form $C_{15}H_{13}NO_2$ [126°].

Phenyl diphenyl-ethyl ketone $C_6H_5.CO.CHPh.CH_2Ph$. [120°]. Formed from phenyl benzyl ketone, NaOEt, and benzyl chloride (V. Meyer a. Oelkers, *B.* 21, 1300). Needles (from alcohol). Yields an oxim [208°].

PHENYL PHENYL-ETHYL KETONE CARBOXYLIC ACID $C_6H_5.CO.CHPh.CH_2.CO_2H$. [152°] (J. a. M.); [161°] (M. a. O.). Formed by oxidising dehydro-acetone-benzil with CrO_3 and HOAc (Japp a. Miller, *B.* 18, 184). Needles.—BaA'_2 2aq.—AgA'.

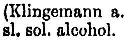
Ethyl ether EtA'. Formed from Ph.CO.CHNaPh and $ClCH_2CO_2Et$ (V. Meyer a. Oelkers, *B.* 21, 1305). When heated it yields an anhydride  $\mathrm{O}<\begin{array}{l}\mathrm{CO\ .CH_2}\\ \mathrm{CPh{:}CPh}\end{array}$ [152°], whence ammonia forms  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\ .CH_2}\\ \mathrm{CPh{:}CPh}\end{array}$ [189°]. Phenyl-hydrazine acting on desylacetic acid forms $C_{22}H_{18}N_2O$ [110°] and $(C_{22}H_{17}N_2O)_2$ [243°]. The former,  $\mathrm{NHPh.N}<\begin{array}{l}\mathrm{CO\ .CH_2}\\ \mathrm{CPh{:}CPh}\end{array}$? may be reduced by Na and isoamyl alcohol to  $\mathrm{NH}<\begin{array}{l}\mathrm{CO—CH_2}\\ \mathrm{CHPh.CHPh}\end{array}$ [207°]. Aniline converts the acid into  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO\ .CH_2}\\ \mathrm{CPh{:}CPh}\end{array}$ [190°] and  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO\ .CH\ .CH\ .CO}\\ \mathrm{CPh\ CPh.CPh{:}CPh}\end{array}>\mathrm{NPh}$ not melted at 300°.

Phenyl phenyl-ethyl ketone carboxylic acid. *Methyl ether* $C_6H_5.CO.CH(CO_2Me).CH_2Ph$. (c. 253° at 50 mm.). Formed from methyl benzoyl-acetate, NaOEt, and benzyl chloride (Perkin a. Calman, *C. J.* 49, 155).

Phenyl di-phenyl-ethyl-ketone carboxylic acid $C_{22}H_{18}O_3$ *i.e.* $C_6H_5.CO.CH_2.CPh_2.CO_2H$. [183°]. Formed by heating the lactone of oxy-tri-phenyl-crotonic acid with alcoholic potash (Japp a. Klingemann, *C. J.* 57, 681). Plates. Reduced by boiling HIAq to tri-phenyl-butyro-lactone. Phenyl-hydrazine in alcoholic solution yields $C_{28}H_{22}N_2O$, which is reduced by Na and isoamyl alcohol to oxy-tri-phenyl-pyrrole di-hydride $C_{22}H_{19}NO$.—NH_4A'.—AgA'. On heating with alcohol and hydroxylamine hydrochloride it forms $C_{22}H_{17}NO_2$ [152°] and $C_{22}H_{17}NO$ [143°].

Methylamide $C_{23}H_{21}NO_2$. [156°]. Formed from tri-phenyl-crotolactone and methylamine.

Ethylamide. [130°]. Needles.

Phenyl tri-phenyl-ethyl ketone carboxylic acid. *Methylamide* $C_6H_5.CO.CHPh.CPh_2.CONHMe$. [260°]. Formed by heating the lactone of oxy-tetra-phenyl-crotonic acid with alcoholic NH_2Me at 100° to 200° (Klingemann a. Laycock, *B.* 24, 514). Plates, sl. sol. alcohol. Yields, on distillation,  $\mathrm{NMe}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{CO\ .CPh_2}\end{array}$ [158°].

PHENYL PHENYL-HEPTYL KETONE $C_6H_5.CO.CHPh.C_6H_{13}$. [59°]. (345°). Needles or plates (from alcohol). Yields an oxim [89°] (Bischoff, *B.* 22, 347).

PHENYL-DI-PHENYL-HYDRAZINE $NHPh.NHC_6H_4Ph$. [127°]. Formed by reducing $C_6H_5.N_2.C_6H_4Ph$ with ammonium sulphide (Locher, *B.* 21, 911). Needles or plates (from dilute alcohol). Yields a di-acetyl derivative [203°].

PHENYL-DI-PHENYL KETONE *v.* PHENYL-BENZOPHENONE.

PHENYL-PHENYL MERCAPTAN $C_{12}H_{10}S$ *i.e.* $C_6H_4Ph.SH$. [111°]. Formed by educing $C_6H_4Ph.SO_2Cl$ with tin and HCl (Gabriel a. Deutsch, *B.* 13, 386).—$Pb(S.C_6H_4Ph)_2$. Reddish-brown pp.—$C_{12}H_9SMe$. [108°]. Needles (*Obermayer, B. 20, 2927*).

DI-PHENYL-DI-PHENYL-METHANE $(C_6H_4Ph)_2CH_2$. [161°]. (360°). Formed from diphenyl, methylal, HOAc, and H_2SO_4 (Weiler, *B.* 7, 1188). Formed also from diphenyl, CH_2Cl_2, and $AlCl_3$; the yield being bad (Adam, *A. Ch.* [6] 15, 254).

DI-PHENYL DI-PHENYL-METHYLENE DISULPHIDE $CPh_2(SPh)_2$. [139°]. Formed by passing dry HCl into a hot mixture of benzophenone, phenyl mercaptan, and $ZnCl_2$ (Baumann, *B.* 18, 889). Prisms (from ether).

PHENYL-PHENYL DI-PHENYL-ETHYL KETONE $C_6H_4Ph.CO.CHPh.CH_2Ph$. [158°]. Formed from $C_6H_4Ph.CO.CH_2Ph$, NaOEt, and benzyl chloride (Päpcke, *B.* 21, 1339). Needles (from alcohol). Yields an oxim [175°].

PHENYL PHENYL-PROPINYL KETONE CARBOXYLIC ACID CPh⋮C.CHBz.CO_2H. [135°]. (c. 275° at 40 mm.). Formed from di-benzoyl-propionic ether and alcoholic potash (Kapf a. Paal, *B.* 21, 1488). Yellow needles or plates, insol. water. Phenyl-hydrazine forms $C_{29}H_{24}N_4O$ [100°]. Boiling with alcohol and HClAq forms di-phenyl-furfurane carboxylic acid [217°]. Alcoholic NH_3 yields di-phenyl-pyrrole carboxylic ether.—KA'2aq: yellow needles (from alcohol).

PHENYL α-PHENYL-PROPYL KETONE $C_6H_5.CO.CHEtPh$. [58°]. (324° cor.). Formed from phenyl benzyl ketone, NaOEt, and EtI (V. Meyer a. Oelkers, *B.* 21, 1299). Needles. Yields an oxim [130°].

Phenyl phenyl-propyl ketone $C_6H_5.CO.CH_2.CHPh.CH_3$ or $C_6H_5.CO.CMe_2Ph$ [70°]. (340°–345° i.V.). Formed by heating acetophenone with HI and P at 140° (Graebe, *B.* 7, 1625). Plates (from alcohol), v. e. sol. ether.

PHENYL DI-PHENYL-PROPYL THIO-UREA $NHPh.CS.NH.CH_2.CHPh.CH_2Ph$. [129°]. Formed from di-phenyl-propyl-amine and phenyl thiocarbimide (Freund a. Remse, *B.* 23, 2862).

PHENYL PHENYL-PYRAZYL KETONE $C_3H_2PhN_2.CO.C_6H_5$. [123°]. Formed by heating phenyl-pyrazole with BzCl at 245° (Balbiano, *G.* 19, 139). Needles (from dilute alcohol). Yields an oxim [154°] and a phenyl-hydrazide [140°].

DI-PHENYL-DI-PHENYL SULPHIDE $C_{24}H_{18}S$ *i.e.* $(C_6H_4Ph)_2S$. [172°]. Formed by distilling $Pb(S.C_6H_4Ph)_2$ (Gabriel a. Deutsch, *B.* 13, 386). Plates, sol. alcohol and ether.

Di-phenyl di-phenyl disulphide $(C_6H_4Ph)_2S_2$. [150°]. Formed by atmospheric oxidation of $C_6H_4Ph.SH$ (G. a. D.). Needles, sol. alcohol and CS_2.

PHENYL-PHENYL SULPHOCYANIDE $C_6H_4Ph.SCN$. [84°]. Formed from $Pb(SC_6H_4Ph)_2$ and ICy (Gabriel a. Deutsch, *B.* 13, 389). White crystals.

DI-PHENYL-DI-PHENYL SULPHONE $(C_6H_4Ph)_2SO_2$. [216°]. Made by oxidising $(C_6H_4Ph)_2S$ with $KMnO_4$ (Gabriel a. Deutsch, *B.* 13, 387). Plates, sl. sol. ether.

PHENYL-PHENYL-SULPHONO-BENZAMIDINE $PhC(NPhH){:}NSO_2Ph$. [139°]. Formed by the action of aniline on the imido-chloride obtained from the anilide of benzene sulphonic acid by the action of PCl_5 (Wallach a. Gossmann, *A.* 214, 214). Narrow plates (from alcohol). Appears not to combine with HCl. On dry distillation it gives di-phenylamine, benzonitrile, SO_2, and phenyl sulphides.

PHENYL-PHENYL-THIOCARBIMIDE $C_6H_4Ph.N:CS$. [58°]. Formed by distilling $(C_6H_4Ph.NH)_2CS$ with P_2O_5 (Zimmermann, *B.* 13, 1964). Needles.

PHENYL PHENYL-THIO-GLYCOLLIC ACID $C_6H_4Ph.S.CH_2.CO_2H$. [170°]. Formed from chloro-acetic acid and $C_6H_4Ph.SNa$ (Gabriel a. Deutsch, *B.* 13, 389). Colourless crystals, sl. sol. water.

Phenyl-phenyl-di-thio-di-glycollic acid $C_{12}H_8(S.CH_2.CO_2H)_2$. [252°]. Formed from $C_{12}H_8S_2Pb$ and $ClCH_2.CO_2H$. Crystals.

DI-PHENYL-DI-PHENYL-THIO-UREA $CS(NH.C_6H_4Ph)_2$ [228°]. Formed from *p*-amido-diphenyl and CS_2 (Zimmermann, *B.* 13, 1963). Plates.

PHENYL PHENYL DI-TOLYL-CARBINYL KETONE *v.* PHENYL-TOLYL-PINACOLIN.

PHENYL-PHENYL-*p*-TOLYL-CARBINYL-UREA $NHPh.CO.NH.CHPh.C_6H_4Me$. [206°]. Formed from $C_6H_4Me.CHPh.NH_2$ and phenyl cyanate (Goldschmidt a. Stöker, *B.* 24, 2802).

PHENYL PHENYL-DI-XYLYL-CARBINYL KETONE *v.* PHENYL-XYLYL-PINACOLIN.

PHENYL PHOSPHATES.

Mono-phenyl di-hydrogen phosphate $C_6H_5O.PO(OH)_2$. *Phenyl-phosphoric acid.* [98°]. A product of the action of P_2O_5 on phenol (Rembold, *Z.* 1866, 652; Jacobsen, *B.* 8, 1519; Rapp, *A.* 224, 157). Deliquescent needles. Partially decomposed by boiling water into phenol and phosphoric acid. Yields phenol and HPO_3 on distillation.—CaA″.—BaA″: prisms.

Chloride $C_6H_5O.POCl_2$. (242°). A product of the action of $POCl_3$ on phenol. Formed also from $C_6H_5O.PCl_4$ and SO_2 (Anschütz a. Emery, *A.* 253, 110).

Di-phenyl hydrogen phosphate $(C_6H_5O)_2PO.OH$. [56°] (R.). A product of the action of P_2O_5 on phenol. Formed also by boiling $(PhO)_3PO$ (1 mol.) with aqueous KOH (1 mol.) (Glutz, *A.* 143, 193), and by decomposing the chloride with water.—BaA'_2.—AgA′.—NH_3PhA'. [c. 160°] (Wallach, *B.* 8, 1235).

Chloride $(C_6H_5O)_2POCl$. (315° at 272 mm.). Formed from phenol and $POCl_3$. Oil, slowly decomposed by water.

Anilide $(C_6H_5O)_2PO.NHPh$. [129°]. Six-sided tables, v. sl. sol. water (W.).

Tri-phenyl phosphate $(C_6H_5O)_3PO$. [45°] (J.). (245° at 11 mm.) (A. a. E.) Formed, together with chloro-benzene, by the action of PCl_5 on phenol (Williamson a. Scrugham, *C. J.* 7, 240). Formed also from phenol and $POCl_3$ (Jacobsen), or PCl_5 (Glutz), followed by water. It is also a product of the action of water on $C_6H_5O.PCl_4$ (Anschütz a. Emery, *A.* 253, 110).

Preparation.—A mixture of phenol (280 pts.) and phosphorus oxychloride (150 pts.) is heated to boiling with an inverted condenser for 16 hours, the excess of phenol is removed by distillation or by shaking with dilute NaOH; the yield is 90 p.c. of the theoretical (Heim, *B.* 16, 1763).

Properties.—Needles, insol. water, sl. sol. alcohol, v. sol. ether.

Reactions.—By distillation with sodium acetate or benzoate it gives phenylacetate or benzoate. Heated with potassium sulphide it yields tri-phenyl-thio-phosphate $PS(OC_6H_5)_3$, together with phenol and some diphenyl and di-phenyl oxide. On distilling with MgO, PbO, ZnO, or CaO the chief product is phenyl, together with some diphenylene-oxide (Kreysler, *B.* 18, 1716). Chlorine passed into its cold ethereal solution forms $(C_6H_5O)_3PCl_2$ (A. a. E.).

Reference.—NITRO-PHENYL-PHOSPHATES.

PHENYL-PHOSPHINE $C_6H_5PH_2$. Mol. w. 110. (161°). S.G. $\frac{15}{15}$ 1·001. A product of the action of alcohol on $C_6H_5PI_3H$ and on $C_6H_5PCl_2$ (Michaelis, *B.* 7, 6; 10, 807; 12, 338; *A.* 181, 303). Pungent liquid.

Reactions.—1. Absorbs oxygen, forming $C_6H_5PHO.OH$ [70°].—2. Sulphur at 100° forms liquid $C_6H_5PH_2S$ and solid $(C_6H_5P)_3S$ [138°].—3. CS_2 at 150° forms $C_{14}H_{12}P_2S_3$.

Salts.—$C_6H_5PH_3I$. Needles.—$B'_2H_2PtCl_6$.

Phenyl-di-chloro-phosphine $C_6H_5PCl_2$. *Phosphenyl chloride.* Mol. w. 179. (225° cor.). S.G. $\frac{0}{4}$ 1·3428 (Thorpe, *C. J.* 37, 347). Formed by passing benzene and PCl_3 through a red-hot tube. Formed also by heating $HgPh_2$ with PCl_3 at 180°, and by the action of $AlCl_3$ on a mixture of benzene and PCl_3 (Michaelis, *B.* 12, 1009; *A.* 181, 280). Pungent fuming liquid, decomposed by water into HCl and $C_6H_5PHO.OH$ [70°]. Chlorine forms $C_6H_5PCl_4$ [73°], which is split up at 180° into C_6H_5Cl and PCl_3, and is converted by water into $C_6H_5PO(OH)_2$. $SbCl_5$ forms $C_6H_5PCl_4SbCl_5$, an unstable yellow crystalline powder. Br yields $C_6H_5PCl_2Br_2$ [208°] and $C_6H_5PCl_2Br_4$. HI forms $C_6H_5PHI_3$. H_2S yields oily $(C_6H_5PS)_2$ and crystalline $C_{24}H_{20}N_2S_3$ [193°]. S forms liquid $C_6H_5PSCl_2$ (270°) (Köhler, *B.* 13, 464).

Phenyl-di-bromo-phosphine $C_6H_5PBr_2$. [257°]. Got from $HgPh_2$ and PBr_3 (Michaelis, *B.* 9, 519). Liquid. Br yields $C_6H_5PBr_4$ [207°] and $C_6H_5PBr_6$.

Di-phenyl-phosphine $(C_6H_5)_2PH$. (c. 280°). S.G. $\frac{12}{12}$ 1·07. Formed, together with the acid $(C_6H_5)_2PO.OH$ by the action of dilute NaOHAq on $(C_6H_5)_2PCl$ (Michaelis a. Gleichmann, *B.* 15, 801; Dörken, *B.* 21, 1508). Oil, v. sol. alcohol. Weak base. Yields $(C_6H_5)_2PO.OH$ on oxidation. CS_2 forms $(C_6H_5)_4P_2H_2CS_2$ [157°].—B′HCl. Crystalline.—$B'_2H_2PtCl_6$.—B′HI.

Di-phenyl-chloro-phosphine $(C_6H_5)_2PCl$. (320°). S.G. $\frac{15}{15}$ 1·229. Formed from $HgPh_2$ and $C_6H_5PCl_2$ at 225° (Michaelis, *B.* 10, 627; 18, 2109; *A.* 207, 208). Formed also by heating $C_6H_5PCl_2$ in a sealed tube for 120 hours at 300° (Dörken, *B.* 21, 1505). Thick liquid, decomposed by water or Na_2CO_3Aq into $(C_6H_5)_2PH$ and $(C_6H_5)_2PO.OH$. Absorbs oxygen from the air forming $(C_6H_5)_2POCl$.

Tri-phenyl-phosphine $P(C_6H_5)_3$. [79°]. (above 360°) (Michaelis, *B.* 15, 802, 1610; *A.* 229, 297). Formed from $C_6H_5PCl_2$, bromo-benzene and Na. Prepared by adding sodium to a mixture of PCl_3 (1 mol.) and C_6H_5Br (3 mols.) diluted with 4 volumes of dry ether and kept cool. The reaction is completed by boiling for 12 hours, and the ether is filtered off and evaporated to crystallisation.

Properties.—Large prisms or tables, sol. alcohol, ether, and benzene, insol. water. Very weak base. Does not combine with CS_2.

Salts.—B′HI. [215°]. Prisms, sol. alcohol, insol. water.—$B'_2H_2PtCl_6$.—$B'HgCl_2$.

Alkylo-halides.—B'MeI. [183°].—B'MeCl aq. [213°]. Crystals, v. e. sol. water and alcohol, insol. ether.—$B'_2Me_2PtCl_6$. [238°]. B'EtI. [165°].—B'PrI. [201·5°].—B'PrI 2aq. [191°].—$B'CH_2PrI$. [177°].—$B'C_5H_{11}I$. [174°].—$B'CH_2PhCl$ aq. [288°].—$B'CH_2PhBr$. [275°].—$B'CH_2PhI$. [253°].—$B'_2CH_2I_2$. [231°].—$B'_2C_2H_4Br_2$. [above 300°].

Benzylo-nitrate $B'C_7H_7NO_3$. [203°]. S. ·338 at 15°. Needles (from water).

Benzylo-picrate $B'C_7H_7C_6H_2N_3O_7$. [248°].

Benzylo-bichromate $(B'C_7H_7)_2Cr_2O_7$.

Benzylo-sulphocyanide $B'C_7H_7SCN$. [189°]. Prisms, v. sol. alcohol, sl. sol. water.

Tri-phenyl-phosphine oxide $(C_6H_5)_3PO$. [153·5°]. (c. 360°). Formed by oxidising tri-phenyl-phosphine with Br_2 and NaOHAq or with conc. HClAq and $KClO_3$. Prisms (containing aq), sl. sol. water, v. e. sol. alcohol. Yields two tri-nitro- compounds [68°] and [242°], the latter of which yields a tri-amido-compound [258°], whence bromine water forms $OP(C_6H_2Br_2(NH_2))_3$ [206°].—$B'HNO_3$. [75°]. Yellow needles, decomposed by water.

Tri-phenyl-phosphine sulphide $(C_6H_5)_3PS$. [157·5°]. Formed from Ph_3P and S in CS_2. Colourless needles, v. sol. alcohol, insol. water.

Tri-phenyl-phosphine selenide $(C_6H_5)_3PSe$. [184°]. Formed from Ph_3P and Se. Needles.

Tetra-phenyl-diphosphine $P_2(C_6H_5)_4$. [67°]. (400°). Formed from $(C_6H_5)_2PCl$ and $(C_6H_5)_2PH$ (Dörken, *B.* 21, 1509). With CS_2 at 138° it forms $Ph_2P.CS.SPH_2Ph_2$ [157°], insol. ether.

PHENYL-PHOSPHINIC ACID *v.* PHENYL-PHOSPHITES.

Di-phenyl-phosphinic acid $(C_6H_5)_2PO.OH$. [190°] (Michaelis, *B.* 8, 922; 11, 885; 15, 802; 18, 2113). Formed by oxidation of $(C_6H_5)_2PCl$ or of di-phenyl-phosphine. Needles, sl. sol. cold alcohol.—CaA'_2 3aq.—AgA': bulky pp.

Ethyl ether EtA'. [165°]. Needles.

Phenyl ether $(C_6H_5)_2PO.OC_6H_5$. [186°]. Formed by oxidising $(C_6H_5)_2POC_6H_5$ (265°–270°), which is got by warming $(C_6H_5)_2PCl$ with phenol. Small needles, sol. hot alcohol, insol. water.

PHENYL PHOSPHITES.

Mono-phenyl dihydrogen phosphite $C_6H_5O.P(OH)_2$. Formed by adding water to $C_6H_5O.PCl_2$ (216°) which is got by the action of PCl_3 on phenol (Noack, *A.* 218, 90; Anschütz, *A.* 239, 310). Uncrystallisable syrup, decomposed by addition of more water into phenol and H_3PO_3.

Isomeride $C_6H_5PO(OH)_2$. *Phenyl phosphinic acid. Phosphenylic acid. Benzene phosphonic acid.* [158°]. S. 23·5 at 15°. Formed by the action of water on $C_6H_5PCl_4$ (Michaelis, *A.* 181, 321). Plates, sol. alcohol and ether. Yields, on nitration, $C_6H_4(NO_2)PO(OH)_2$ [132°], which may be reduced to crystalline $C_6H_4(NH_2).PO(OH)_2$.—NaHA″*x*aq.—Na_2A'' 12aq.—$CaH_2A''_2$.—CaA″ 2aq.—$SrH_2A''_2$aq.—CuA″.—$Fe_2A''_3$ 2½aq.

Ethers.—Me_2A''. (247°).—Et_2A''. (267°).—EtHA″.—EtAgA″.—PhHA″. [57°]. Formed from $C_6H_5POCl_2$ by successive treatment with phenol and boiling water. Needles, sl. sol. water.—Ph_2A''. [63·5°]. Formed from phenol and $C_6H_5PCl_4$.

Chloride $C_6H_5POCl_2$. (258°). Formed from $C_6H_5PCl_4$ and water, and also from $C_6H_5PCl_2$ and O. Thick liquid.

Di-phenyl hydrogen phosphite $(C_6H_5O)_2POH$. Formed by adding a little water to the compound $(C_6H_5O)_2PCl$ (295° at 731 mm.) which is got from phenol and PCl_3 (N.). Uncrystallisable. Decomposed by more water into H_3PO_3 and phenol.

Tri-phenyl phosphite $(C_6H_5O)_3P$. (220° at 11 mm.). S.G. $\frac{15}{15}$ 1·184. Formed by heating phenol (3 mols.) with PCl_3 (1 mol.) at 230° in a current of dry CO_2 (Noack, *A.* 218, 91; Anschütz a. Emery, *A.* 239, 311). Neutral liquid, v. sol. alcohol. Decomposed by water into phenol and H_3PO_3. Dry bromine forms $(C_6H_5O)_3PBr_2$, which is converted by water into $(C_6H_5O)_3PO$.

PHENYL-PHTHALIDE *v. Anhydride* of OXY-BENZYL-BENZOIC ACID.

Di-phenyl-phthalide *i.e.* $C_6H_4<\begin{smallmatrix}CPh_2\\CO\end{smallmatrix}>O$. *Phthalophenone. Tri-phenyl-carbinol carboxylic anhydride.* [115°]. Formed by the action of $AlCl_3$ on a mixture of benzene and phthalyl chloride (Friedel a. Crafts, *A. Ch.* [6] 1, 523, Baeyer, *B.* 12, 612; *A.* 202, 50) or of benzene with [1:2] $C_6H_4Bz.CO.OAc$ (Von Pechmann, *B.* 14, 1866). Got also by heating phthalyl chloride with $HgPh_2$ (Noelting, *B.* 17, 387). Plates (from alcohol). Insol. KOHAq, sol. boiling alcoholic potash, but reppd. by acids.

Reference.—DI-AMIDO-DI-PHENYL-PHTHALIDE.

DI-PHENYL-PHTHALIDE CARBOXYLIC ACID *v. Anhydride* of TRI-PHENYL-CARBINOL DI-CARBOXYLIC ACID.

PHENYL-PHTHALIMIDE *v. Phenyl-imide* of PHTHALIC ACID.

PHENYL-PHTHALIMIDINE $C_{14}H_{11}NO$ *i.e.* $C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>NPh$. [160°]. Got by heating phthalide with aniline at 210° (Hessert, *B.* 10, 1450; 11, 239; Racine, *A.* 239, 88). Formed also by reducing the phenylimide of phthalic acid with tin and HClAq (Graebe, *A.* 217, 305). Plates (from alcohol), v. sl. sol. hot water.

PHENYL-PIPERAZINE *v.* PHENYL-PYRAZINE HEXAHYDRIDE.

PHENYL-PIPERIDINE *v.* PHENYL-PYRIDINE HEXAHYDRIDE.

PHENYL-PROPANE *v.* CUMENE.

Di-phenyl-propane $CH_2(CH_2Ph)_2$. *Di-benzyl-methane.* (290°–300°). Formed by heating di-benzyl ketone with HIAq and P at 180° (Graebe, *B.* 7, 1623). Got also from $CH_2Cl.CHCl.CH_2Cl$, benzene, and $AlCl_3$ (Claus, *B.* 18, 2935). Liquid.

Di-phenyl-propane $CH_2Ph.CHPh.CH_3$. (291°–295°). S.G. $\frac{0}{0}$ ·996. Formed from benzene, $AlCl_3$, and propylene chloride or allyl chloride (Silva, *C. R.* 89, 606). Formed also by adding H_2SO_4 to a cooled mixture of toluene and styrene (Kraemer, Spilker, a. Ebenhardt, *B.* 23, 3274). Oil, sol. alcohol and ether.

Di-phenyl-propane CMe_2Ph_2. (282°). Formed by the action of benzene and $AlCl_3$ on CCl_2Me_2 or $CH_2{:}CCl.CH_3$ (Silva, *Bl.* [2] 34, 674; 35, 289).

Tri-phenyl-propane $C_3H_5(C_6H_5)_3$. (340°). Formed by the action of $AlCl_3$ upon a mixture of benzene and glyceryl tri-bromide or tri-chloride (Claus a. Mercklin, *B.* 18, 2935). Oil.

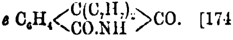
PHENYL-PROPANE TRICARBOXYLIC ACID $CH_2Ph.C(CO_2H)_2.CH_2.CO_2H$. [168·5°]. Formed from benzyl-malonic ether, NaOEt, and chloro-acetic ether (Fittig, *A.* 256, 92).

Small prisms, m. sol. warm water. Yields benzyl-succinic acid [161°] when boiled with water.—$Ca_3A'''_2$ 6½aq.—$Ba_3A'''_2$ 2½aq.—Ag_3A'''.

Ethyl ether Et_3A'''. (336° cor.). S.G. $\frac{20}{4}$ 1·1079. $\mu_D = 1{\cdot}484$ at 20°. Formed from sodium ethane tricarboxylic ether and benzyl chloride (Bischoff a. Mintz, *B.* 23, 653).

Di-phenyl-propane tetra-carboxylic acid. *Di-nitrile of the di-ethyl ether* $(CO_2Et)_2C(CH_2.C_6H_4.CN)_2$. [86°]. Formed from sodium malonic ether and $[1:2]C_6H_4(CN).CH_2Cl$ (Hausmann, *B.* 22, 2019). Prisms.

Tri-phenyl-propane dicarboxylic acid.



Imide $C_6H_4{<}\begin{matrix}C(C_7H_7)_2\\CO.NH\end{matrix}{>}CO$. [174°]. Formed from $C_6H_4{<}\begin{matrix}CH_2.CO\\CO\ .NH\end{matrix}$, benzyl chloride, and NaOEt (Pulvermacher, *B.* 20, 2193). Yellow plates (from alcohol).

Benzyl-imide $C_{30}H_{25}NO_2$. [109°].

PHENYL PROPARGYL OXIDE C_9H_8O *i.e.* $C_6H_5.O.C_3H_3$. (210°). S.G. $\frac{0}{0}$ 1·216. Formed by the action of alcoholic potash on the bromo-allyl derivative of phenol (Henry, *C. R.* 96, 1233). Liquid.

PHENYL-PROPARGYL-UREA $C_{10}H_{10}N_2O$ *i.e.* $CH{:}C.CH_2.NH.CO.NHPh$. [133°]. Formed from propargylamine oxalate, phenyl cyanate, and K_2CO_3Aq (Paal a. Hempel, *B.* 24, 3012). Needles.

PHENYL-PROPENYL-AMIDINE $C_9H_{12}N_2$. [98°]. Formed from propionitrile, HCl, and aniline (Michael a. Wing, *Am.* 7, 72). Hexagonal plates, sol. alcohol and ether.—$B'_2H_2PtCl_6$.

PHENYL PROPENYL METHYL KETONE CARBOXYLIC ACID $C_{12}H_{12}O_3$ *i.e.* $CH_3.CO.C(CH_2.CO_2H){:}CHPh$. [125°]. S. 3 at 100°; ·5 at 15°. Formed by boiling benzoic aldehyde with acetyl-propionic acid and NaOAc (Erdmann, *A.* 254, 187).—$BaA'_2$5aq.—$CdA'_2$2aq.—MgA'_2.—$CaA'_2$3½aq: groups of needles.

Methyl ether MeA'. (c. 215° at 38 mm.).

PHENYL PROPENYL SULPHIDE $C_6H_5.S.CMe{:}CH_2$. (208°). Formed by heating phenyl-sulphydro-crotonic acid (Autenrieth, *A.* 254, 232). Yellowish oil, volatile with steam.

TRI-PHENYL PROPENYL TRISULPHONE $C_3H_5(SO_2Ph)_3$. [226°]. Got from $CHBr(CH_2Br)_2$ and sodium benzene sulphinate (Stuffer, *B.* 23, 1413). Needles, m. sol. hot alcohol.

DI-PHENYL-PROPENYL-DI-UREA

$CEt{\lessgtr}\begin{matrix}N\ .CO.NHPh\\NH.CO.NHPh\end{matrix}$. [170°]. Formed from propionamidine and phenyl cyanate (Pinner, *B.* 23, 2924). Needles, m. sol. alcohol. Yields di-phenyl-urea [234°] when boiled for a long time with alcohol. Boiling dilute HOAc forms $NHPh.CO.NH.CO.C_2H_5$ [137°].

PHENYL-PROPIOLIC ACID $C_9H_6O_2$ *i.e.* $C_6H_5.C{:}C.CO_2H$. Mol. w. 146. [137°].

Formation.—1. By the action of Na and CO_2 on ω-bromo-styrene (Glaser, *Z.* [2] 4, 328; *A.* 154, 140).—2. By boiling αβ-di-bromo-phenyl-propionic acid or its ether with alcoholic potash (G.; Perkin, jun., *C. J.* 45, 173; Weger, *A.* 221, 70; Roser, *A.* 247, 138).—3. By boiling α-bromo-cinnamic acid with alcoholic potash (G.; Bairisch, *J. pr.* [2] 20, 181).

Properties.—Trimetric twin crystals. Reduced by zinc and HOAc to cinnamic acid (Aronstein a. Hollemann, *B.* 22, 1181) and by sodium-amalgam to phenyl-propionic acid. Dry HCl passed through its solution in HOAc forms two chloro-cinnamic acids [142°] and [132°] (Michael, *J. pr.* [2] 40, 63).

Salts.—KA'.—BaA'_2aq: square tables.—$BaA'_2$2aq: needles.—$BaA'_2$3aq.—$CuA'_2$4aq.—AgA': sparingly soluble pp.

Ethyl ether EtA'. (260°-270°).

References.—AMIDO- and NITRO- PHENYL-PROPIOLIC ACID.

α-PHENYL-PROPIONIC ACID $C_9H_{10}O_2$ *i.e.* $CH_3.CHPh.CO_2H$. *Hydratropic acid.* (268°). Formed by reducing atropic acid (15 g.) with (5 p.c.) sodium-amalgam (90 g.) (Trinius, *A.* 227, 262; *cf.* Kraut, *A.* 148, 244; Fittig, *A.* 195, 165). Got also from acetophenone by treatment with HCy, the resulting $CH_3.CPh(OH).CN$ being saponified and the oxy-phenyl-propionic acid reduced by HI and P (Janssen, *A.* 250, 135). Oil, with characteristic odour. Yields atrolactic acid $CH_3.CPh(OH).CO_2H$ on oxidation by alkaline $KMnO_4$.—$BaA'_2$2aq.—$CaA'_2$3aq.—$CaA'_2$2aq.—AgA': plates (from hot water).

Methyl ether MeA'. (221°).

Ethyl ether EtA'. (230°). S.G. $\frac{20}{4}$ 1·0147. R_∞ = 83·3 (Brühl).

Amide $CHMePh.CONH_2$. [92°]. Plates.

Nitrile CHMePh.CN. (232°). Formed by the action of PCl_5 on the amide, and from sodium phenyl-acetonitrile and MeI (Oliveri, *G.* 18, 572).

β-Phenyl-propionic acid $CH_2Ph.CH_2.CO_2H$. *Hydrocinnamic acid.* Mol. w. 150. [48·7°]. (280° i.V.). H.C.v. 1,084,600. H.C.p. 1,085,500. H.F. 105,500 (Stohmann, *J. pr.* [2] 40, 135). S. ·6 at 20°. A product of the putrefaction of albumen, 20 g. being got from 5 kilos of ox-brain (Stöckly, *J. pr.* [2] 24, 17).

Formation.—1. By reduction of cinnamic acid by sodium-amalgam or HI (Erlenmeyer, *A.* 121, 375; 137, 327; Popoff, *Bl.* [2] 4, 375; Giacosa, *H.* 8, 108).—2. By reducing αβ-di-bromo-phenyl-propionic acid (Schmitt, *A.* 127, 319).—3. From ethyl-benzene *viâ* $CH_2Ph.CH_2Cl$ and $CH_2Ph.CH_2.CN$ (Fittig, *Z.* 1869, 166; *A.* 156, 249).—4. By oxidising phenyl-propyl alcohol (W. von Miller, *B.* 9, 274).—5. By heating benzyl-malonic acid (Conrad, *A.* 204, 176).

Properties.—Needles (from water), sol. alcohol and ether; volatile with steam. When taken internally it is secreted as hippuric acid (E. a. H. Salkowski, *B.* 12, 653).

Salts.—NH_4A'. Plates, v. e. sol. water.—CaA'_2 1½aq.—$CaA'_2$2aq.—$BaA'_2$2aq.—PbA'_2aq. ZnA'_2.—AgA'. Phenyl-hydrazine salt: [57°]; silky needles (Liebermann, *B.* 24, 1107).

Methyl ether MeA'. (239° cor.). S.G. $\frac{0}{0}$ 1·0455. S.V. 196·0. Liquid, with peculiar odour.

Ethyl ether EtA'. (248° cor.). S.G. $\frac{0}{0}$ 1·0343. S.V. 221·5 (Lossen, *A.* 254, 63).

n-Propyl ether PrA'. (262° cor.). S.G. $\frac{0}{0}$ 1·0152 (Weger, *A.* 221, 79). S.V. 246.

Isoamyl ether $C_5H_{11}A'$. (292°). S.G. $\frac{0}{0}$ ·981; ^{49} ·952 (E.).

Benzyl ether C_7H_7A'. (c. 300°). S.G. $\frac{21}{17{\cdot}5}$ 1·074. Formed by warming benzyl acetate with sodium (Conrad a. Hodgkinson, *B.* 10, 254; *A.* 193. 300).

Amide $C_9H_{11}NO$. [105°]. Formed by heating the ammonium salt at 230° (Hofmann, *B.* 18, 2740). Small needles.

Nitrile C_9H_9N. (261° cor.). S.G. $\frac{15}{15}$ 1·0014.

Occurs in the oil of *Nasturtium officinale* (Hofmann, *B.* 7, 520).

Di-α-phenyl-propionic acid $CH_3.CPh_2.CO_2H$. [178°]. (above 300°). Made by oxidation of the (β)-pinacolin of acetophenone $CPh_2Me.CO.CH_3$ [41°] with chromic acid mixture (Thörner a. Zincke, *B.* 11, 1993). Formed also by dissolving pyruvic acid and benzene in H_2SO_4 at 0° (Böttinger, *B.* 14, 1595). White leaflets, sol. ether, alcohol, and hot water.—KA′—CaA′$_2$ 1½aq.—BaA′ 2aq.—AgA′: white pp.

αβ-Di-phenyl-propionic acid $CH_2Ph.CHPh.CO_2H$. [84°]. Formed by the action of sodium-amalgam on a mixture of benzyl chloride and $ClCO_2Et$ (Wurtz, *C. R.* 70, 350). Got also by reducing phenyl-cinnamic acid (Oglialoro, *J.* 1878, 821). Needles, sl. sol. boiling water.—CaA′$_2$.—PbA′$_2$. [146°].—AgA′.

Nitrile $CH_2Ph.CHPh.CN$. [58°]. (c. 335°) (Janssen, *A.* 250, 133).

Di-β-phenyl-propionic acid $CHPh_2.CH_2.CO_2H$. [145°]. Formed from allo-cinnamic acid, benzene, and H_2SO_4 (Liebermann a. Hartmann, *B.* 25, 960). Needles.—CaA′$_2$.

ααβ-Tri-phenyl-propionic acid $CH_2Ph.CPh_2.CO_2H$. [162°]. Formed by saponifying the nitrile with HOAc and fuming HClAq at 220° (Neure, *A.* 250, 147). White needles, v. sl. sol. water.—AgA′: white insoluble powder.

Nitrile $CH_2Ph.CPh_2.CN$. [126°]. Formed from $CHPh_2.CN$, benzyl chloride, and NaOEt.

Tri-β-phenyl propionic acid $Ph_3C.CH_2.CO_2H$. [177°]. Formed from $Ph_3C.CH(CO_2Et)_2$ by boiling with alcoholic potash (Henderson, *C. J.* 51, 226; *B.* 20, 1014). Prisms (from alcohol), v. sl. sol. water.—KA′aq.—NaA′aq.—BaA′$_2$aq.—AgA′. Minute needles.

Ethyl ether EtA′. [81°].

References.—AMIDO-, AMIDO-SULPHO-, BROMO-, BROMO-SULPHO-, BROMO-AMIDO-, BROMO-NITRO-, CHLORO-, IODO-, IODO-OXY-, NITRO-AMIDO-, NITRO-OXY-, NITRO-, OXY-AMIDO- and OXY- PHENYL-PROPIONIC ACID.

PHENYL-PROPIONIC ALDEHYDE $C_6H_5.CH_2.CH_2.CHO$. [208°]. Formed from *n*-cumene by successive treatment with CrO_2Cl_2 and water (Étard, *A. Ch.* [5] 22, 254). Oil. Forms a crystalline compound with $NaHSO_3$.

Oxim. Oil. Yields a solid hydrochloride. Ac_2O rapidly forms phenyl-propionitrile; hence it is a *syn-* oxim (Dollfus, *B.* 25, 1918).

PHENYL-PROPYL ALCOHOL $C_9H_{12}O$ *i.e.* $CHPhEt.OH$. Mol. w. 136. (216°). S.G. ^{0} 1·016. Formed by reducing phenyl ethyl ketone with sodium-amalgam (Errera, *G.* 16, 322; *cf.* Barry, *B.* 6, 1007. Got also from benzoic aldehyde by successive treatment with $ZnEt_2$ and water (Wagner, *Bl.* [2] 42, 330). Yields $CHPhEt.OAc$ (228° i.V.) and oily $CHPhEtCl$.

Phenyl-propyl alcohol $CH_2Ph.CH_2.CH_2OH$. (235° uncor.) (213° at 360 mm.). S.G. $\frac{20}{4}$ 1·0079. μ_β 1·5478. $R_\infty = 68·79$ (Brühl, *A.* 200, 191). Occurs in storax as phenyl-propyl cinnamate (Miller, *A.* 188, 202). Prepared by reducing cinnamyl alcohol with sodium-amalgam (Rügheimer, *B.* 6, 214; *A.* 172, 123; Hatton a. Hodgkinson, *C. J.* 39, 319; Errera, *G.* 16, 310). Viscid oil. Heating with conc. HClAq yields $CH_2Ph.CH_2.CH_2Cl$ (219°), whence NaOEt forms $CH_2Ph.CH_2.CH_2OEt$ (220°).

Acetyl derivative $C_3H_6Ph.OAc$. (245°).

Phenyl-isopropyl alcohol $CH_2Ph.CH(OH).CH_3$. *Methyl-benzyl-carbinol.* (215°). Got by reducing benzyl methyl ketone (E.). Liquid, with pleasant odour.

Di-phenyl-propyl alcohol $CH_2Ph.CHPh.CH_2OH$. (301°). Formed by warming di-phenyl-propylamine nitrite (Freund a. Remse, *B.* 23, 2863). Oil, sol. alcohol.

PHENYL-PROPYL-AMINE $C_9H_{13}N$ *i.e.* $CH_2Ph.CH_2.CH_2NH_2$. (222° i.V.). Formed by reducing the phenyl-hydrazide (20 g.) of cinnamic aldehyde dissolved in alcohol (300 g.) by (2½ p.c.) sodium-amalgam (700 g.) and HOAc (70 g.) at about 30°, the yield being 30 p.c. of the theoretical (Tafel, *B.* 19, 1930; 22, 1857). Liquid, m. sol. water, miscible with alcohol and ether. Absorbs CO_2 from air, forming a crystalline mass. The aqueous solution is strongly alkaline.—B′HCl. [218°]. Plates.—B′H_2SO_4.—B′$_2H_2C_2O_4$. [156°]. Needles.—B′$H_2C_2O_4$.—B′$_2H_2PtCl_6$. Plates, sol. hot water.

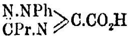
Phenyl-isopropyl-amine $CH_2Ph.CHMe.NH_2$. (203°). Formed by the action of Br and KOHAq on the amide of phenyl-isobutyric acid (Edeleano, *B.* 20, 618). Liquid.—B′$_2H_2PtCl_6$. Needles.

Isomeride *v.* CUMIDINE.

Di-phenyl-propyl-amine $CH_2Ph.CHPh.CH_2NH_2$. (316°). Formed by reducing the nitrile (30 g.) of phenyl-cinnamic acid dissolved in alcohol by treatment with Na (75 g.) (Freund a. Remse, *B.* 23, 2860). Liquid, sol. alcohol. Forms with $HgCl_2$ a crystalline compound [107°].—B′HCl. [190°]. Needles.—Aurochloride [145°].

Di-acetyl derivative. [85°]. Needles.

PHENYL-*n*-PROPYL-TRIAZOLE CARBOXYLIC ACID

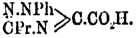


$\left.\begin{array}{l}\text{N.NPh}\\ \text{CPr.N}\end{array}\right\rangle\text{C.CO}_2\text{H}$. [161°].

Formed by saponifying the nitrile which is made from phenyl-hydrazine dicyanide and butyric anhydride (Bladin, *B.* 25, 179). Cubes (from alcohol) or prisms (from benzene).—CuA′$_2$ ½aq.—AgA′. Bulky white pp.

Amide $C_2N_3PhPr.CO.NH_2$. [122·5°]. The thio-amide $C_2N_3PhPr.CS.NH_2$ [130·5°] is got by the action of alcoholic ammonium sulphide on the nitrile.

Phenyl-isopropyl-triazole carboxylic acid



$\left.\begin{array}{l}\text{N.NPh}\\ \text{CPr.N}\end{array}\right\rangle\text{C.CO}_2\text{H}$. [155°]. Formed in like manner (B.). Prisms.—HA′HCl. Needles.—CuA′$_2$ 2½aq.—AgA: minute tables.

Methyl ether MeA′. [76°].

Amide. [128°]. Needles. The thio-amide $C_2N_3PhPr.CS.NH_2$ [148°], formed by the action of alcoholic NH_3 and H_2S on the crude nitrile, crystallises in yellow needles.

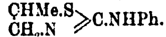
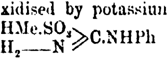
DI-PHENYL-DI-ISOPROPYL-TETRAZONE $NPhPr.N{:}N.NPhPr$. [79°]. Formed by oxidising phenyl-isopropyl-hydrazine with HgO (Michaelis a. Philips, *A.* 252, 281). Octahedra.

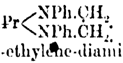
DI-PHENYL-PROPYL TRICYANIDE

$\text{CPh}\left\langle\begin{array}{l}\text{N.CPr}\\ \text{N:CPh}\end{array}\right\rangle\text{N}$. [78·5°]. (239° at 15 mm.).

Formed from benzonitrile, butyryl chloride, and $AlCl_3$ at 75° (Krafft a. Von Hansen, *B.* 22, 807). Decomposed by dilute H_2SO_4 into NH_3, butyric acid, and HOBz.—B′$_2H_2PtCl_6$. Needles.

PHENYL-PROPYLENE *v.* ALLYL-BENZENE.

PHENYL PROPYLENE - ψ - THIO - UREA $C_{10}H_{12}N_2S$ *i.e.*  $\left.\begin{matrix}\mathrm{CHMe.S}\\ \mathrm{CH_2.N}\end{matrix}\right>\mathrm{C.NHPh}$. [117°]. Formed from the isomeric phenyl-allyl-thio-urea [95°] and HClAq at 100° (Prager, *B.* 22, 2992). Oxidised by potassium chlorate and HClAq to  $\left.\begin{matrix}\mathrm{CHMe.SO_3}\\ \mathrm{CH_2{-}{-}{-}N}\end{matrix}\right>\mathrm{C.NHPh}$ [192°]. — $B'_2H_2PtCl_6$. — $B'C_6H_3N_3O_7$. [154°]. Yellow needles.

DI - PHENYL - ISOPROPYL - GLYOXALINE TETRA - HYDRIDE  $\mathrm{CHPr}\left<\begin{matrix}\mathrm{NPh.CH_2}\\ \mathrm{NPh.CH_2}\end{matrix}\right.$. [95°]. Formed from di-phenyl-ethylene-diamine and isobutyric aldehyde (Moos, *B.* 20, 734). Crystalline groups (from alcohol), sl. sol. water.

PHENYL-PROPYL-HYDRAZINE $C_9H_{14}N_2$ *i.e.* $C_6H_5NH.NHPr$. [158°]. Formed by heating propionamide with phenyl-hydrazine (Freund, *B.* 21, 2461). Plates (from chloroform).

Phenyl-isopropyl-hydrazine $C_6H_5NPr.NH_2$. (233°). Formed from sodium phenyl-hydrazine and isopropyl bromide (Michaelis a. Philips, *B.* 20, 2485; *A.* 252, 278). – B'HCl. [135°]. Crystalline. Yields a tetrazone [85°]. Phenyl-thio-carbimide forms NPhPr.NH.CS.NHPh. [116°].

Acetyl derivative. [102°]. Needles.

DI-PHENYL-PROPYLIDENE DISULPHIDE $Me_2C(SPh)_2$. [56°]. Formed from phenyl-mercaptan and acetone (E. Baumann, *B.* 19, 2804). Crystals, insol. water, v. sol. alcohol.

DI-PHENYL-PROPYLIDENE DISULPHONE $Me_2C(SO_2Ph)_2$. [97°] (B.); [182°] (F.). Formed by oxidising $Me_2C(SPh)_2$ (Baumann, *B.* 19, 2810), and also by treating $CH_2(SPh)_2$ with NaOH and MeI (Fromm, *A.* 253, 162). Crystals, almost insol. cold water.

PHENYL PROPYL KETONE $C_{10}H_{12}O$ *i.e.* Ph.CO.Pr. Mol. w. 148. (221°). S.G. ^{15} ·992.

Formation. – 1. By distilling calcium butyrate with calcium benzoate (Schmidt a. Fieberg, *B.* 6, 498).—2. By the action of $AlCl_3$ on a mixture of benzene and butyryl chloride (Burcker, *Bl.* [2] 37, 4).—3. By boiling benzoyl-acetic acid with dilute alcoholic potash (Baeyer a. Perkin, *B.* 16, 2131; *C. J.* 45, 181).

Properties. — Oil. Does not unite with $NaHSO_3$. Oxidised by CrO_3 and H_2SO_4 to benzoic and propionic acids (Popoff, *B.* 6, 560). CrO_2Cl_2 forms $C_{10}H_{12}O2CrO_2Cl_2$, a brown powder.

Phenyl isopropyl ketone Ph.CO.Pr. (209°–217°). Formed by distilling calcium isobutyrate with calcium benzoate (Popoff, *B.* 6, 1255). Liquid. Yields benzoic acid, CO_2, and HOAc on oxidation.

Oxim.—Ph.C(NOH)Pr. [58°]. Plates (from ligroïn) (Rattner, *B.* 20, 506).

PHENYL PROPYL KETONE CARBOXYLIC ACID *v. Ethyl-benzoyl-acetic acid*, vol. i. p. 482.

Phenyl isopropyl ketone *o*-**carboxylic acid** $C_{11}H_{12}O_3$ *i.e.* $Pr.CO.C_6H_4.CO_2H$. [121°]. Formed by boiling isopropylidene-phthalide with alcohol and KOHAq (Roser, *B.* 17, 2777). Crystals.

PHENYL - PROPYL METHYL KETONE CARBOXYLIC ACID $CH_2Ph.CHAc.CH_2.CO_2H$. [99°]. (235° at 40 mm.). Formed by reducing benzylidene-β-acetyl-propionic acid with sodium-amalgam in presence of H_2SO_4 (Erdmann, *A.* 254, 203). Needles. It yields on oxidation $\mathrm{CHMe}\left<\begin{matrix}\mathrm{CH(C_3H_7)}\\ \mathrm{O\ .\ CO}\end{matrix}\right>\mathrm{CH_2}$ [86°]. — CaA'_2 3aq. — AgA'.

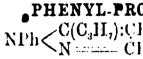
PHENYL METHYLENE PROPYL DI-KETONE *v.* BUTYRYL-ACETOPHENONE.

PHENYL-PROPYL METHYL KETONE $CH_3.CO.CHMe.CH_2Ph$. (239°). Formed by distilling calcium acetate with calcium phenyl-isobutyrate (Von Miller, *B.* 23, 1884). Oil.

PHENYL - PROPYL METHYL KETONE CARBOXYLIC ACID *v.* BENZYL-METHYL-ACETO-ACETIC ACID, vol. i. p. 25.

Di-phenyl-isopropyl methyl ketone tricarboxylic acid. *Ethyl ether of the dinitrile* $CO_2Et.C(CH_2.C_6H_4.CN)_2.CO.CH_3$. [120°]. Formed from sodium acetoacetic ether and the nitrile [1:2] $CH_2Cl.C_6H_4.CN$ (Gabriel a. Hausmann, *B.* 22, 2018). Prisms (from alcohol).

Hexa-phenyl-isopropyl methyl ketone carboxylic acid $C_{42}H_{19}O_4$ *i.e.* $(CPh_3)_2C(CO_2H).CO.CH_3$. [160°]. Formed from sodium acetoacetic ether and $BrCPh_3$ (Allen a. Kölliker, *A.* 227, 111). Crystals (from ether).

PHENYL-PROPYL-PYRAZOLE $C_{12}H_{14}N_2$ *i.e.*  $\mathrm{NPh}\left<\begin{matrix}\mathrm{C(C_3H_7){:}CH}\\ \mathrm{N{=}{=}{=}{=}CH}\end{matrix}\right.$ (280°). S.G. ^{15} 1·0435. Formed from butyryl-acetic aldehyde and phenyl-hydrazine (Claisen a. Stylos, *B.* 21, 1148). Liquid.

PHENYL PROPYL SULPHONE $Ph.SO_2.Pr$. [44°]. Formed by the action of KOHAq at 100° on $Ph.SO_2.CHEt.CO_2H$ [124°], which is made from α-bromo-butyric acid and sodium benzene sulphinate (Michael a. Palmer, *Am.* 7, 67; *cf.* Otto, *B.* 21, 998). Pearly plates, v. sol. alcohol.

TRI - PHENYL - DI - PROPYL - DI - THIO - BIURET $C_2S_2N_3Ph_3Pr_2$. [154°]. Formed by the action of aniline (1 mol.) on NPhPr.CSCl (2 mols.) (Billeter a. Strohl, *B.* 21, 109). Yellow needles.

PHENYL - PROPYL - THIO - CARBAMIC CHLORIDE NPhPr.CS.Cl. [36°]. Formed from propyl-aniline and $CSCl_2$ (Billeter a. Strohl, *B* 21, 102). Prisms (from ligroïn).

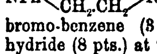
DI - PHENYL - ISOPROPYL - THIO - SEMI - CARBAZIDE NHPh.CS.NH.NPhPr. [116°]. Formed from phenyl-thiocarbimide and phenyl-isopropyl-hydrazine (Michaelis a. Philips, *A.* 252, 280). Crystalline.

PHENYL-PROPYL-THIO-UREA $C_{10}H_{14}N_2S$ *i.e.* $NHPh.CS.NHC_3H_7$. [63°]. Formed from aniline and propyl-thio-carbimide and also from propyl-amine and phenyl thiocarbimide (O. Hecht, *B.* 23, 286). Pearly plates (from dilute alcohol).

Di-phenyl-propyl-thio-urea CSN_2HPh_2Pr. [104°]. Formed by heating propyl-aniline with phenyl-thio-carbimide on the water-bath (Billeter a. Strohl, *B.* 21, 109). Needles.

Di-phenyl-di-propyl-thio-urea $CS(NPhPr)_2$. [103°]. Formed from propyl-aniline and $CSCl_2$ (B. a. S.). Large plates.

DI-PHENYL-PROPYL-UREA $C_{16}H_{18}N_2O$ *i.e.* $NH_2.CO.NH.CH_2.CHPh.CH_2Ph$. [112°]. Formed from di-phenyl-propylamine hydrochloride and potassium cyanate solution (Freund a. Remse, *B.* 23, 2861). Needles, sol. alcohol and ether.

PHENYL-PYRAZINE. *Hexahydride*  $\mathrm{NPh}\left<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}\right>\mathrm{NH}$. Formed by heating bromo-benzene (8 pts.) with pyrazine hexahydride (8 pts.) at 270° (Schmidt a. Wichmann, *B.* 24, 3239). Thick liquid, v. sol. water.

Di-phenyl-pyrazine $C_{16}H_{12}N_2$, *i.e.* $\mathrm{N}\!<\!\begin{matrix}\mathrm{CH{:}CPh}\\\mathrm{CPh.CH}\end{matrix}\!>\!\mathrm{N}$. *Iso-indole.* [196° cor.]. V.D. 7·95 (Treadwell a. Meyer, *B.* 16, 342). Formed by the action of cold alcoholic NH_3 on ω-bromo-acetophenone or on amido-acetophenone (Staedel a. Kleinschmidt, *B.* 11, 1744; 13, 837; Möhlau, *B.* 18, 163; Wolff a. Röders, *B.* 20, 432; Goedeckemeyer, *B.* 21, 2687). Broad yellow needles (from alcohol). — $B'_2H_2PtCl_6$. Bronzed plates (from HClAq) quickly decomposed by water.

Hexahydride $C_{16}H_{18}N_2$. [109°] and [123°]. Formed by reducing di-phenyl-pyrazine with Na and isoamyl alcohol. Occurs in two forms. The (α)-variety [123°] crystallises from ligroïn in white needles, and yields $B''2HCl$ [c. 310°], $B''H_2PtCl_6\frac{1}{2}aq$, and a nitrosamine $C_{16}H_{16}N_6O_4$ [143°]. The (β)-variety [109°] crystallises from alcohol in white needles and yields $B''2HCl$ [c. 295°] and $B''H_2PtCl_6 2aq$.

Di-phenyl-pyrazine $\mathrm{N}\!<\!\begin{matrix}\mathrm{CPh.CPh}\\\mathrm{CH:CH}\end{matrix}\!>\!\mathrm{N}$. [119°]. (c. 340°). Formed by distilling the dihydride (M.). Needles (from ligroïn), ppd. by adding water to its solution in HClAq.—$B'_2H_2PtCl_6$.

Dihydride $\mathrm{N}\!<\!\begin{matrix}\mathrm{CPh.CPh}\\\mathrm{CH_2.CH_2}\end{matrix}\!>\!\mathrm{N}$. [181°]. Formed by boiling benzil with ethylene-diamine and alcohol (Mason, *B.* 20, 268; *C. J.* 55, 97). Prisms (from alcohol), insol. water. Split up by HClAq into the parent substances.

Di-phenyl-pyrazine. *Hexahydride v.* DI-PHENYL-DI-ETHYLENE-DIAMINE.

Tetra-phenyl-pyrazine $\mathrm{N}\!<\!\begin{matrix}\mathrm{CPh{:}CPh}\\\mathrm{CPh.CPh}\end{matrix}\!>\!\mathrm{N}$. *Di-tolane-azotide.* [241°] (P.); [247°] (G.). Formed by heating benzoïn with ammonium acetate (vol. i. p. 477). Formed also by reducing the di-oxim of di-phenyl-glyoxal in alcoholic solution by sodium-amalgam (Polonowska, *B.* 21, 489), and by heating benzoic aldehyde with $CPhH(NH_2).CPhH(NH_2)$ (Grossmann, *B.* 22, 2302). White needles (from HOAc), v. sl. sol. alcohol. Conc. H_2SO_4 gives a blood-red colour.

PHENYL-PYRAZOLE $C_9H_8N_2$ *i.e.* $\begin{matrix}\mathrm{NPh.CH}\\\mathrm{N{=}{=}CH}\end{matrix}\!>\!\mathrm{CH}$. [11°]. (247° cor.). S.G. $\frac{18}{0}$ 1·113. Formed by boiling epichlorhydrin with phenyl-hydrazine and benzene (Balbiano, *G.* 17, 176; 18, 354). Got also by distilling its tricarboxylic acid (Knorr a. Laubmann, *B.* 22, 180). Oil, sol. alcohol and ether. — $B'_2H_2PtCl_6 2aq$: needles, decomposing at 175°.

Ethylo-iodide B'EtI. [117°]. Prisms.

Dihydride $\begin{matrix}\mathrm{NPh.CH_2}\\\mathrm{N{=}{=}CH}\end{matrix}\!>\!\mathrm{CH_2}$. [52°]. (274° at 754 mm.). Formed from phenyl-hydrazine (120 g.) dissolved in ether (600 g.) by addition of arcoleïn (50 g.) in ether (100 g.) (Fischer a. Knoevenagel, *A.* 239, 196). Sl. sol. hot water, v. sol. alcohol, ether, and benzene. Sl. sol. dilute acids, sol. conc. HCl. May be distilled with steam. $K_2Cr_2O_7$ colours its solution in dilute H_2SO_4 reddish-violet, or, in very dilute solutions, blue. Gives no indole derivative when fused with $ZnCl_2$.

Reference. — DI-BROMO-PHENYL-PYRAZOLE DIHYDRIDE.

Tetra-hydride $\begin{matrix}\mathrm{NPh.CH_2}\\\mathrm{NH.CH_2}\end{matrix}\!>\!\mathrm{CH_2}$. (210° at 165 mm.). Formed from tri-methylene bromide, sodium phenyl-hydrazine, and benzene (Michaelis a. Lampe, *B.* 24, 3738). Liquid. — $B'C_6H_3N_3O_7$. Short yellow needles.

Di-phenyl-pyrazole $C_{15}H_{12}N_2$ *i.e.* $\begin{matrix}\mathrm{CH{:}CH}\\\mathrm{CPh{:}N}\end{matrix}\!>\!\mathrm{NPh}$ or $\begin{matrix}\mathrm{CH{:}CPh}\\\mathrm{CH{:}N}\end{matrix}\!>\!\mathrm{NPh}$. [56°]. (336°). Formed by distilling its carboxylic acids (Beyer a. Claisen, *B.* 20, 2187; Knorr a. Laubmann, *B.* 21, 1212; 22, 176). White crystals.

Dihydride $C_{15}H_{14}N_2$. [136°]. Formed by reducing the base. Small needles. An isomeric or identical body [138°], got by distilling the phenyl-hydrazide of cinnamic aldehyde; differs by fluorescing slightly in alcoholic solution.

Tri-phenyl-pyrazole $C_{21}H_{16}N_2$. [206°]. A product of the action of phenyl-hydrazine on anhydro-acetophenone-benzil (Japp a. Klingemann, *C. J.* 57, 709). Stellate groups of needles.

Tri-phenyl-pyrazole $\begin{matrix}\mathrm{CH{:}CPh}\\\mathrm{CPh{:}N}\end{matrix}\!>\!\mathrm{NPh}$. [138°]. Got by warming CH_2Bz_2 with phenyl-hydrazine (Knorr a. Laubmann, *B.* 21, 1205). Plates (from ether). Weak base.

Methylo-iodide B'MeI. [176°].

Dihydride $\begin{matrix}\mathrm{CH_2.CHPh}\\\mathrm{CPh{-}{-}N}\end{matrix}\!>\!\mathrm{NPh}$. [135°]. Got by reduction or by warming benzylidene-acetophene with phenyl-hydrazine and alcohol. Yields $C_{21}H_{15}Br_4N_2$ [179°].

PHENYL-PYRAZOLE CARBOXYLIC ACID $C_{10}H_8N_2O_2$. [220°]. Formed by distilling the tricarboxylic acid (Knorr a. Laubmann, *B.* 22, 180). Needles (from Aq), v. sol. alcohol, sl. sol. ether. May be sublimed. AgA': amorphous pp.

Phenyl-pyrazole dicarboxylic acid $\begin{matrix}\mathrm{C(CO_2H){:}N}\\\mathrm{CH{:}C(CO_2H)}\end{matrix}\!>\!\mathrm{NPh}$. [256°] (B.); [266°] (C. a. R.). Formed by oxidising phenyl-di-methyl-pyrazole or phenyl-methyl-pyrazole carboxylic acid with alkaline $KMnO_4$ (Balbiano, *B.* 23, 1449; Claisen a. Roosen, *B.* 24, 1892). Small white plates in spherical groups (from alcohol). — $(NH_4)_2A''$. [212°].—PbA''.—Ag_2A''.

Methyl ether MeA''. [128°].

Amide $C_3N_2HPh(CO.NH_2)_2$. [190°].

Phenyl-pyrazole tri-carboxylic acid $\begin{matrix}\mathrm{CO_2H.C{=}{=}N}\\\mathrm{CO_2H.C{:}C(CO_2H)}\end{matrix}\!>\!\mathrm{NPh}$. [184°]. Formed by oxidising phenyl-methyl-pyrazole dicarboxylic acid with alkaline $KMnO_4$ (K. a. L.). White needles (containing aq) (from ether), sol. water and alcohol.—$BaHA'''\frac{1}{2}aq$: plates.

Di-phenyl-pyrazole carboxylic acid $C_{16}H_{12}N_2O_2$ *i.e.* $\begin{matrix}\mathrm{CPh{=}{=}N}\\\mathrm{CH{:}C(CO_2H)}\end{matrix}\!>\!\mathrm{NPh}$ or $\begin{matrix}\mathrm{CO_2H.C{=}{=}N}\\\mathrm{CH{:}CPh}\end{matrix}\!>\!\mathrm{NPh}$. Got by saponification of its ether, which is obtained by boiling benzoyl-pyruvic ether $CH_2Bz.CO.CO_2Et$ (20 pts.) with HOAc (100 pts.) and phenyl-hydrazine (10 pts.) (Beyer a. Claisen, *B.* 20, 2185). Crystals (containing EtOH), which melt at 185°, v. sol. acetone.

Ethyl ether EtA'. [90°]. (c. 400°).

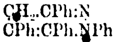
Di-phenyl-pyrazole dicarboxylic acid $C_{17}H_{12}N_2O_4$ *i.e.* $\begin{matrix}\mathrm{CPh{=}N}\\\mathrm{CO_2H.C.C(CO_2H)}\end{matrix}\!>\!\mathrm{NPh}$. [218°]. Got by oxidation of di-phenyl-methyl-pyrazole carboxylic acid (Knorr a. Laubmann, *B.* 22, 175). Satiny needles (containing $\frac{1}{2}$ aq) (from HOAc).—NH_4HA''. [c. 270°].—BaA'' aq.—CaA'' 2aq.

References.—OXY- and OXY-AMIDO- PHENYL-PYRAZOLE CARBOXYLIC ACID.

DI-PHENYL-PYRAZOLONE *v.* OXY-DI-PHENYL-PYRAZOLE.

PHENYL-PYRAZYL METHYL KETONE $C_3N_2H_2Ph.CO.CH_3$. [122° cor.]. Formed by heating ν-phenyl-pyrazole with AcCl at 150° (Balbiano, *G.* 19, 136). Small needles. Yields an oxim [131°] and a phenyl-hydrazide [144°].

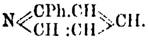
TETRA-PHENYL-PYRIDAZINE DIHYDRIDE $C_{28}H_{22}N_2$ *i.e.*



$\begin{matrix}\mathrm{CH_2.CPh{:}N}\\ \mathrm{CPh{:}CPh.NPh}\end{matrix}$

? [149°]. Formed from desyl-acetophenone, phenyl-hydrazine, and HOAc (Smith, *C. J.* 57, 649). Yellow needles (from alcohol), v. sol. hot HOAc. According to Klingemann (*A.* 269, 106), this body is probably phenyl-amido-tri-phenyl-pyrrole, since on boiling with HOAc it yields tetra-phenyl-pyrrole.

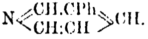
(α)-PHENYL-PYRIDINE



$\mathrm{N}\left<\begin{matrix}\mathrm{CPh.CH}\\ \mathrm{CH{:}CH}\end{matrix}\right>\mathrm{CH}$.

(270°). A product of the distillation of its di-carboxylic acid with lime (Skraup a. Cobenzl, *M.* 4, 472). Heavy oil. Yields picolinic acid on oxidation.—$B'_2H_2PtCl_6$ 2aq.—Picrate [c. 170°].

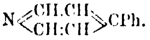
(β)-Phenyl-pyridine



$\mathrm{N}\left<\begin{matrix}\mathrm{CH.CPh}\\ \mathrm{CH{:}CH}\end{matrix}\right>\mathrm{CH}$.

(270°). Formed by distilling its carboxylic acid with lime (Skraup a. Cobenzl, *M.* 4, 453). Got also by heating pyrrole with benzylidene chloride and NaOEt (Ciamician a. Silber, *B.* 20, 191). Heavy oil. Yields nicotinic acid on oxidation. — $B'_2H_2PtCl_6$ 3aq. — $B'C_6H_3N_3O_7$. [163°]. Groups of yellow needles.

(γ)-Phenyl-pyridine

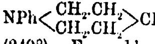


$\mathrm{N}\left<\begin{matrix}\mathrm{CH.CH}\\ \mathrm{CH{:}CH}\end{matrix}\right>\mathrm{CPh}$.

[78°]. (275° uncor.). Formed by distilling its tetra-carboxylic acid with lime (Hantzsch, *B.* 17, 1518). Plates (from water). Yields iso-nicotinic acid [304°] on oxidation.—$B'_2H_2PtCl_6$.—$B'_2H_2Cr_2O_7$. [155°]. Orange needles. — Picrate. [196°]. Yellow needles.

Hexahydride $C_5H_{10}PhN$. [58°]. (256° at 727 mm.). Got by reducing the base (Bally, *B.* 20, 2590). Strong base, almost insol. water.—B'HCl. Needles.—$B'_2H_2PtCl_6$. [204°–207°].

ν-Phenyl-pyridine hexahydride

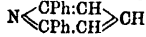


$\mathrm{NPh}\left<\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}\right>\mathrm{CH_2}$.

Phenyl-piperidine. (249°). Formed by heating piperidine with iodo-benzene or bromo-benzene at 260° (Lellmann, *B.* 20, 680; 21, 2279. Alkaline oil, v. sol. alcohol and ether.—$B'_2H_2PtCl_6$ 2aq: needles or plates.—$B'H_2Cr_2O_7$: plates.

References.—AMIDO- and NITRO- PHENYL-PIPERIDINE.

Di-(α)-phenyl-pyridine $C_{17}H_{13}N$ *i.e.*



$\mathrm{N}\left<\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh.CH}\end{matrix}\right>\mathrm{CH}$.

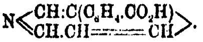
[82°] (P. a. S.); [73°] (D.). Formed by distilling its carboxylic acids with soda-lime (Paal a. Strasser, *B.* 20, 2764; Doebner, *A.* 249, 121). Yellow needles, v. sol. alcohol. Yields an oily hexahydride.—$B'_2H_2PtCl_6$. [205°].—$B'HAuCl_4$. [202°].—$B'_4H_4Cr_3O_{11}$. Orange-red needles.

Methylo-iodide B'MeI. [203°].

Tri-phenyl-pyridine $C_{23}H_{17}N$. [135°]. Formed by passing NH_3 through acetophenone, and adding P_2O_5 (Engler, *B.* 6, 639; 19, 40; *A.* 238, 27).—$B'_2H_2PtCl_6$.

Reference.—OXY-PHENYL-PYRIDINE.

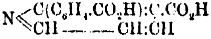
PHENYL-PYRIDINE *o*-CARBOXYLIC ACID $C_{12}H_9NO_2$ *i.e.*



$\mathrm{N}\left<\begin{matrix}\mathrm{CH{:}C(C_6H_4.CO_2H)}\\ \mathrm{CH.CH{=\!=\!=}CH}\end{matrix}\right>$.

[185°]. Formed by heating the dicarboxylic acid at 185° (Skraup a. Cobenzl, *M.* 4, 450). Needles, sl. sol. cold water. Yields nicotinic acid on oxidation.—CaA'_2 2aq: long needles, v. sol. cold water.

(α)-Phenyl-pyridine dicarboxylic acid $C_{13}H_9NO_4$ *i.e.*

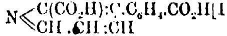


$\mathrm{N}\left<\begin{matrix}\mathrm{C(C_6H_4.CO_2H){:}C.CO_2H}\\ \mathrm{CH{-\!-\!-}CH{:}CH}\end{matrix}\right.$

[230°–235°]. Formed by oxidation of (α)-naphtho-quinoline (Skraup a. Cobenzl, *M.* 4, 463). Minute crystals, gives off indigo-blue vapours when heated. When distilled with CaO it yields (α)-phenyl-pyridine and the compound $C_{12}H_7NO$ [140°–142°] (315°), which crystallises from alcohol in yellow plates and yields $B'_2H_2PtCl_6$. Yields a di-bromo- derivative [205°].

Salts. — CaA″ 2aq. — CuA″ 4aq: violet crystalline pp. — Ag_2A'' 1½aq. — H_2A''HCl. — $(H_2A'')_2H_2PtCl_6$ 3aq.

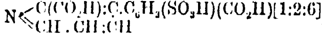
(β)-Phenyl-pyridine dicarboxylic acid



$\mathrm{N}\left<\begin{matrix}\mathrm{C(CO_2H){:}C.C_6H_4.CO_2H[1{:}2]}\\ \mathrm{CH.CH{:}CH}\end{matrix}\right.$

. [207°]. Formed by oxidation of (β)-naphthoquinoline (Skraup a. Cobenzl, *M.* 4, 442). Prisms (containing aq), sl. sol. cold water. Salts. — HA′HCl. — $(HA')_2H_2PtCl_6$ 2½aq. — K_2A'' 3aq. — KHA″ 2aq. — CaA″ 3aq. BaA″ 4½aq. — CuA″ 4aq. — $Cu_2H_2A''_3$. —$AgH_3A''_2$.

Sulphonic acid $C_{13}H_9NSO_7$ *i.e.*

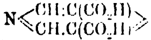


$\mathrm{N}\left<\begin{matrix}\mathrm{C(CO_2H){:}C.C_6H_3(SO_3H)(CO_2H)[1{:}2{:}6]}\\ \mathrm{CH.CH{:}CH}\end{matrix}\right.$.

Formed, as well as $C_{12}H_8(SO_3H)NO$ aq, by oxidation of (β)-naphtho-quinoline sulphonic acid with alkaline $KMnO_4$ (Immerheiser, *B.* 22, 405). Crystals (from water). — K_3A'''. — $Ba_3H_3A'''_3$.— $Pb_4A'''_2(OH)_2$. — Ag_3A''' (dried at 100°).

The by-product $C_{12}H_8(SO_3H)NO$ aq yields KA′ aq, BaA'_2 2aq, PbA'_2 3aq, AgA′ aq, an oxim [290°] and a phenyl-hydrazide [c. 295°].

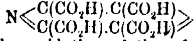
Phenyl-pyridine dicarboxylic acid



$\mathrm{N}\left<\begin{matrix}\mathrm{CH{:}C(CO_2H)}\\ \mathrm{CH.C(CO_2H)}\end{matrix}\right>\mathrm{CPh}$.

[230°] (hydrated); [246°] (anhydrous). Formed by heating the tetra-carboxylic acid at 170° (Weber, *A.* 241, 13). Greenish-yellow plates (containing aq). — CuA″ 2aq: blue pp.

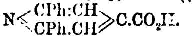
(γ)-Phenyl-pyridine tetra-carboxylic acid



$\mathrm{N}\left<\begin{matrix}\mathrm{C(CO_2H).C(CO_2H)}\\ \mathrm{C(CO_2H).C(CO_2H)}\end{matrix}\right>\mathrm{CPh}$.

[207°]. Formed by oxidation of the phenyl-di-methyl-pyridine dicarboxylic acid, which is got from acetoacetic ether, NH_3, and benzoic aldehyde (Hantzsch, *B.* 17, 1515). Crystals (containing 3aq), v. sol. water. KH_3A^{iv} aq: small prisms or pyramids, sl. sol. cold water.—$Ba_3(NH_4)_2A^{iv}_2$ 6aq: minute tables. —Cu_2A^{iv} 7aq.

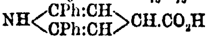
Di-phenyl-pyridine (γ)-carboxylic acid



$\mathrm{N}\left<\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh.CH}\end{matrix}\right>\mathrm{C.CO_2H}$.

[275°]. Formed by heating $(CH_2Bz)_2C(CO_2H)_2$ with alcoholic NH_3 at 120° (Paal a. Strasser, *B.* 20, 2761). Needles (from alcohol).—AgA′: pp., sl. sol. hot water.

Dihydride $C_{18}H_{15}NO_2$ *i.e.*



$\mathrm{NH}\left<\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh{:}CH}\end{matrix}\right>\mathrm{CH.CO_2H}$.

Crystalline flakes.—NH_4A'. [270°]. Formed from $(CH_2Bz)_2CH.CO_2H$ and alcoholic NH_3 in the cold. Needles, v. sol. water.

Hexahydride
$\mathrm{NH}<\begin{matrix}\mathrm{CHPh.CH_2}\\ \mathrm{CHPh.CH_2}\end{matrix}>\mathrm{CH.CO_2H}$. [339°]. Formed, in small quantity, when di-benzoyl-di-methyl-malonic acid is heated with alcoholic NH_3 at 120° (P. a. S.). Crystals, v. sl. sol. water. Yields a nitrosamine [159°].

Di-phenyl-pyridine tricarboxylic acid $\mathrm{N}\leqslant\begin{matrix}\mathrm{C(C_6H_4.CO_2H):C.CO_2H}\\ \mathrm{CPh.CH{=}C.CO_2H}\end{matrix}$. [250°]. Formed by oxidising phenyl-naphthoquinoline carboxylic acid with alkaline $KMnO_4$ below 50° (Doebner, *A.* 249, 120). Needles (from dilute alcohol).—Ag_3A''': white flocculent pp.

At 100° the chief product is phenylene phenyl-pyridylene ketone carboxylic acid $C_{19}H_{11}NO_3$ [226°], which on distillation with soda-lime yields $\mathrm{CO}<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_5H_2PhN}\end{matrix}$ [68°], which forms an oxim [84°] and B'_2CrO_3.

Reference.—OXY-PHENYL-PYRIDINE CARBOXYLIC ACID.

PHENYL PYRIDYL KETONE $C_{12}H_9NO$ *i.e.* $C_6H_5.CO.C_5H_4N$. (307°). Formed by heating its carboxylic acid (Bernthsen a. Mettegang, *B.* 20, 1209). Liquid. Yields a phenyl-hydrazide [143·5°].—$B'_2H_2PtCl_6$.

PHENYL (β)-PYRIDYL KETONE CARBOXYLIC ACID $C_6H_5.CO.C_5H_3N.CO_2H$. [147°]. Formed from quinolinic anhydride, benzene, and $AlCl_3$ (Bernthsen a. Mettegang, *B.* 20, 1209). Prisms, v. e. sol. hot water.

DI-PHENYL-PYRONE $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CPh}\\ \mathrm{CH{:}CPh}\end{matrix}>\mathrm{O}$. [139·5°]. Formed by heating its carboxylic acid (Feist, *B.* 23, 3734). Got also by heating de-hydro-benzoyl-acetic acid with HClAq at 245°. Needles resembling asbestos (from benzene). Its solution in conc. H_2SO_4 exhibits violet fluorescence. Alcoholic NH_3 converts it, on heating, into oxy-di-phenyl-pyridine.

DI-PHENYL-PYRONE CARBOXYLIC ACID $\mathrm{CO}<\begin{matrix}\mathrm{C(CO_2H){:}CPh}\\ \mathrm{CH{=}CPh}\end{matrix}>\mathrm{O}$. [201°]. Formed by warming chloro-dehydro-benzoyl-acetic acid (1 pt.) in H_2SO_4 (3 pts.) at 140° (Feist, *B.* 23, 3730). Small crystals (from benzene), v. sol. chloroform.—NH_4A'. [135°].—BaA'_2 6aq.—$Ag_2A'_2AgNO_3$: curdy pp.

Di-phenyl-pyrone dicarboxylic ether $\mathrm{CO}<\begin{matrix}\mathrm{C(CO_2Et){:}CPh}\\ \mathrm{C(CO_2Et){:}CPh}\end{matrix}>\mathrm{O}$. [140°]. Formed by allowing a mixture of cupric benzoyl-acetic ether (24 g.), $COCl_2$ (10 g.), and toluene (40 g.) to stand for six weeks (F.). Got also from acetone dicarboxylic ether, Et_2O, Na, and BzCl (Dünschmann a. Pechmann, *A.* 261, 189). Plates, v. sol. most solvents.

PHENYL-PYROTARTARIC ACID $C_6H_5.CH_2.CH(CO_2H).CH_2.CO_2H$. *Benzyl-succinic acid.* [161°]. Got by heating phenyl-propane tricarboxylic acid and by reducing phenyl-itaconic acid (Bischoff, *B.* 23, 653; Fittig a. Roeders, *A.* 256, 87; *cf.* Baeyer a. Perkin, *B.* 17, 449). White plates, sl. sol. cold water. Yields an anhydride [102°].—BaA'' ½aq.—CaA''.—Ag_2A''.

Phenyl-pyrotartaric acid $CO_2H.CHPh.CHMe.CO_2H$. Two varieties [171°] and [193°] are formed by saponifying the product of the reaction of NaOEt on a mixture of α-cyano-propionic acid and α-bromo-phenyl-acetic ether (Zelinsky a. Buchstab, *B.* 24, 1877). At 320° it forms an anhydride which on treatment with water yields a mixture of the two isomeric phenyl-methyl-succinic acids.

Reference.—OXY-AMIDO-PHENYL-PYROTARTARIC ACID.

PHENYL-PYROXIMIDINE DIHYDRIDE $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2.O}\\ \mathrm{CH_2.N}\end{matrix}\geqslant\mathrm{CPh}$. Formed from γ-bromo-propyl-benzamide by shaking with hot water (Gabriel, *B.* 24, 3214). Liquid, sl. sol. cold water.—$B'_2H_2PtCl_6$. [185°].—$B'C_6H_3N_3O_7$. [151°].

DI-PHENYL-PYRROLE $\mathrm{NH}<\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh{:}CH}\end{matrix}$. [143°]. Formed by the action of alcoholic potash on its carboxylic ether (Paal, *B.* 21, 3061). Got also by heating the dicarboxylic acid $C_4NH_3(C_6H_4.CO_2H)_2$ with lime (Baumann, *B.* 20, 1490). Plates (from HOAc or dilute alcohol). Forms a red solution in H_2SO_4. Colours pine-wood, moistened with HClAq, red.

Tri-phenyl-pyrrole $\mathrm{NPh}<\begin{matrix}\mathrm{CPh{:}CH}\\ \mathrm{CPh.CH}\end{matrix}$. [229°]. Formed by heating its carboxylic acid or its di-carboxylic acid $C_4NH_2Ph(C_6H_4.CO_2H)_2$ with lime (P.; B.). Needles, sl. sol. ether and alcohol.

Tri-phenyl-pyrrole $\mathrm{NH}<\begin{matrix}\mathrm{CPh{:}CPh}\\ \mathrm{CPh{:}CH}\end{matrix}$. [141°]. Formed by heating desyl-acetophenone with alcoholic NH_3 at 150° (Smith, *C. J.* 57, 645). Slender needles with violet fluorescence.

Tetra-phenyl-pyrrole $C_{28}H_{21}N$ *i.e.* $\mathrm{NH}<\begin{matrix}\mathrm{CPh{:}CPh}\\ \mathrm{CPh{:}CPh}\end{matrix}$. [214·5°]. Formed from both bidesyls by heating with alcoholic NH_3 at 150° (Garrett, *B.* 21, 3107; Fehrlin, *B.* 22, 553; Magnanini a. Angeli, *B.* 22, 855). Got also by distilling its phenyl-ν-amido- derivative (Klingemann, *A.* 269, 122). Needles or plates.

Acetyl derivative. [226°]. Needles.

Tetra-phenyl-pyrrole $\mathrm{NPh}<\begin{matrix}\mathrm{CPh{:}CPh}\\ \mathrm{CPh{:}CH}\end{matrix}$. [197°]. Formed by boiling desyl-acetophenone with aniline and HOAc (Smith, *C. J.* 57, 646). White silky needles, v. sl. sol. cold alcohol.

DI-PHENYL-PYRROLE CARBOXYLIC ACID $\mathrm{NH}<\begin{matrix}\mathrm{CPh{:}C.CO_2H}\\ \mathrm{CPh{:}CH}\end{matrix}$. [261°]. Formed by saponifying the ether, which is got by the action of alcoholic NH_3 or of boiling NH_4OAc and HOAc on di-β-benzoyl-propionic ether (Kapf a. Paal, *B.* 21, 1491, 3061). Orange needles, sl. sol. alcohol.

Ethyl ether EtA'. [159°]. Needles.

Amide $C_{17}H_{14}N_2O$. [217°].

Di-phenyl-pyrrole di-*o*-carboxylic acid $\mathrm{NH}<\begin{matrix}\mathrm{C(C_6H_4.CO_2H){:}CH}\\ \mathrm{C(C_6H_4.CO_2H){:}CH}\end{matrix}$. [232°]. Formed by heating $C_2H_4(CO.C_6H_4.CO_2H)_2$ with alcoholic NH_3 (Gabriel, *B.* 19, 840). Slender needles. Yields a nitrosamine $C_{18}H_{12}N_2O_5$ [c. 210°] crystallising from HOAc.

Tri-phenyl-pyrrole carboxylic acid $\mathrm{NPh}<\begin{matrix}\mathrm{CPh{:}C.CO_2H}\\ \mathrm{CPh{:}CH}\end{matrix}$. [273°]. Formed by saponifying the ether, which is got by boiling di-benzoyl-propionic ether with aniline and HOAc (Paal, *B.* 21, 3061). Needles (from HOAc).

Ethyl ether EtA'. [170°]. Needles.

Tri-phenyl-pyrrole di-carboxylic acid $\mathrm{NPh}<\begin{matrix}\mathrm{C(C_6H_4.CO_2H){:}CH}\\ \mathrm{C(C_6H_4.CO_2H){:}CH}\end{matrix}$. [295°]. Formed by rming $C_6H_4(CO.C_6H_4.CO_2H)_2$ with aniline Baumann, *B.* 20, 1487). Crystals, insol. water. g_2A'': bulky pp.

Ethyl ether Et_2A''. [122°]. Needles.

DI-α-PHENYL-β-PYRROYL-PROPIONIC ACID $C_4H_4N.CO.CH_2.CPh_2.CO_2H$. [216°]. Formed by saponification of di-phenyl-pyrryl-crotolactone $\begin{matrix}CH:C(C_4H_4N)\\CPh_2.CO\end{matrix}\!\!>O$ [184°] which is got by warming (α)-pyrryl methyl ketone with benzil and conc. KOHAq (Angeli, *B.* 23, 1356). Colourless crystals, almost insol. water.—KA'.—AgA': light-yellow pp.

PHENYL PYRRYL KETONE $C_{11}H_9NO$ *i.e.* $NC_4H_4.CO.C_6H_5$. [78°]. Formed by heating pyrrole with NaOBz and Bz_2O (Ciamician a. Dennstedt, *B.* 17, 2955). Yields $C_{11}H_8AgNO$.

PHENYL-PYRUVIC ACID *v.* PHENYL-GLYCIDIC ACID.

PHENYL-QUINAZOLINE $C_6H_4<\begin{matrix}CH:N\\N{=}CPh\end{matrix}$. [101°]. Got by distilling *o*-amido-benzyl-benzamide (Gabriel a. Jansen, *B.* 23, 2810). Yellow needles. Weak base.

Phenyl-quinazoline. *Dihydride.* $C_{14}H_{12}N_2$ *i.e.* $C_6H_4<\begin{matrix}CH_2.NPh\\N{=}CH\end{matrix}$. [95°]. Formed by reducing $[1:2]C_6H_4(NO_2).CH_2.NPh.CHO$ with zinc and HClAq (Paal a. Busch, *B.* 22, 2686; Donner, *Ph.* [3] 20, 43). Six-sided tables (from ether-ligroïn), almost insol. water and alkalis. Split up into aniline and benzonitrile by heating with zinc-dust.—B'HCl 2aq. [80°] when hydrated; [221°] when anhydrous. Concentric needles, sol. water.—$B'HSnCl_3$. [130°-134°]. White crystals.—$B'_2H_2PtCl_6$. [208°]. Yellow crystals.—$B'_2H_2SO_4$ 2aq. [79°]. Melts at 140°-143° when anhydrous.

Methylo-iodide B'MeI. [170°] and [180°].—$B'MeI_2$. [157°]. Golden plates.

Tetrahydride $C_6H_4<\begin{matrix}CH_2.NPh\\NH.CH_2\end{matrix}$. [117°]. Got by reduction. Needles. Yields a crystalline acetyl derivative and a brick-red nitrosamine.

Di-phenyl-quinazoline. *Dihydride.* $C_{20}H_{16}N_2$ *i.e.* $C_6H_4<\begin{matrix}CH_2.NPh\\N{=}CPh\end{matrix}$. [115°]. Formed by reduction of the benzoyl derivative of *o*-nitro-benzyl-aniline in HOAc with tin and HCl (Lellmann a. Stickel, *B.* 18, 1608). Small needles, v. sol. alcohol.—B'HCl: silky needles.

Reference.—OXY-PHENYL-QUINAZOLINE.

(*B.* 2)-**PHENYL-QUINOLINE** $\begin{matrix}CPh:CH.C.CH:CH\\CH:CH.C.N{=}CH\end{matrix}$ *p-Phenyl-quinoline.* [111°]. (260° at 77 mm.). S.G. ^{22} 1·1945. Prepared by heating *p*-amido-diphenyl with glycerin, nitrobenzene, and H_2SO_4 (La Coste, *B.* 15, 562; *A.* 230, 8). Trimetric plates (from ether).—$B'_2H_2PtCl_6$. Orange crystalline powder.—$B'_2H_2Cr_2O_7$. [136°].—**Tartrate** $B'C_4H_6O_6$ 3aq. [153°]. Needles.

Methylo-iodide B'MeI 2aq. [194°].

Ethylo-iodide B'EtI 2aq. [169°].

Tetrahydride $C_9H_{10}PhN$. Got by reduction. Unstable pp. Yields a nitrosamine $C_9H_9Ph(NO)N$ [112°], an acetyl derivative [100°], and a benzoyl derivative [137°].—B'HCl $1\frac{1}{2}$aq. [204°].—$B'C_6H_3N_3O_7$. [165°].

(*B.* 4)-**Phenyl-quinoline** $\begin{matrix}CH:CH\ .C.CH:CH\\CH:CPh.C.N{=}CH\end{matrix}$ *o-Phenyl-quinoline.* (273° at 80 mm.). Got in like manner, using *o*-amido-diphenyl (C.). Oil, with yellowish-green fluorescence.—$B'_2H_2PtCl_6$.—$B'_2H_2Cr_2O_7$. [126°]. Orange plates.

Methylo-iodide B'MeI. [163°]. Crystals, v. sol. water.—$B'_2Me_2PtCl_6$ [193°].

(*Py.* 1)-**Phenyl-quinoline** $C_6H_4<\begin{matrix}CPh:CH\\N{=}CH\end{matrix}$. [62°]. Got by heating its carboxylic acid (Königs a. Nef, *B.* 19, 2430). Needles (from ether or ligroïn). Solutions of its sulphate and hydrochloride fluoresce blue.—$B'H_2CrO_4$: needles.—$B'_2H_2PtCl_6$: yellow four-sided tables.

(*Py.* 2)-**Phenyl-quinoline** $C_6H_4<\begin{matrix}CH:CPh\\N{=}CH\end{matrix}$. Formed by adding a little NaOH to a solution of *o*-amido-benzoic aldehyde and phenyl-acetic aldehyde in dilute alcohol (Friedländer a. Gohring, *B.* 16, 1836). Oil, sparingly volatile with steam.—B'HCl. [93°].—$B'_2H_2PtCl_6$.

(*Py.* 3)-**Phenyl-quinoline** $C_6H_4<\begin{matrix}CH:CH\\NCPh\end{matrix}$. [86°]. (above 360°).

Formation.—1. By heating cinnamic aldehyde (30 pts.) with aniline (20 pts.) and conc. HClAq (20 pts.) for two hours at 210° (Grimaux, *C. R.* 96, 584; Doebner a. Miller, *B.* 16, 1665; 19, 1194).—2. By warming *o*-amido-benzoic aldehyde with acetophenone, dilute alcohol, and a little NaOH (Friedländer a. Gohring, *B.* 16, 1835).—3. By distilling *m*-oxy-phenyl-quinoline or di-oxy-phenyl-quinoline with zinc-dust (Miller a. Kinkelin, *B.* 18, 1908; Weidel, *M.* 9, 157).—4. By distilling its carboxylic acid with soda-lime (Doebner, *B.* 20, 280; *A.* 242, 294; Pfitzinger, *J. pr.* [2] 38, 583).

Properties.—Silky needles (from dilute alcohol), sol. ether, sl. sol. water. Yields $NHBz.C_6H_4.CO_2H$ [1:2] [182°] on oxidation by $KMnO_4$ in acid solution.

Salts.—$B'_2H_2PtCl_6$ 2aq.—$B'HAuCl_4$. [160°].—$(B'HCl)_2AuCl_3$. [204°]. Needles.—$B'H_2Cr_2O_7$: stable golden plates.—$B'C_6H_3N_3O_7$. [188°].

Alkylo-iodides B'MeI. [197°].—B'EtI. [195°].—$B'_2Et_2PtCl_6$.—B'EtCl 2aq.—$B'_2Et_2PtCl_6$.

Tetrahydride $C_{15}H_{15}N$. (342°). Got by reducing the base with tin and HClAq (Doebner, *B.* 19, 1198). Oil, yielding an oily nitrosamine.—B'HCl. Needles (from alcohol), v. sl. sol. water.

(*Py.* 1,3)-**Di-phenyl-quinoline** $C_6H_4<\begin{matrix}CPh:CH\\N-CPh\end{matrix}$. [112°]. Formed by heating the anilide of CH_2Bz_2 with H_2SO_4 (Beyer, *B.* 20, 1772). Mass of white crystals.—$B'_2H_2PtCl_6$ 2aq.—$B'H_2SO_4$. Needles, v. sl. sol. dilute H_2SO_4.

(*Py.* 2,3)-**Di-phenyl-quinoline** $C_6H_4<\begin{matrix}CH:CPh\\N-CPh\end{matrix}$. [96°]. (c. 420°). Formed by reducing [1:2] $C_6H_4(NO_2).CH_2.CHPh.CO.C_6H_5$ with iron and HOAc (Buddeberg, *B.* 23, 2075). Large crystals, sol. alcohol.—$B'_2H_2PtCl_6$.

(*Py.* 2)-**PHENYL-ISOQUINOLINE** $C_{15}H_{11}N$ *i.e.* $C_6H_4<\begin{matrix}CH:CPh\\CH:N\end{matrix}$. [105°]. Obtained by reduction of the (*Py.* 4)-chloro- derivative by heating it with HI and P at 170° for three hours; also by distilling phthalimide with zinc-dust (Gabriel, *B.* 18, 3477). Rhombic plates. Slightly volatile with steam.—$B'_2H_2Cl_2PtCl_4$: needles.

Tetrahydride $C_6H_4<\begin{array}{l}CH_2.CHPh.\\CH_2.NH\end{array}$ [45°-48°]. Formed by reduction of an alcoholic solution of the (*Py.*)-mono- or di- chloro-derivatives by boiling with (3 p.c.) sodium-amalgam (Gabriel, *B.* 18, 3479). Crystals, v. sol. alcohol.

References. — AMIDO-, CHLORO-, CHLORO-NITRO-, NITRO-, OXY-AMIDO-, and OXY- PHENYL-QUINOLINE.

(*Py.* 1) - **PHENYL - QUINOLINE** (*Py.* 3)-**CARBOXYLIC ACID** $C_{16}H_{11}NO_2$ *i.e.* $C_6H_4<\begin{array}{l}CPh:CH\\N{=}C.CO_2H\end{array}$. [171°]. Got by oxidation of phenyl-methyl-quinoline-phthalone with chromic acid mixture (Kœnigs a. Nef, *B.* 19, 2428). Yellow needles (from dilute alcohol), sol. acids and alkalis.

(*Py.* 3)-**Phenyl-quinoline** (*Py.* 1)-**carboxylic acid** $C_6H_4<\begin{array}{l}C(CO_2H):CH\\N{=\!=\!=\!=}CPh\end{array}$. [207°]. Formed by warming pyruvic acid with benzoic aldehyde, aniline, and alcohol (Doebner, *B.* 20, 280; *A.* 242, 291). Formed also by heating isatin with acetophenone and alcoholic potash (Pfitzinger, *J. pr.* [2] 83, 538). Needles, m. sol. cold alcohol. Yields phenyl-quinoline [84°] on distillation with soda-lime. — $(HA')_2H_2PtCl_6$. — PbA'_2aq. — CuA'_2aq. — ZnA'_2aq. — AgA': white pp.

Phenyl - quinoline - *o* - di - carboxylic acid $C_9H_4(C_6H_5)N(CO_2H)_2$ *i.e.* $C_6H_4<\begin{array}{l}CPh:C.CO_2H\\N=C.CO_2H\end{array}$. Formed by oxidation of phenyl-acridine with $KMnO_4$.

Salts.—$BaA''4aq$: glistening needles (Claus a. Nicolaysen, *B.* 18, 2706).

(*Py.* 2,3) - **Di - phenyl - quinoline carboxylic acid** $C_6H_4<\begin{array}{l}C(CO_2H):CPh\\N{=\!=\!=\!=}CPh\end{array}$. [191°]. Formed by the action of isatin and alcoholic potash on deoxybenzoïn (Pfitzinger, *J. pr.* [2] 38, 583). Needles, insol. water, v. sol. hot alcohol.

(*Py.* 3)-**PHENYL-QUINOLINE** (*B.* 2)-**SULPHONIC ACID** $\begin{array}{l}SO_3H.C:CH.C.CH:CH\\\quad\quad HC:CH.C.N{=}CPh\end{array}$. Got, together with the more soluble (*B.* 3)-sulphonic acid, by heating (*Py.* 3)-phenyl-quinoline with H_2SO_4 and SO_3 at 100° (Murmann, *M.* 13, 60).—Plates, sl. sol. water, almost insol. alcohol. Gives oxy-phenyl-quinoline [238°] when fused with potash at 250°.—BaA'_2: plates. —NH_4A': plates. —AgA': granules.

(*Py.* 3) - **Phenyl - quinoline** (*B.* 3) - **sulphonic acid.** Formed as above (M.). Granules. Yields oxy-phenyl-quinoline [156°] on fusion with potash. — $KA'aq$. — $BaA'_2 1\frac{1}{2}aq$: needles. — $AgA' 1\frac{1}{2}aq$: needles.

(*B.* 2) - **Phenyl - quinoline** *p* - **sulphonic acid** $C_{15}H_{11}NSO_3$ *i.e.* $\begin{array}{l}[1:4]SO_3H.C_6H_4.C:CH.C.CH:CH\\\quad\quad\quad\quad\quad\quad\quad HC:CH.C.N{=}CH\end{array}$. Formed, together with the following more soluble isomeride, by sulphonation of *p*-phenyl-quinoline (La Coste a. Sorger, *A.* 230, 30). Needles (containing 2aq). Turns brown, without fusion, at 300°. Alkaline $KMnO_4$ gives quinolinic acid and *p*-sulpho-benzoic acid.—NH_4A'. [above 310°].—$NaA'aq$.—HgA'_2: white pp.

(*B.* 2) - **Phenyl - quinoline** (*β*) - **sulphonic acid.** Formed as above. Plates (containing aq), not melted at 300°.—NH_4A': small scales.

PHENYL-DIQUINOLYL-METHANE. *Octohydride* $CHPh(C_9H_{10}N)_2$. [153°]. Formed from quinoline tetrahydride, benzoic aldehyde, and $ZnCl_2$ in alcohol (Einhorn, *B.* 19, 1243). Its solution in HClAq is coloured green by $FeCl_3$.

Di-phenyl-(*B.* 1)-**quinolyl-methane** $\begin{array}{l}CHPh_2.C:CH.C.CH:CH\\\quad\quad HC:CH.C.N{=}CH\end{array}$. [104°]. Formed by Skraup's method from amido-tri-phenyl-methane (Fischer a. Fränkel, *B.* 19, 749; *A.* 241, 364). Prisms, v. sol. alcohol. Yields a nitro- derivative [213°].—$B'_2H_2PtCl_6$ (dried at 100°).

DI-PHENYL-(*Py.* 3)-**QUINOLYL-UREA** $C_9H_6N.NPh.CO.NHPh$. [150°]. Formed by heating carbostyril with phenyl isocyanate and benzene at 220° (Goldschmidt a. Meissler, *B.* 23, 276). Needles (from benzene), sol. HClAq and re-ppd. by NH_3.

DI-PHENYL-QUINONE $C_{18}H_{12}O_2$ *i.e.* $CPh\Big<\begin{array}{l}CH.CO\\CO.CH\end{array}\Big>CPh$. [214°]. Formed by heating phenyl methyl diketone with NaOHAq and a little K_3FeCy_6 at 100° (Müller a. Pechmann, *B.* 22, 2130). Orange-yellow plates, m. sol. benzene. Zinc-dust and HOAc reduce it to di-phenyl-hydroquinone [219°].

DI-PHENYL-QUINOXALINE $C_6H_4<\begin{array}{l}N:CPh\\N:CPh\end{array}$. [126°]. Formed by heating benzoïn with *o*-phenylene-diamine in the air at 165° (Fischer, *B.* 24, 720). Needles.

Dihydride $C_6H_4<\begin{array}{l}NH.CHPh\\N{=}CPh\end{array}$. [149°]. Formed by heating benzoïn with *o*-phenylene-diamine at 165° with exclusion of air. Prisms. Its solutions in ether and benzene fluoresce yellowish-green.

Phenylo-hydroxide $C_6H_4<\begin{array}{l}NPh(OH):CPh\\N{=\!=\!=\!=}CPh\end{array}$. [135°]. Formed from benzil and *o*-phenylene-phenyl-diamine (Kehrmann a. Messinger, *B.* 24, 1239). — $C_{26}H_{19}N_2ClFeCl_3$. Golden prisms, m. sol. cold water, insol. ether. — $(C_{26}H_{19}N_2Cl)_2PtCl_4$. — $C_{26}H_{19}N_2HgCl_3$. Yellow scales.

Tri-phenyl-quinoxaline. *Dihydride* $C_6H_4<\begin{array}{l}NPh.CHPh\\N{=\!=}CPh\end{array}$. [117°]. Got by heating benzoïn with *o*-phenylene-phenyl-diamine in a sealed tube at 175° (Kehrmann a. Messinger, *B.* 24, 1875). Crystalline, v. sol. ether. Its solutions fluoresce bluish-green.

Tetra-phenyl-diquinoxaline, so-called. $\begin{array}{l}CPh:N.C.CH:C.N:CPh\\CPh:N.C.CH:C.N:CPh\end{array}$. [289°]. Formed from tetra-amido-benzene and benzil (Nietzki a. Müller, *B.* 22, 446). V. sol. hot HOAc. Forms a blue solution in conc. H_2SO_4.

DI-PHENYL-QUINOXALINE CARBOXYLIC ACID $C_{21}H_{14}N_2O_2$, *i.e.* $\left[4\begin{smallmatrix}2\\1\end{smallmatrix}\right]C_6H_3(CO_2H)<\begin{array}{l}N:CPh\\N:CPh\end{array}$. [288°]. Formed by mixing benzil and di-amido-benzoic acid, both dissolved in hot HOAc (Zehra, *B.* 23, 3627). Yellow plates or needles. — $BaA'_2 3aq$: needles, sl. sol. hot water.

Ethyl ether EtA'. [151°]. Needles.

TETRA-PHENYL-DIQUINOXALYL $C_{40}H_{26}N_4$, *i.e.* $\begin{array}{l}CPh:N\\CPh:N\end{array}\Big>C_6H_3.C_6H_3\Big<\begin{array}{l}N:CPh\\N:CPh\end{array}$. [above 270°]. Formed by mixing acetic acid solutions of benzil and tetra-amido-diphenyl $\{C_6H_3(NH_2)_2[1:3:4]\}_2$ (Brunner a. Witt, *B.* 20, 1026). Crystals (from phenol-HOAc). Forms a bright-red solution in conc. H_2SO_4.

PHENYL SELENIDE *v. Organic compounds* of SELENIUM.

TETRA-PHENYL-SILICANE *v. Organic compounds* of SILICON.

PHENYL SILICATE $Si(OPh)_4$. [48°]. (420°). Prepared by heating phenol with $SiCl_4$; the yield being 78 p.c. of the theoretical amount (Hertkorn, *B.* 18, 1679). Long colourless prisms, v. sol. alcohol. Decomposed by hot water into phenol and silicic acid. Boiling alcohol forms ethyl silicates and phenol.

TRI-PHENYL-STIBINE *v.* vol. i. p. 294.

PHENYL-STYRYL-HYDRAZINE $C_{15}H_{16}N_2$ *i.e.* $CHPh{:}CH.CH_2.NPh.NH_2$. [54°]. Formed from styryl bromide and sodium phenyl-hydrazide (Michaelis a. Claessen, *B.* 22, 2239). Crystals, v. sol. alcohol and ether.

PHENYL-STYRYL KETONE *v.* BENZYLIDENE-ACETOPHENONE. Its carboxylic ether is described as *Benzylidene-benzoyl-acetic ether*, vol. i. p. 481.

PHENYL-SUCCINIC ACID $C_{10}H_{10}O_4$, *i.e.* $CO_2H.CHPh.CH_2.CO_2H$. [167°].

Formation.—1. By saponification of the nitrile which is got from ω-chloro-styrene and KCy (Rügheimer, *B.* 14, 428).—2. By saponification of the product of the action of α-bromo-phenyl-acetic ether on sodium acetoacetic ether (R.).—3. At 191° from $CO_2H.CHPh.CH(CO_2H)_2$, got from α-chloro-phenyl-acetic ether and sodium malonic ether (Spiegel, *B.* 14, 873, 1693; *A.* 219, 32; Alexander, *A.* 258, 74).—4. From hydrocornicularic acid by potash-fusion (S.).

Properties.—Needles, sol. hot water and alcohol, sl. sol. chloroform. Br and PBr_3 yield a bromo- derivative [119°] converted by hot water into phenyl-maleïc acid.

Salts.—CaA''.—Ag_2A''.

Anhydride $C_{10}H_8O_3$. [c. 54°].

(α)-Di-phenyl-succinic acid $C_{16}H_{14}O_4$ *i.e.* $CO_2H.CHPh.CHPh.CO_2H$. [222°] (when dry); [183°] (when hydrated). H.C. 1,848,300 (Ossipoff, *C. R.* 109, 223). S. (alcohol) 41 at 21°.

Formation.—1. By heating α-bromo-phenyl-acetic acid with KCy (Franchimont, *B.* 5, 1018). 2. Together with the isomeric (β)-acid, by reduction of di-phenyl-maleïc anhydride with sodium-amalgam or Zn and HCl. Separated through the sparing solubility of the Ba salt (Reimer, *B.* 14, 1802; Anschütz, *A.* 259, 67).—3. By heating the (β)-isomeride with baryta-water at 200° (R.).

Properties.—Prisms (containing aq) or needles (from dilute HOAc). Yields di-phenyl-ethane and di-phenyl-ethylene when distilled with lime. HClAq at 200° converts it into the (β)-acid.

Salts.—BaA'' 2aq. S. 32 at 18°.—BaA'' 4aq.—Ag_2A'': white pp.

Mono-ethyl ether HEtA''. [140°].

Di-ethyl ether Et_2A''. [84°]. Needles.

Anhydride $C_{16}H_{12}O_3$. [116°]. (240° at 11 mm.). Formed when either of the two *s*-di-phenyl-succinic acids is heated. Got also by heating the (α)- acid with AcCl at 120° (Tillmanns, *A.* 258, 87). Trimetric crystals; *a*:*b*:*c* = ·508:1:·546. V. sol. chloroform. Yields the (α)- acid on boiling with water, and a mixture of (α)- acid (86 p.c.) and (β)- acid (14 p.c.) when treated with KOHAq.

Nitrile CN.CHPh.CHPh.CN. [160°]. Formed, together with the (β)- isomeride by heating phenyl-acetonitrile with mandelic nitrile and alcoholic KCy at 55° (Chalanay a. Knoevenagel, *B.* 25, 289). V. e. sol. alcohol. Converted into the (β)- isomeride by boiling with HOAc.

Phenylimide $C_{22}H_{17}NO_2$. [231°]. Got by heating either the (α)- or the (β)- anhydride with aniline.

Phenyl-amic acid $C_{22}H_{19}NO_3$ *i.e.* $CO_2H.CHPh.CHPh.CO.NHPh$. [220°]. Got by boiling the phenylimide with baryta (Anschütz a. Bendix, *A.* 259, 92).

(β)-Di-phenyl-succinic acid $CO_2H.CHPh.CHPh.CO_2H$. [230°]. H.C. 1,822,900. S. (alcohol) 1·24 at 21°.

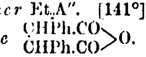
Formation.—1. By heating its nitrile with HClAq at 200°.—2. By reduction of di-phenyl-maleïc anhydride. 3. By heating the α-isomeride with HClAq at 200°.

Properties.—Needles, sol. alcohol, sl. sol. benzene, insol. water. On distillation *in vacuo* at 250° it yields a mixture of the (α)- anhydride (89 p.c.) and the (β)- anhydride (11 p.c.).

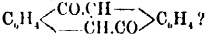
Reactions.—1. Yields *s*-di-phenyl-ethane and di-phenyl-ethylene on distillation with lime (Reimer, *B.* 14, 1802).—2. Baryta-water at 200° converts it into the (α)- isomeride.

Salts.—BaA'' 7aq. S. 21 at c. 18°.—Ag_2A''.

Ethyl ether Et_2A''. [141°]. Needles.

Anhydride 
$\begin{matrix}CHPh.CO\\CHPh.CO\end{matrix}\!\!>\!O$. [c. 107°]. Formed by heating the (β)- acid with AcCl at 100°, and also by the action of AcCl on its salts. When boiled with water it yields the (α)- acid (75 p.c.) and some (β)- acid (25 p.c.). Cold KOHAq forms only the (β)- acid. On heating with aniline it gives the phenylimide [231°].

Diphensuccindone


$C_6H_4\!<\!\begin{matrix}CO.CH—\\—CH.CO\end{matrix}\!>\!C_6H_4$? [202°].

Formed by heating the acid (5 g.) with conc. H_2SO_4 (8 g.) until dissolved, and then pouring into water (Roser, *A.* 247, 153). White crystals, insol. water, sol. alcohol. Yields a dioxim $C_{16}H_{10}(NOH)_2$ [254°] and a phenyl-hydrazide $C_{16}H_{10}(N_2HPh)_2$ [c. 265°]. Reduced by HI and P to $C_{16}H_{14}$ [100°].

Nitrile CN.CHPh.CHPh.CN. [240°]. Accompanies the (α)- isomeride (*v. supra*). Colourless needles, sol. hot alcohol.

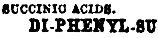
Tetra-phenyl-succinic acid $CO_2H.CPh_2.CPh_2.CO_2H$. [262°]. Formed by heating α-chloro-di-phenyl-acetic ether with finely-divided silver at 125° (Bickel, *B.* 22, 1538). Insol. water, v. sol. alcohol and ether.

Ethyl ether Et_2A''. [89°].

Nitrile $CN.CPh_2.CPh_2.CN$. [c. 230°]. Formed by the action of NaOEt and I on di-phenyl-acetonitrile (Auwers a. V. Meyer, *B.* 22, 1227; *cf.* Anschütz a. Romig, *A.* 233, 349). Formed also by the action of nitrous acid on di-phenyl-acetonitrile (Neure, *A.* 250, 148). Flat needles (from HOAc), v. sl. sol. hot alcohol. Liquefied by heating for a long time at 180°.

Phenyl-isosuccinic acid *v.* BENZYL-MALONIC ACID.

References.—NITRO- and OXY- PHENYL-SUCCINIC ACIDS.

DI-PHENYL-SUCCINIMIDINE $C_{16}H_{15}N_3$ *i.e.* 
$C_2H_4\!<\!\begin{matrix}C(NH)\\C(NPh)\end{matrix}\!>\!NPh$. Formed from ethylene

cyanide and aniline hydrochloride at 154° (Blochmann, *B.* 20, 1856). Greyish-yellow crystals, insol. water. Yields the phenylimide of succinic acid when boiled with HClAq.—B'HCl.—$B'_2H_2PtCl_6$.—$B'H_2SO_4$.—B'HBr.—B'HI.

PHENYL-SULPHAMIC ACID $C_6H_7NSO_3$ *i.e.* $C_6H_5NH.SO_3H$. Formed as a salt from $ClSO_3H$ (1 mol.), aniline (3 mols.) and chloroform in the cold. Got also by the action of solid fuming sulphuric acid on aniline in $CHCl_3$ at a low temperature (Wagner, *B.* 19, 1157; Traube, *B.* 23, 1655; 24, 360).—NaA'.—KA': leaflets, sol. hot alcohol.—$BaA'_2$2aq: leaflets or needles, sol. hot water. Decomposed by acids into aniline and H_2SO_4.—NH_2PhHA'. [192°]. Plates.

PHENYL SULPHATE.

Hydrogen phenyl sulphate $C_6H_5O.SO_2.OH$. *Phenyl-sulphuric acid.* Occurs in urine of horses, men, and dogs (Baumann, *B.* 9, 55; 11, 1907; *H.* 2, 335), the quantity being greatly increased by administration of phenol. The K salt is formed by adding $K_2S_2O_7$ (125 pts.) to a solution of phenol (100 pts.) and KOH (60 pts.) in water (90 pts.) at 65°. The free acid quickly splits up, in aqueous or alcoholic solution, into phenol and H_2SO_4.—KA'. S. 14 at 15°. Plates (from alcohol). Not attacked by potash. The dry salt changes at 150°-160° into phenol *p*-sulphonic acid.—$BaA'_2$3aq: needles.

DI-PHENYL SULPHAZIDE *v. Phenyl-hydrazide* of BENZENE SULPHONIC ACID.

DI-PHENYL SULPHIDE $C_{12}H_{10}S$ *i.e.* Ph_2S. Mol. w. 186. (293°). S.G. 1·119.

Formation.—1. By the dry distillation of sodium benzene sulphonate (Stenhouse, *Pr.* 14, 351; *A.* 140, 288).—2. From $S(C_6H_4.NH_2)_2$ by elimination of NH_2 by the diazo-reaction (Krafft, *B.* 7, 384, 1164).—3. By distilling $Pb(SPh)_2$ (Kekulé a. Szuch, *C. R.* 64, 752).—4. By the action of Na on $SO(C_6H_5)_2$ (Colby a. McLoughlin, *Am.* 9, 67).—5. By the action of NaSPh on $C_6H_5.N_2Cl$ in molecular proportions (Ziegler, *B.* 23, 2471).—6. By heating benzene with S and $AlCl_3$ at 80° (Friedel a. Crafts, *A. Ch.* [6] 14, 438).

Preparation.—Ammonium sulphide is slowly added to an acid solution of diazobenzene, cooled with ice, the oil which separates is cohobated for 2 or 3 hours to decompose the disulphide, and finally distilled; the yield is good (Graebe a. Mann, *B.* 15, 1683).

Properties.—Oil, with slightly alliaceous odour, v. sol. hot alcohol, miscible with ether. Its alcoholic solution is not ppd. by $AgNO_3$ or $HgCl_2$. Yields di-phenyl-sulphone on oxidation.

Di-phenyl disulphide Ph_2S_2. Mol. w. 218. [61°]. (310°).

Formation.—1. By oxidising phenyl mercaptan with dilute HNO_3 (Vogt, *A.* 119, 142; Otto, *A.* 143, 213), with chromic acid mixture (Kekulé, *Z.* 1867, 194), and by exposure of its ammoniacal solution to air.—2. From NaSPh and CyCl (Clemm, *J. pr.* [2] 1, 147).—3. Together with mercury by distilling $Hg(SPh)_2$ (Dreher a. Otto, *A.* 154, 178).—4. From NaSPh and I (Hübner a. Alsberg, *A.* 156, 330).—5. In small quantity by adding zinc-dust to a mixture of S_2Cl_2 and benzene (Schmidt, *B.* 11, 1173).—6. By reducing $C_6H_5.SO_2Cl$ with HI (Cleve, *B.* 21, 1100).—7. By heating $C_6H_5SO_2H$ with HSPh (Otto, *B.* 9, 1589).—8. By passing SO_2 into a solution of phenyl-hydrazine in benzene, and heating to boiling (Michaelis a. Ruhl, *B.* 23, 476).

Properties.—Needles, with faint odour, insol. water, v. sol. alcohol and ether.

Reactions.—1. Reduced by zinc and dilute H_2SO_4 to C_6H_5SH.—2. Oxidised by nitric acid to benzene sulphonic acid.—3. Split up by long boiling into Ph_2S and S (Graebe, *A.* 174, 189).—4. Alcoholic potash forms KSPh and $C_6H_5SO_2K$. 5. Alcoholic K_2S forms KSPh.—6. Bromine forms crystalline Ph_2SBr_2.

Di-phenyl tetra-sulphide $(C_6H_5)_2S_4$. S.G. $\frac{14·5}{}$ 1·297. Formed by the action of H_2S on a conc. alcoholic solution of benzene sulphinic acid (Otto, *J. pr.* [2] 37, 208). Formed also by the action of S_2Cl_2 on phenyl mercaptan. Thick yellow oil, m. sol. alcohol, v. sol. ether.

Di-phenyl hexasulphide $(C_6H_5)_2S_6$. An amorphous solid formed by heating benzene (20 g.) with S_2Cl_2 (10 g.) and iodine (1 g.) for 100 hours at 120° (Onufrovitch, *B.* 23, 3368).

References.—AMIDO-, AMIDO-IMIDO-, BROMO-, CHLORO-, CHLORO-NITRO-, IODO-, NITRO-, and OXY-DI-PHENYL SULPHIDES. *V.* also DI-PHENYL-DI-PHENYL SULPHIDE.

DI-PHENYL SULPHIDE *o*-CARBOXYLIC ACID $C_6H_5.S.C_6H_4.CO_2H$. Formed by the action of alkalis on the product of the action of NaSPh on diazotised *o*-amido-benzoic acid (Ziegler, *B.* 23, 2471). Plates (from benzene), insol. water.

PHENYL SULPHINIC ACID is BENZENE SULPHINIC ACID.

Diphenyl sulphinic acid $C_6H_4Ph.SO_2H$. Got by reducing $C_{12}H_9.SO_2Cl$ in ether with sodium-amalgam (Gabriel a. Deutsch, *B.* 13, 388). Crystalline powder, decomposing at about 70°.

PHENYL SULPHITE (Schall, *B.* 25, 1490, 1875). The salt $NaSO_2.OPh$ is formed from NaOPh and SO_2, and exhibits the following reactions:—1. *Alkyl iodides* convert it into phenyl ethers of the sulphonic acids $R.SO_2.OH$.—2. *Benzyl ether* forms phenyl benzyl oxide, SO_2, and NaCl at 180° (yield 16 p.c.).—3. $COCl_2$ forms $CO(OPh)_2$, SO_2, and NaCl at 180°.—4. *Iodoform* (1 mol.) heated with $NaSO_2.OPh$ (3 mols.) at 180° forms MeI, $CH_3.SO_2.OPh$, and 'rubbadin.'

Rubbadin $C_{44}H_{32}S_4O_8$, mol. w. 830 (by Raoult's method, calc. 806). Rub. crystallises from dilute alcohol in minute brownish-red plates, S. (alcohol) 43 at 20°, and forms a claret-coloured solution in alkalis. Its solution in NH_3Aq dyes silk and wool pale-claret colour, and cotton yellowish-violet.

Reactions.—1. Reduced by zinc-dust and NaOHAq to $C_{44}H_{34}S_4O_8$.—2. Conc. HNO_3, free from nitrous fumes, at 0° forms $C_{44}H_{26}(NO_2)_6S_4O_8$, a red crystalline powder, m. sol. hot alcohol, which may be reduced to $C_{44}H_{26}(NO_2)_4(NH_2)_2S_4O_8$, a glittering black crystalline powder (from ether-phenol) which yields a black crystalline di-acetyl derivative.—3. HClAq at 200° forms phenol (2 mols.), H_2S (2 mols.), and $C_{32}H_{20}S_2O_8$, a reddish-brown crystalline powder which yields the derivatives $C_{32}H_{18}Ac_2S_2O_8$, $C_{32}H_{18}Me_2S_2O_8$, and $C_{32}H_{14}Br_4Ac_2S_2O_8$.—4. Fusion with NaOH forms $SO(C_6H_4.OH)_2$ [96°] and salicylic acid.

Di-acetyl derivative $C_{44}H_{30}Ac_2S_4O_8$. Dark-brown powder, decomposed by heat without previous fusion. Split up by long boiling with alcohol into $C_{32}H_{21}S_2O_8$, sol. alcohol and $C_{24}H_{22}S_2O_4$, insol. alcohol. Br in chloroform converts the di-acetyl derivative into $C_{44}H_{24}Br_6Ac_2S_4O_8$.

Di-methyl-rubbadin $C_{44}H_{30}Me_2S_4O_8$. Got from rubbadin, KOHAq, and MeI. Dark reddish-brown powder.

PHENYL SULPHOCYANIDE $C_6H_5.SCN$. (231° cor.). S.G. $\frac{17.5}{}$ 1·155. Formed from $Pb(SPh)_2$ and CyCl. Prepared by adding cuprous sulphocyanide to a solution of diazobenzene sulphate and potassium sulphocyanide (Billeter, *B.* 7, 1753; Gattermann a. Haussknecht, *B.* 23, 738). Liquid. Yields phenyl mercaptan when heated with alcoholic potash.

Polymeride $(Ph.SCy)_3$. [97°]. Got from PhSNa and cyanuric chloride (Klason, *J. pr.* [2] 33, 120). Prisms (from HOAc).

Reference.—NITRO-PHENYL SULPHOCYANIDE.

PHENYL SULPHOCYANO-ETHYL KETONE $C_{10}H_9NSO$ *i.e.* $C_6H_5.CO.C_2H_4.SCy$. Got from $C_6H_5.CO.C_2H_4Br$ and KSCy in alcohol (Pampel a. Schmidt, *B.* 19, 2897). Liquid.

DI-PHENYL SULPHONE $(C_6H_5)_2SO_2$. *Sulphobenzide.* Mol. w. 218. [128°]. (376°) at 722 mm.

Formation. — 1. From benzene and SO_3 (Mitscherlich, *P.* 31, 628; Freund, *A.* 120, 76; Otto, *A.* 136, 160), fuming H_2SO_4 (Berthelot, *B.* 9, 349), or HSO_3Cl (Knapp, *Z.* [2] 5, 41). - 2. By oxidation of Ph_2S (Stenhouse, *A.* 140, 290; Kekulé a. Szuch, *Bl.* [2] 8, 204).—3. By distilling benzene sulphonic acid (F.). - 4. From benzene, $C_6H_5SO_2Cl$, and $AlCl_3$; the yield being 80 p.c. of the theoretical amount (Beckurts a. Otto, *B.* 11, 2066).—5. By heating benzene (200 c.c.) with conc. H_2SO_4 (300 c.c.), the yield being 6 p.c. of the benzene employed (Istrati, *Bl.* [3] 1, 492).—6. By heating $C_6H_5.SO_2Cl$ with $HgPh_2$ (Otto, *B.* 18, 248).—7. By oxidation of di-phenyl sulphoxide with $KMnO_4$ and HOAc (Colby a. McLoughlin, *Am.* 9, 67).

Properties.—Monoclinic prisms (from benzene) or plates (from alcohol), v. sol. ether. PCl_5 at 160° forms $C_6H_5SO_2Cl$ and chloro-benzene. Converted by potash-fusion into phenol, diphenyl, Ph_2S, PhSH, and other bodies (Otto, *B.* 19, 2425). Hot fuming H_2SO_4 forms benzene sulphonic acid.

References. — AMIDO-, BROMO-, CHLORO-, NITRO-, OXY-AMIDO-, and OXY- DI-PHENYL SULPHONES.

PHENYL SULPHONE ACETIC ACID *v.* PHENYL-SULPHONO-ACETIC ACID.

DI-PHENYL SULPHONE *o*-**CARBOXYLIC ACID** $C_{13}H_{10}SO_4$ *i.e.* $C_6H_5.SO_2.C_6H_4.CO_2H$. [152°]. Formed by oxidising $PhS.C_6H_4.CO_2H$ with HNO_3 (Graebe a. Schultess, *A.* 263, 7). Needles (containing aq). Melts at 99° when hydrated.

Di-phenyl sulphone *p*-**carboxylic acid.** [above 300°]. Got by oxidation of phenyl tolyl sulphone with $KMnO_4$ (Michael a. Adair, *B.* 11, 119). Prisms (from alcohol), sl. sol. hot water.—AgA′.

Di-phenyl sulphone di-carboxylic acid $SO_2(C_6H_4.CO_2H)_2$. [above 300°]. Got by oxidising di-*p*-tolyl sulphone (M. a. A.). Small prisms, sol. nitrobenzene.

DI-PHENYL SULPHONE *m*-**SULPHONIC ACID** $C_6H_5.SO_2.C_6H_4.SO_3H$. Got by heating di-phenyl sulphone (1 mol.) with $HO.SO_2Cl$ (1 mol.) at 150° (Otto, *B.* 11, 2075; 19, 2417). Fibrous crystalline mass, v. sol. water. — KA′aq.—NaA′3aq.—$CaA'_2$7aq.—$BaA'_2$4½aq.—$PbA'_2$3½aq.—$CuA'_2$7½aq.

Chloride. [99°]. White needles.

Amide $Ph.SO_2.C_6H_4.SO_2NH_2$. [154°].

Anilide. [131°]. Hard nodules.

Ethers.—EtA′. [89°].—PhA′. [106°].

Di-phenyl sulphone di-sulphonic acid $SO_2(C_6H_4.SO_3H)_2$. Formed from di-phenyl sulphone (1 mol.) and $HO.SO_2Cl$ (2 mols.) at 155° (Otto, *B.* 19, 3124). Deliquescent mass.—K_2A''aq.—Na_2A''3aq.—CaA″6½aq.—BaA″5aq.—PbA″3aq.—CuA″3½aq.

Chloride $C_{12}H_8S_3O_6Cl_2$. [176°]. Plates.

Amide. [242°]. Nearly insol. ether.

Anilide. [212°]. Lustrous plates.

Ethers Et_2A''. [82°].—Ph_2A''. [193°].

DIPHENYL SULPHONIC ACID $C_{12}H_{10}SO_3$ *i.e.* $C_6H_4Ph.SO_3H$. Formed, together with the di-sulphonic acid, by heating diphenyl with H_2SO_4 (Engelhardt a. Latschinoff, *B.* 4, 561; 6, 193).—KA′aq. Crystals (from 40 p.c. alcohol).—BaA'_2.—$CuA'_2$6aq.

Ethyl ether EtA′. [74°]. Needles.

Chloride $C_{12}H_9.SO_2Cl$. [115°].

Amide $C_{12}H_9.SO_2NH_2$. [227°-230°]. Slender needles (Gabriel a. Deutsch, *B.* 13, 386).

Diphenyl di-*o*-sulphonic acid $C_{12}H_{10}S_2O_6$ *i.e.* $SO_3H.C_6H_4.C_6H_4.SO_3H$. Formed by elimination of NH_2 from benzidine disulphonic acid (Limpricht, *A.* 261, 327). Viscid mass. Yields di-oxy-diphenyl [99°] by potash-fusion. BaA″6½aq.—PbA″5aq: needles, v. e. sol. water.

Chloride $C_{12}H_8(SO_2Cl)_2$. [138°]. Prisms.

Amide $C_{12}H_8(SO_2NH_2)_2$2aq. Prisms.

Anilide $C_{12}H_8(SO_2NHPh)_2$. [157°].

Diphenyl di-*p*-sulphonic acid $C_{12}H_8(SO_3H)_2$. [72·5°]. Formed by sulphonating diphenyl (Fittig, *A.* 132, 209; Engehardt, *Z.* 1871, 260). Deliquescent prisms. — K_2A''2½aq.—CaA″.—BaA″.

Chloride. [203°] (G. a. D.). Prisms.

Amide. [above 300°]. Needles.

References.—NITRO-, OXY-AMIDO-, and OXY-DIPHENYL SULPHONIC ACID.

PHENYL-SULPHONO-ACETIC ACID $C_8H_8SO_4$ *i.e.* $C_6H_5.SO_2.CH_2.CO_2H$. [112°].

Formation.—1. From sodium benzene sulphinate and chloro-acetic acid (Gabriel, *B.* 14, 834).—2. By saponifying its ether, which is got by boiling sodium benzene sulphinate with chloro-aceto-acetic ether (Otto a. Rössing, *B.* 23, 755).—3. By oxidising phenyl-thio-glycollic acid (Claesson; Blomstrand, *B.* 4, 712; 8, 120; Otto, *B.* 19, 3138).—4. By warming phenyl oxy-ethyl sulphone (1 vol.) with H_2SO_4 (1 vol.), diluted with water (2 vols.), and extracting with ether (Otto, *J. pr.* [2] 30, 340).

Properties.—Monoclinic crystals, m. sol. water, but separated by addition of NaCl. Sol. alcohol and ether.

Reactions.—1. Reduced by sodium amalgam to benzene sulphinic and acetic acids.—2. Gives off CO_2 above 160°, forming phenyl methyl sulphone.—3. *Chlorine*, passed into its warm aqueous solution, forms $CHCl_2.SO_2.C_6H_5$ [59°].—4. PCl_5 gives the chloride [58°], and at 110° forms $C_6H_5.SO_2.CCl_2.COCl$, which on treatment with water gives $C_6H_5.SO_2.CHCl_2$ (Otto, *J. pr.* [2] 40, 540).

Salts.—$BaA'_2$2aq.—$CuA'_2$2aq.—$CaA'_2$2½aq.—$PbA'_2$2aq.—AgA′. Sparingly soluble needles.

Methyl ether MeA′. Oil (Otto, *J. pr.* [2] 36, 436).

Ethyl ether EtA′. [42°] (O.). Readily saponified by NaOHAq, while KOHAq gives phenyl methyl sulphone. Bromine at 90°, followed by NaOHAq, forms $C_6H_5.SO_2.CHBr_2$ [76°]. Alcoholic potash forms $Ph.SO_2.Me$ (Michael a. Milner, *Am.* 7, 65). NaOEt forms the compound $C_6H_5.SO_2.CHNa.CO_2Et$, which yields Ph_2S_2, Ph_2S, PhSEt, and $Ph.SO_2Me$ on distillation (Otto a. Rössing, *B.* 22, 1453; 23, 1647).

Chloride $Ph.SO_2.CH_2.COCl$. [58°].

Amide $Ph.SO_2.CH_2.CONH_2$. [153°]. Needles (from water). Yields $Hg(C_8H_8NSO_3)_2$ [215°] on boiling with HgO.

PHENYL-SULPHONO-ACETONE *v.* PHENYL METHYLENE METHYL SULPHONE-KETONE.

Di-phenyl-di-sulphono-acetone *v.* DI-PHENYL DI-METHYLENE DISULPHONE-KETONE.

PHENYL-SULPHONO-ANGELIC ETHER $C_{13}H_{16}SO_4$ *i.e.* $C_6H_5.SO_2.CH(C_3H_5)CO_2Et$. [64·5°]. Got from $PhSO_2.CHNa.CO_2Et$ and allyl iodide (Michael, *Am.* 7, 67). Prisms (from alcohol).

PHENYL-SULPHONO-*n*-BUTYRIC ACID $C_6H_5.SO_2.CHEt.CO_2H$. [124°]. Formed from benzene sulphinic acid, α-bromo-butyric acid, and Na_2CO_3Aq (Otto, *B.* 21, 996). Needles, m. sol. water. Yields phenyl propyl sulphone on heating.

Di-phenyl-di-sulphono-butyric ether $(C_6H_5.SO_2)_2CMe.CH_2.CO_2Et$. [97°]. Got by oxidation of $(PhS)_2CMe.CH_2.CO_2Et$ (Autenrieth, *A.* 259, 367). Small crystals, insol. water. Converted by KOHAq into benzene sulphinic acid and β-phenyl-isocrotonic acid.

PHENYL-SULPHONO-CROTONIC ACID $C_6H_5.SO_2.CMe{:}CH.CO_2H$. [158°]. S. ^{15} ·38; ^{100} 25. Formed by heating the Na salt of β-chloro-crotonic acid [94·5°] with sodium benzene sulphinate in aqueous solution at 170° (Autenrieth, *A.* 259, 343). Plates (from water), m. sol. ether. At 210° it slowly changes to the following isomeride [127°].—KA′ $1\frac{1}{2}$aq.—BaA′$_2$ aq.—MgA′$_2$ 7aq.—ZnA′$_2$ 6aq.—CuA′$_2$ aq.—AgA′. [200°]. Matted needles (from water).

Phenyl-sulphono-isocrotonic acid $C_6H_5.SO_2.CMe{:}CH.CO_2H$. [127°]. S. ·26 at 15°; 5 at 100°. Formed by heating β-chloro-isocrotonic acid with sodium benzene sulphinate in aqueous solution at 145°. Got also by saponifying di-phenyl-di-sulphono-isobutyric ether (Autenrieth, *A.* 259, 335). Feathery needles. Yields benzene sulphinic acid [81°] on boiling with potash.—KA′ 3aq.—BaA′$_2$ $2\frac{1}{2}$aq.—MgA′$_2$ 6aq.—ZnA′$_2$ 6aq. [120°] (hydrated).—AgA′. [c. 243°].

Ethyl ether EtA′. Oil.

DI-PHENYL-DI-SULPHONO-DI-ETHYL OXIDE $C_{16}H_{18}S_2O_5$ *i.e.* $O(C_2H_4.SO_2Ph)_2$. [70°]. Formed from $C_6H_5.SO_2.C_2H_4Cl$ and dry Ag_2O (Otto, *J. pr.* [2] 30, 202). Needles, sol. benzene. A polymeride [88°] is got by heating the compound $(C_6H_5.SO_2)_2C_2H_4$ with KOHAq.

DI-PHENYL-DI-SULPHONO-DI-ETHYL SULPHIDE $S(C_2H_4.SO_2Ph)_2$. [124°]. Got from $C_6H_5.SO_2.C_2H_4Cl$ and alcoholic KSH (Otto, *J. pr.* [2] 30, 348). Needles (from dilute alcohol).

DI-PHENYL-DI-SULPHONO-HEXOIC ETHER $(C_6H_5.SO_2)_2CMe.CHEt.CO_2Et$. [111°]. Got by oxidising $(PhS)_2CMe.CHEt.CO_2Et$ (Autenrieth, *A.* 259, 372). Crystals, v. sol. alcohol.

DI-PHENYL-DI-SULPHONO-DI-PHENYL OXIDE $(C_6H_5.SO_2.C_6H_4)_2O$. [70°]. (above 200°). Got by heating $C_6H_4(SO_2Ph)_2$ with alcoholic potash at 165° (Otto a. Rössing, *B.* 20, 187). Needles, v. e. sol. alcohol, insol. water.

PHENYL-α-SULPHONO-PROPIONIC ACID $C_6H_5.SO_2.CHMe.CO_2H$. [116°]. Formed by heating α-bromo-propionic ether with sodium benzene sulphinate and ether. Minute needles.—NaA′.—BaA′$_2$ 2aq.—EtA′. [c. 17°].

Phenyl-β-sulphono-propionic acid $C_6H_5.SO_2.CH_2.CH_2.CO_2H$. [124°]. Got from β-bromo-propionic acid, benzene sulphinic acid, and Na_2CO_3Aq (Otto, *B.* 21, 89). Plates, sl. sol. cold water.

DI-PHENYL SULPHOXIDE $(C_6H_5)_2SO$. [71°]. Formed by the action of SO_2 or $SOCl_2$ on benzene in presence of $AlCl_3$ (Colby a. McLoughlin, *Am.* 9, 67; *B.* 20, 195). Triclinic crystals, v. sol. alcohol. Oxidised by $KMnO_4$ to Ph_2SO_2. Reduced by sodium to Ph_2S. $NaNO_2$ and H_2SO_4 give $SO(C_6H_4.NO_2)_2$ [116°] and $SO_2(C_6H_4.NO_2)_2$ [163°].

Di-phenyl-di-sulphoxide *v. Phenyl ether* of BENZENE THIOSULPHONIC ACID.

PHENYL-SULPHURIC ACID *v.* PHENYL SULPHATE and PHENOL, *Reaction* 19.

PHENYL SULPHUROUS ACID *v.* BENZENE SULPHONIC ACID.

PHENYL SULPHYDRATE *v.* PHENYL MERCAPTAN.

PHENYL-SULPHYDRO-ACETIC ACID *v.* PHENYL-THIOGLYCOLLIC ACID.

PHENYL-SULPHYDRO-ACETOPHENONE $C_6H_5.CO.CH_2.SPh$. [53°]. Formed from ω-bromo-acetophenone and NaSPh (Delisle, *B.* 22, 306). Crystals, v. sol. ether and acetone.

DI-PHENYL-DI-SULPHYDRO-BUTYRIC ETHER $C_{18}H_{20}S_2O_2$ *i.e.* $(PhS)_2CMe.CH_2.CO_2Et$. [58°]. Got by passing HCl into a mixture of acetoacetic ether and phenyl mercaptan (Escales a. Baumann, *B.* 19, 1790). Pearly plates (from alcohol), v. sol. ether.

PHENYL-SULPHYDRO-CROTONIC ACID $CH_3.CH{:}C(SPh).CO_2H$. [86°]. Formed by the action of Na and phenyl mercaptan on the Na salt of α-chloro-crotonic acid [97°] (Autenrieth, *A.* 254, 246). Needles or plates. Its K salt is hygroscopic, S. (alcohol) 20·8.

Isomeride $CHMe{:}C(SPh).CO_2H$. [80°]. Got in like manner from the stereo-isomeric liquid chloro-crotonic acid. White plates. Its K salt is hygroscopic, S. (alcohol) 10·4.

Phenyl-β-sulphydro-crotonic acid $CH_3.C(SPh){:}CH.CO_2H$ or $CH_2{:}C(SPh).CH_2.CO_2H$. [177°]. S. (alcohol) 2 in the cold. Formed, together with small quantities of an isomeride [145°], by warming di-phenyl-di-sulphydro-butyric ether with alcoholic soda (Escales a. Baumann, *B.* 19, 1791). Plates (from alcohol), insol. water.—BaA′$_2$ 2aq.—AgA′: amorphous pp.

Isomeride $CH_3.C(SPh){:}CH.CO_2H$. [158°]. Formed from phenyl mercaptan and the Na salt of chloro-crotonic acid [95°] (Autenrieth, *A.* 254, 230). Both acids form a cherry-red solution in H_2SO_4.

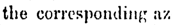
DI-PHENYL SULPHYDRO-ETHYLIDENE DISULPHONE. *Phenyl derivative* $(C_6H_5.SO_2)_2CMe.SPh$. [194°]. Got by heating $(C_6H_5.SO_2)_2CH.SPh$ with alcoholic soda and

MeI at 100° (Laves, *B.* 23, 1416). Crystals (from chloroform).

DI-PHENYL-DI-SULPHYDRO-HEXOIC ETHER $CH_3.C(SPh)_2.CHEt.CO_2Et$. [71°]. Got from ethyl-acetoacetic ether, phenyl mercaptan, and HCl (Autenrieth, *A.* 259, 371). Shining crystals, v. sol. ether and alcohol.

DI-PHENYL SULPHYDRO-METHENYL DISULPHONE. *Phenyl derivative* $(C_6H_5.SO_2)_2CH.SPh$. [175°]. Got by the action of $KMnO_4$ and dilute H_2SO_4 on $CH(SPh)_3$ dissolved in benzene (Laves, *B.* 23, 1414). Silky needles, m. sol. chloroform, nearly insol. water and alcohol, sol. alcoholic NaOH. May be oxidised to $CH(SO_2Ph)_3$ [215°].

DI-PHENYL-DI-SULPHYDRO-PHENYL-ACETIC ACID $C_6H_5.C(SPh)_2.CO_2H$. [143°]. Formed from phenyl-glyoxylic acid, phenyl-mercaptan, and HCl (Escales a. Baumann, *B.* 19, 1789). Insol. water, v. sol. ether. Crystallises from benzene with $\frac{1}{2}C_6H_6$.—KA′ 1½aq.

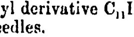
PHENYL-SULPHYDRO-PHENYL-THIO-BIAZYL-HYDRAZINE 
$\begin{smallmatrix}\mathrm{NPh.N}\\ \mathrm{CS-S}\end{smallmatrix}\!>\!\mathrm{C.NH.NHPh}$.
[142°]. Got by reducing the corresponding azo-compound with alcoholic ammonium sulphide (Freund a. Kuh, *B.* 23, 2830). Plates, sl. sol. alcohol.

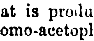
DI-PHENYL-DI-SULPHYDRO-PROPIONIC ACID $CH_3.C(SPh)_2.CO_2H$. [117°]. Got from pyruvic acid, phenyl mercaptan, and HCl (Escales a. Baumann, *B.* 19, 1787). Needles (from ligroïn).—NaA′.—BaA′$_2$2aq: v. sol. hot Aq.

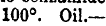
Amide. [93°]. Needles (from alcohol).

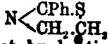
DI-PHENYL SULPHYDRO-PROPYLENE DISULPHONE. *Phenyl derivative* $C_6H_5.SO_2.CH_2.CMe(SPh).SO_2.C_6H_5$. [119°]. Formed by oxidising $C_6H_5.SO_2.CH_2.CMe(SPh)_2$ with $KMnO_4$ in the cold (Otto a. Rössing, *B.* 24, 234). Crystalline granules, sl. sol. cold alcohol.

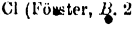
DI-PHENYL-DI-SULPHYDRO-VALERIC ACID $CH_3.C(SPh)_2.CH_2.CH_2.CO_2H$. [69°]. Got from phenyl mercaptan, β-acetyl-propionic acid and HCl (Escales a. Baumann, *B.* 19, 1795). Prisms (from chloroform-ether).—BaA′$_2$.

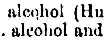
PHENYL-TETRIC ACID $C_{11}H_{10}O_3$ *i.e.* 
$\begin{smallmatrix}\mathrm{CH_2Ph.CH.CO}\\ \mathrm{CO.CH_2}\end{smallmatrix}\!>\!\mathrm{O}$. Formed by heating bromo-benzylacetoacetic ether (Moscheles, *B.* 21, 2608). Not affected by HClAq at 170°. Yields a benzoyl derivative $C_{11}H_9BzO_3$ [110°] crystallising in needles.

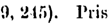
PHENYL-THIAZOLE C_9H_7NS *i.e.* 
$\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{CH\ .S}\\ \mathrm{CPh:CH}\end{smallmatrix}$. [52°]. (273° cor.). Got by the diazo- reaction from the amido-phenyl-thiazole that is produced by the action of thio-urea on bromo-acetophenone (Popp, *A.* 250, 279; *cf.* Arapides, *A.* 249, 25). Sl. sol. cold water.—B′HCl. [80°]. Needles.—B′$_2$H$_2$PtCl$_6$ 2aq. [196°].—B′HHgCl$_3$. [153°].—**Picrate.** [165°].—B′HAuCl$_4$. [175°]. Needles (from alcohol).

μ-Phenyl-thiazole 
$\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{CPh.S}\\ \mathrm{CH\ :CH}\end{smallmatrix}$. (269°). Formed by heating thio-benzamide with di-chloro-di-ethyl oxide at 100°. Oil.—B′HCl 2aq. [62°].—B′$_2$H$_2$PtCl$_6$2aq. [175°] (when anhydrous).—**Picrate.** [125°]. Yellow needles.

Dihydride 
$\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{CPh.S}\\ \mathrm{CH_2.CH_2}\end{smallmatrix}$. *Phenyl-thiazoline.* (276). Got by heating thio-benzamide with ethylene bromide (Gabriel a. Heymann, *B.* 23, 158; 24, 784). Formed also by the action of PCl_5 on $S_2(C_2H_4.NHBz)_2$ (Gabriel a. Coblentz, *B.* 24, 1124). Oil. Yields a crystalline dibromide. — B′$_2$3HCl. — B′$C_6H_3N_3O_7$. [172°]. Yellow needles.—B′$_2$H$_2$PtCl$_6$.

ν-Phenyl-thiazole. *Tetra-hydride* 
$\mathrm{NPh}\!<\!\begin{smallmatrix}\mathrm{CH_2.S}\\ \mathrm{CH_2.CH_2}\end{smallmatrix}$. Got by reducing ethylene phenyl-di-thio-carbamate [128°] with tin and HCl (Förster, *B.* 21, 1871). Oil.—B′$_2$H$_2$PtCl$_6$.

Di-phenyl-thiazole 
$\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{CPh.S}\\ \mathrm{CPh:CH}\end{smallmatrix}$ [93°]. (above 360°). Got from thiobenzamide and bromo-acetophenone in alcohol (Hubacher, *A.* 259, 237). Plates, v. sol. alcohol and ether.

Tri-phenyl-thiazole 
$\mathrm{N}\!<\!\begin{smallmatrix}\mathrm{CPh.S}\\ \mathrm{CPh:CPh}\end{smallmatrix}$ [87°]. Got from thiobenzamide and bromo-deoxybenzoïn (Hubacher, *A.* 259, 245). Prisms (from ether), m. sol. alcohol, nearly insol. HClAq.

Reference.—OXY-PHENYL-THIAZOLE.

PHENYL-DITHIENYL $C_4H_3S.C_4H_2PhS$. [209°]. A product of the action of S on toluene at a red heat (Renard, *C. R.* 111, 48). Plates, v. sl. sol. alcohol and ether. Gives a blue colour with isatin and H_2SO_4, and a green colour with phenanthraquinone and H_2SO_4. Gives rise to $C_{14}H_7Br_5S_2$ [320°] and $C_{14}H_8(NO_2)_2S_2$ [273°].

PHENYL THIENYL KETONE *v.* THIENYL PHENYL KETONE.

(α)-PHENYL-(β)-THIO-ALLOPHANIC ACID *Ethyl ether.* $C_{10}H_{12}N_2SO_2$ *i.e.* $NH_2.CS.NPh.CO_2Et$. [127°]. Formed from NHAc.CS.NHPh and $ClCO_2Et$ (Seidel, *J. pr.* [2] 32, 275). Monoclinic tablets, converted by alcoholic NH_3 at 100° into phenyl-thio-urea.

(β)-Phenyl-thio-allophanic acid. *Ethyl ether* $NHPh.CS.NH.CO_2Et$. Got from phenyl-thio-urea and $ClCO_2Et$ (Seidel, *J. pr.* [2] 32, 270). Oil. AcCl at 60° forms NHAc.CS.NHPh [170°].

Phenyl di-thio-allophanic acid. *Isoamyl ether* $NHPh.CS.NH.CO.SC_5H_{11}$. [102°]. Formed from phenyl-thio-urea and $Cl.CO.SC_5H_{11}$ (Schöne, *J. pr.* [2] 32, 256). Needles. Very unstable. Forms an acetyl derivative [240°].

Di-phenyl-thio-allophanic acid. *Ethyl ether* $NHPh.CS.NPh.CO_2Et$. [95°]. Formed from di-phenyl-thio-urea and $ClCO_2Et$ (Seidel, *J. pr.* [2] 32, 262). Prisms (from alcohol). Alcoholic $AgNO_3$ ppts. $C_{16}H_{16}N_2SO_2AgNO_3$.

Reactions.—1. *Caustic potash* regenerates $CS(NHPh)_2$.—2. Aqueous ammonia at 100° forms $NHPh.CS.NH_2$ and $NHPh.CO_2Et$. — 3. Alcoholic *aniline* at 100° forms $CS(NHPh)_2$ and $NHPh.CO_2Et$.—4. HgO in presence of alcoholic ammonia forms $(NHPh.CO.NPh.CO_2Et)_2HgO$ [129°], a crystalline body that is reconverted by H_2S into di-phenyl-thio-allophanic ether.—5. By heating in a current of HCl it is converted into $CS(NHPh)_2$, aniline, and phenyl-thiocarbimide.

Di-phenyl-di-thio-allophanic acid. *Isoamyl ether* $NPhH.CS.NPh.CO.SC_5H_{11}$. [87°]. Got from di-phenyl-thiurea and $Cl.CO.SC_5H_{11}$ (Schöne, *J. pr.* [2] 32, 258). Needles (from alcohol). It is insoluble in cold water, but decomposed by hot water. Its alcoholic solution is ppd. by $AgNO_3$, $HgCl_2$ or $PtCl_4$. HgO and NH_3

convert it (in alcoholic solution) into di-phenyl-guanidine, [147°].

TRI-PHENYL-THIO-AMMELINE $C_{21}H_{17}N_5S$ *i.e.* $C(SH)\left\langle\begin{matrix}N-C(NPh)\\NPh.C(NPh)\end{matrix}\right\rangle NH$. [238°]. Formed from phenyl-cyanamide and phenyl-thiocarbimide, and got also by heating tri-phenyl-biguanide with CS_2 at 100°, and by heating di-phenyl-guanidine with phenyl-thiocarbimide, alcohol, and mercury sulphocyanide (Rathke, *B.* 20, 1065; 23, 1673). Plates (from chloroform). Converted by alcoholic potash into tri-phenyl-ammeline. Alcohol and EtBr at 100° form $C_{21}H_{16}EtN_5SHBr$, crystallising from alcohol in plates.—B'HCl.—$AgC_3HPh_3N_5S$: yellow pp.

DI-PHENYL-THIO-BENZAMIDE $Ph.CS.NPh_2$. Formed by heating di-phenyl-benzamidine with H_2S or CS_2 at 130° (Bernthsen, *A.* 192, 88). Yellow triclinic crystals (from benzene); $a:b:c = \cdot927:1:\cdot766$, $\alpha = 93° 29'$, $\beta = 100° 55'$, $\gamma = 84° 14'$. Insol. cold water, sl. sol. cold alcohol.

PHENYL-DI-THIO-BIURET $C_8H_9N_3S_2$ *i.e.* $NHPh.CS.NH.CS.NH_2$. [174°]. Formed by heating aniline with perthiocyanic acid (Glutz, *A.* 154, 44). Got also by boiling carbimido-phenyl-thio-urea with ammonium sulphide (Wunderlich, *B.* 19, 452). Prepared by adding phenyl-thiocarbimide (36 g.) to an alcoholic solution of cyanamide (11 g.) and Na (6 g.), and decomposing the pp. by dissolving in a solution of NH_4Cl (14·5 g.) containing NH_3Aq (50 c.c.), passing in H_2S, and heating to boiling (Hecht, *B.* 25, 756). Pearly plates, sl. sol. hot water.—B'HCl.—$B'HNO_3$.

Ethyl derivative $C_8H_8EtN_3S_2$. [109°]. Got by adding alcohol, NH_3Aq, and EtI to the base (Tursini, *B.* 17, 584). Trimetric tables.

PHENYL-THIO-CARBAMIC ACID NHPh.CO.SH. *Methyl ether* NHPh.CO.SMe. [84°]. Formed by heating di-phenyl-methyl-ψ-thio-urea NHPh.C(NPh).SMe with dilute H_2SO_4 (Will, *B.* 15, 339). Plates, sol. alcohol, ether, and benzene. Decomposed by KOH into aniline, MeSH, and CO_2. Boiling alcoholic NH_3 forms MeSH and phenyl-urea. Aniline gives methyl mercaptan and $CO(NHPh)_2$.

Ethyl ether NHPh.CO.SEt. [73°]. Needles. Got by heating NHPh.C(NPh).SEt with dilute H_2SO_4 and by the action of aniline on Cl.CO.SEt (Will).

Isoamyl ether $NHPh.CO.SC_5H_{11}$. [67°]. Got from aniline and $Cl.CO.SC_5H_{11}$ (Schöne, *J. pr.* [2] 32, 249). Needles (from ether).

Ethylene ether $CO\left\langle\begin{matrix}NPh.CH_2\\S-CH_2\end{matrix}\right.$. [79°]. Got by heating di-phenyl-ethylene-ψ-thio-urea with dilute HClAq at 200° (W.). Formed also by the action of chloro-acetic acid on the ethylene ether of phenyl-di-thio-carbamic acid (Evers, *B.* 21, 976). Needles, sol. alcohol and ether, insol. acids and alkalis.

Phenyl ether NHPh.CO.SPh. [125°]. Formed by heating phenyl mercaptan with phenyl cyanate (Snape, *C. J.* 47, 778; *B.* 18, 2432). Needles, v. sol. alcohol and ether.

Phenyl-ψ-thio-carbamic acid NHPh.CS.OH.

Ethyl ether $C_9H_{11}NSO$ *i.e.* NHPh.CS.OEt or NPh:C(SH).OEt. [72°]. Formed by heating phenyl-thiocarbimide with alcohol (Hofmann, *B.* 2, 120; 3, 772; Bamberger, *B.* 15, 2164). Formed also by the action of alcoholic potash on phenyl-thiocarbimide (R. Schiff, *B.* 9, 1316). Triclinic prisms, sol. alkalis and reppd. by CO_2. Resolved by distillation into alcohol and phenyl-thiocarbimide. Oxidised by alkaline K_3FeCy_6 to $C_{18}H_{20}N_2O_2S_2$ or $S_2(C(NPh).OEt)_2$ [102°], which is also got by the action of I on $C_9H_{10}NOSAg$ (Liebermann a. Natanson, *B.* 13, 1575; Jacobsen, *B.* 19, 1076).—$(C_9H_{10}NO.S)_2Pb\,2aq$: small needles.—$C_9H_{10}NOSAg$.—$C_9H_{10}NOSHgClHCl$: needles.—$(C_9H_{10}NOS)_2Hg$. [78°] (Stephanovitch, *B.* 7, 692).—$(C_9H_{10}NOS)_2HgAgNO_3$. Needles.—$C_9H_{10}NOSMe$. (260°–265°). Oil.—$C_9H_{10}NOSEt$. [30°]. (275°). Prisms; decomposed by dilute H_2SO_4 at 200° into aniline and CO(OEt)(SEt) (Liebermann, *B.* 13, 682; *A.* 207, 148).—$C_9H_{10}NOSC_4H_9$. [75°] (Mylius, *B.* 5, 977).

Phenyl ether NHPh.CS.OPh. Got by heating phenyl-thiocarbimide with phenol at 145° (Dixon, *C. J.* 57, 268). Sulphur-yellow octahedra; decomposed by heat.

Phenyl di-thio-carbamic acid NHPh.CS.SH. Splits up into CS_2 and aniline when set free from its salts.

Salts.—The salt NHPh.CS.SK is formed by boiling potassium xanthate EtO.CS.SK (1 mol.) with an alcoholic solution of aniline (1 mol.) (Rathke, *B.* 11, 958). Prepared from CS_2, aniline, ether, and alcoholic potash (Losanitsch, *B.* 24, 3024). Yellow monoclinic needles, v. e. sol. water and alcohol, insol. ether. Yields $CS(NHPh)_2$ when heated. Boiling water forms phenyl-thiocarbimide and $CS(NHPh)_2$.—$NHPh.CS.SNH_4$. Yellow prisms. Converted by I into $(NHPh.CS)_2S$ [138°]. BaA'_2: yellowish plates.—NiA'_2.

Methyl ether NHPh.CS.SMe. [93·5°]. Formed from the NH_4 salt and MeI (L.) and also by heating NHPh.C(NPh).SMe with CS_2 at 160° (Will, *B.* 15, 342). Decomposed by alkalis into MeSH and aniline.

Ethyl ether NHPh.CS.SEt. [60°]. Formed from phenyl-thiocarbimide and mercaptan at 150° (Hofmann, *B.* 2, 120; Will, *B.* 15, 1305), and also by the action of EtI on the ammonium salt (L.). Tables, v. sol. alcohol, sol. alkalis.

Isoamyl ether $C_5H_{11}A'$. [171°].

Ethylene derivative $CS\left\langle\begin{matrix}NPh.CH_2\\S-CH_2\end{matrix}\right.$. [234°]. Formed, together with phenyl-thiocarbimide, by heating $C(NPh)\left\langle\begin{matrix}NPh.CH_2\\S-CH_2\end{matrix}\right.$ with CS_2 at 200° (W.). Needles. Converted by MeI into $C_9H_9NS_2MeI$ [149°].

References.—BROMO-, CHLORO-, and NITRO-PHENYL-THIO-CARBAMIC ACID.

PHENYL-THIOCARBAMINE-CYAMIDE *v.* CARBIMIDO-PHENYL-THIO-UREA.

PHENYL-THIOCARBAMINE-ETHYL-CYAMIDE *v.* ETHYL-CARBIMIDO-PHENYL-THIO-UREA.

PHENYL-THIO-CARBAZIC ACID NHPh.NH.CO.SH. The phenyl hydrazine salt $NHPh.NH.CO.SN_2H_3Ph$ [84°] is formed from phenyl-hydrazine and COS (Heller, *A.* 263, 269).

Phenyl di-thio-carbazic acid NHPh.NH.CS.SH. Formed, as phenyl-hydrazine salt $NHPh.NH.CS.SN_2H_3Ph$ [97°] by adding CS_2 to an ethereal solution of phenyl-hydrazine (Fischer, *A.* 190, 114). Plates, v. sol. alcohol and ether. Readily decomposed by heat into $CS(N_2H_3Ph)_2$, CS_2, H_2S, and NH_3.

PHENYL-THIO-SEMICARBAZIDE $C_7H_9N_3S$ *i.e.* $NH_2.CS.NH.NHPh$. [201°] (F.; P.); [190°] (S. a. R.).

Formation.—1. By warming di-phenyl-thio-carbazide with alcoholic or aqueous alkalis (Fischer, *A.* 212, 324).—2. By heating phenyl-hydrazine sulphocyanide.—3. By heating phenyl-hydrazine with thio-urea or with phenyl-thio-urea (Pellizzari, *G.* 16, 203; Skinner a. Ruhemann, *C. J.* 53, 550; *B.* 20, 3373).

Properties.—Needles, insol. ether, sl. sol. hot water, v. sol. hot alcohol. Conc. HClAq at 120° forms phenyl-thiocarbizine $C_7H_6N_2S$. $COCl_2$ forms $CO:N_2Ph.CS.NH_2$ [c. 270°] crystallising from HOAc (Freund, *A.* 21, 2465).

Acetyl derivative NHPh.NH.CS.NHAc. [179°]. Formed by mixing solutions of acetyl-thiocarbimide and phenyl-hydrazine in dry benzene (Dixon, *C. J.* 55, 303). Small prisms.

Benzoyl derivative $C_{14}H_{13}N_3SO$. Silky needles. Does not melt at 220°.

Di-phenyl-thiocarbazide $CS(NH.NHPh)_2$. [c. 150°]. Formed by heating the compound of phenyl-hydrazine and CS_2 at 110°–140° (Fischer). Formed also from phenyl-hydrazine and $CSCl_2$ (Heller, *A.* 263, 278). Triangular prisms (from alcohol). Dissolves in hot aniline, forming a solution which is green in thin layers, but red in thick layers. Hot alcoholic potash also forms this dichroic substance, di-phenyl-thiocarbazone $C_{13}H_{12}N_4S$ or $CS(N_2Ph)NH.NHPh$, which yields $(C_{13}H_{12}N_4S)_2ZnO$, and may be reduced by zinc-dust and NaOHAq to phenyl-thio-semicarbazide and aniline. Di-phenyl-thio-carbazone may be oxidised by ppd. MnO_2 in presence of alcoholic potash to red needles of di-phenyl-thiocarbodiazone $CS(N_2Ph)_2$.

Di-phenyl-thio-semicarbazide NHPh.NH.CS.NHPh. [177°]. Formed from phenyl-hydrazine and phenyl-thiocarbimide in alcoholic solution (Fischer, *A.* 190, 122). Prisms (from alcohol), sl. sol. ether. $COCl_2$ forms $CO:N_2Ph.CS.NHPh$ [188°], crystallising in needles (Freund, *B.* 21, 2466).

Butyryl derivative $C_4H_7O.NPh.NH.CS.NHPh$. [156°]. Formed from sodium phenyl-hydrazine, phenyl thiocarbimide, and *n*-butyryl chloride (Michaelis a. Schmidt, *A.* 252, 309). V. sol. hot alcohol.

Benzoyl derivative NPhBz.NH.CS.NHPh. [310°]. Obtained from $NPhBz.NH_2$ and phenyl-thiocarbimide (M. a. S.).

Reference.—NITRO-DI-PHENYL-THIO-SEMICARBAZIDE.

DI-PHENYL-THIO-SEMICARBAZIDE CARBOXYLIC ACID $C_{14}H_{13}N_3O_2S$ *i.e.* $NHPh.CS.NH.NHC_6H_4.CO_2H$. [204°]. Formed by warming *m*-hydrazido-benzoic acid with phenyl thiocarbimide and HOAc (Roder, *A.* 236, 173). Colourless needles.

PHENYL-THIOCARBIMIDE C_7H_5NS *i.e.* $C_6H_5N.CS$. Mol. w. 135. (220°) at 750 mm. (Schiff, *B.* 19, 568). S.G. $\frac{4}{4}$ 1·059 (Nasini a. Scala, *G.* 17, 66). S.V. 143·4 (Schiff; Lossen *A.* 254, 73).

Formation.—1. By distilling phenyl-thio-urea with P_2O_5 (Hofmann, *Pr.* 9, 274, 487; *C. J.* 13, 309; *B.* 15, 980).—2. By heating di-phenyl-thio-urea with conc. HClAq at 165° (Merz a. Weith, *Z.* 1869, 589).—3. By the action of I on a benzene solution of tri-phenyl-guanidine (Hofmann, *B.* 2, 453; Rudneff, *J. R.* 10, 184).—4. By heating phenyl cyanate or phenyl-carbamic ether with P_2S_5 at 160° (Michael a. Palmer, *Am.* 6, 258).—5. Formed, together with *o*- or *p*- tolyl-thiocarbimide, by heating phenyl-*o*- or *p*- tolyl-cyanamide ($C_6H_5N:C:NC_7H_7$) with CS_2 at 180°–200° (Huhn, *B.* 19, 2409).

Properties. — Pungent oil, volatile with steam.

Reactions. — 1. *Alcohol* at 100° forms NHPh.CS.OEt, while mercaptan gives rise to NHPh.CS.SEt. — 2. *Alcoholic potash* forms $CS(NHPh)_2$ and $CO(NHPh)_2$. — 3. *Ammonia* forms $CS(NHPh)(NH_2)$, *aniline* gives $CS(NHPh)_2$, and other amines act in like manner.—4. PEt_3 acts violently, and forms $C_{13}H_{20}NPS$, while PMe_3 forms oily $C_{10}H_{14}NPS$, which yields crystalline B'HCl.—5. *Chlorine* passed into its solution in chloroform forms $(PhNCS)_2Cl_2$ [150°–160°] and $PhNCCl_2$ (212°). The chloride $(PhNCS)_2Cl_2$ is converted by H_2S into $CS(NHPh)_2$, and by warm spirit into $(PhNCS)_2O$, crystallising in yellow needles [118°] (Helmers, *B.* 20, 786). 6. *Bromine* in chloroform or HOAc forms red crystals of $(PhNCSBr_2)_2$, decomposed at 100° into pale-yellow plates $(PhNCSBr)_2$ [190°] (Helmers; *cf.* Proskauer a. Sell, *B.* 9, 1262).—7. SO_3 forms $C_7H_5NS_2O_3$ [180°–183°], crystallising from benzene, and converted by water at 100° into amido-benzene *p*-sulphonic acid, CO_2, and H_2S (Magatti, *B.* 11, 2267).—8. PCl_5 at 100° forms $C_6H_5NCCl_2$ and $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{S}{>}CCl$ (248°) (Hofmann, *B.* 12, 1126).—9. $ClSO_3H$ forms $C_{14}H_{10}N_2S_3$ [151°], insol. water, and $SO_3H.C_6H_4.NOS$ aq, sol. water (Pawlewski, *B.* 22, 2200).—10. Reduced *copper* at 200° forms benzonitrile.—11. H_2S forms phenyl-thio-urea. — 12. Boiling *water* forms $CS(NHPh)_2$, CO_2, and H_2S (Bamberger, *B.* 14, 2642). — 13. HOAc forms, on heating, $CO(NHPh)_2$, Ac_2O, H_2S, and CO_2; the di-phenyl-urea being further split up into aniline and CO_2, with formation of Ac_2O (Cain a. Cohen, *C. J.* 59, 327; *cf.* Gumpert, *J. pr.* [2] 32, 294).—14. *Chloro-acetic acid* and alcohol at 170° form $PhN:C{<}\genfrac{}{}{0pt}{}{S.CH_2}{O.CO}$ [148°], which yields aniline, CO_2, and thioglycollic acid on boiling with water (Liebermann a. Voeltzkoff, *B.* 13, 276).—15. *Sodium malonic ether* in presence of alcohol forms $C_{14}H_{16}SNO_4Na$, whence acids liberate $C_{14}H_{17}SNO_4$, or $(CO_2Et)_2CH.CS.NHPh$ [60°] (Michael, *J. pr.* [2] 35, 451).—16. *Sodium cyanamide* and alkyl iodides form cyano-phenyl-alkyl-thio-ureas (Hecht, *B.* 23, 1664). In this way the following compounds may be prepared: NHPh.CS.NMeCy [186°], NHPh.CS.NEtCy [144°], $NHPh.CS.NCyC_3H_5$ [100°], crystallising in needles, $NHPh.CS.NCyC_3H_7$ [108°], crystallising in needles, and $NHPh.CS.NCy.CH_2Ph$ [182°]. 17. *Aldehyde-ammonia* forms $C_{22}H_{21}N_3S_2O_2$ [148°], crystallising from alcohol in silvery needles (R. Schiff, *B.* 9, 567; *G.* 6, 244).—18. *Benzamidine* hydrochloride and dilute NaOHAq form CPh(NH).NH.CS.NHPh [125°] (Pinner, *B.* 22, 1609). Prisms.

References.—BROMO-, CHLORO-, IODO-, NITRO-, and OXY- PHENYL-THIOCARBIMIDE.

PHENYL-THIOCARBIZINE $C_7H_6N_2S$ *i.e.* $CS{<}\genfrac{}{}{0pt}{}{NH}{NPh}$. [129°]. Formed by heating phenyl-thio-semicarbazide (10 g.) with dilute (20 p.c.) HClAq (80 c.c.) for 12 hours at 130° (E. Fischer, *A.* 212, 826). Plates (from water), v. e. sol. alcohol. May be distilled. MeI forms $C_7H_5MeN_2S$ [123°]. Does not reduce Fehling's solution. HIAq at 200° forms aniline, H_2S, CO_2, and NH_3. Aqueous NaOCl forms a violet pp. which dissolves in H_2SO_4 with deep-red colour. Br in chloroform gives $C_7H_5BrN_2S$ [210°] crystallising in needles.

Salts. — B'HCl. [240°]. Needles. — $B'_2H_2PtCl_6$. Yellow prisms.—$C_7H_5N_2SAg$: flocculent pp. got by adding ammoniacal $AgNO_3$.

Acetyl derivative $C_7H_5AcN_2S$. [187°]. Got by heating phenyl-thiocarbizine with Ac_2O (F.). An isomeride [74°] (275°), got by heating acetyl-phenyl-hydrazine with $CSCl_2$ and benzene (Freund, *B.* 21, 2468), is converted by boiling with alcohol and HgO into acetyl-phenyl-carbizine.

Benzoyl derivative $C_7H_5BzN_2S$. [180°]. Got from the base and BzCl (Fischer). An isomeride [110°] is got by heating NHBz.NPhH with $COCl_2$ in benzene at 100° (F.).

PHENYL THIOCARBONATE $CS(OPh)_2$. [97°]. Formed from NaOPh and $CSCl_2$ (Bergreen, *B.* 21, 346). White crystals, sol. alcohol.

PHENYL-TRI-THIO-ORTHOFORMATE $CH(SPh)_3$. [40°]. Got by boiling aqueous NaSPh with chloroform (Gabriel, *B.* 10, 185). Thick prisms, sol. ether. Split up by fuming HClAq at 100° into formic acid and PhSH.

PHENYL-THIOGLYCOLLIC ACID $C_8H_8SO_2$, *i.e.* $CH_2(SPh).CO_2H$. [62°]. Formed by saponifying its ether, which is got by adding $ClCO_2Et$ to a solution of NaSPh in absolute alcohol (Claesson, *Bl.* [2] 23, 441; Gabriel, *B.* 12, 1639). Thin tables, sl. sol. cold water. Oxidised by $KMnO_4$ to phenyl methyl sulphone (Otto, *B.* 19, 3138). *Salts.*—KA'.—NaA'.—BaA'_2.—CaA'_2.—MgA'_2 3aq.—CdA'_2 aq.—ZnA'_2 2aq.—PbA'_2. [60°].—MnA'_2 5aq.—CuA'_2.—AgA' aq: crystalline pp.

Ethyl ether EtA'. (277°). S.G. $\frac{0}{4}$ 1·136; ^{15} 1·127.

Amide. [104°]. Tables (from alcohol).

References. — Amido- and Bromo- Phenyl-thioglycollic acids.

(a)-PHENYL-THIOHYDANTOÏC ACID $C_9H_{10}N_2SO_2$, *i.e.* $NH_2.C(NPh).S.CH_2.CO_2H$. [148°–152°]. Got by heating aniline with ammonium sulphocyanide, chloro-acetic acid, and alcohol (Claesson, *B.* 14, 732). Needles (from HOAc); m. sol. hot water and ether. Cold NaOHAq converts it into $C_{18}H_{17}N_3S_2O_4$ [112°–115°] (Liebermann, *A.* 207, 129).

(β)-Phenyl-thio-hydantoïc acid $NHPh.C(NH).S.CH_2.CO_2H$. Got by evaporating an alcoholic solution of ammonium chloro-acetate and phenyl-thio-urea at 100° (Meyer, *B.* 14, 1659). Decomposes on heating without melting. Insol. water, alcohol, and ether. Boiling dilute HCl forms $CO\left<\begin{array}{l}NPh.CO\\S—CH_2\end{array}\right.$ [148°].

Isomeride *v.* Phenyl-thio-hydantoïn.

Di-phenyl-hydantoïc acid $NHPh.C(NPh).S.CH_2.CO_2H$. Got from potassium chloro-acetate and di-phenyl-thio-urea (Lange, *B.* 12, 597). Yellow octahedra.

PHENYL-THIO-ψ-HYDANTOÏN $C_9H_8N_2OS$, *i.e.* $C(NH)\left<\begin{array}{l}NPh.CO\\S=CH_2\end{array}\right.$. [178°]. Got from chloro-acetic anilide and thio-urea, and obtained also by boiling (β)-phenyl-hydantoïc acid with HOAc or conc. NH_3Aq (Meyer, *B.* 14, 1661), and by the action of phenyl-cyanamide on thioglycollic acid (Andreasch, *B.* 15, 324). Needles, sol. NaOHAq.

Phenyl-thio-hydantoïn $CS\left<\begin{array}{l}NPh.CO\\NH.CH_2\end{array}\right.$. Got by melting glycocoll with phenyl-thiocarbimide (Aschan, *B.* 17, 424). Monoclinic plates, decomposing near 200°. Boiling alcoholic potash converts it into a salt of an oily phenyl-thio-hydantoïc acid $NHPh.CS.NH.CH_2.CO_2H$ which, when set free, rapidly changes again to phenyl-thio-hydantoïn.

Di-phenyl-thio-hydantoïn $C_{15}H_{12}N_2SO$, *i.e.* $CS\left<\begin{array}{l}NPh.CO\\NPh.CH_2\end{array}\right.$? [176°]. Got from chloro-acetic acid and di-phenyl-thio-urea (Lange, *B.* 12, 595). Iridescent plates, insol. water, v. sol. hot alcohol. Boiling dilute HClAq forms the compound $C_9H_7NSO_2$ [148°].—$B'_2H_2PtCl_6$. Yellow needles.

Di-phenyl-thio-hydantoïn $CS\left<\begin{array}{l}NPh.CO\\NH.CHPh\end{array}\right.$. [233°]. Formed by the action of alkalis on $NHPh.CS.NH.CHPh.CO_2Et$ (Kossel, *B.* 24, 4152).

Reference.—Oxy-di-phenyl-thiohydantoïn.

PHENYL-DI-THIO-DI-METHYL-KETURET $NH\left<\begin{array}{l}CHPh.S\\C(NH).S\end{array}\right>CMe_2$. [239°]. Formed from phenyl-di-thio-biuret and acetone (Fromm, *B.* 25, 1278). Sol. alkalis. Converted by benzyl chloride into $C_7H_7N\left<\begin{array}{l}CHPh—S\\C(NC_7H_7).S\end{array}\right>CMe_2$ [128°] which is insol. alkalis.

DI-PHENYL-THIO-OXAMIDE $C_2S_2(NHPh)_2$. [133°]. Formed from di-phenyl-oxamide by successive treatment with PCl_5 and H_2S (Wallach, *B.* 13, 527). Golden plates.

(a)-PHENYL-THIOPHENE $C_{10}H_8S$ *i.e.* C_4SH_3Ph. [41°]. Formed by heating either $CH_2Bz.CH(CO_2H)_2$ or β-benzoyl-propionic acid with P_2S_5 (Kues a. Paal, *B.* 19, 3141). Small tables, insol. water, v. e. sol. ether, v. sol. alcohol. Volatile with steam. With isatin and cold H_2SO_4 it gives a splendid bluish-violet colour, changing to dark blue. Bromine gives rise to $C_{10}H_6Br_2S$ [56°] and $C_4SBr_3.C_6H_4Br$ [1:4] [146°].

(β)-Phenyl-thiophene C_4H_3PhS. [170°]. (330°). A product of the passage of the vapours of toluene and sulphur through a red-hot tube (Renard, *C. R.* 109, 699). White spangles, m. sol. cold alcohol. Gives a blue colour with isatin and H_2SO_4, and a green colour with phenanthraquinone and H_2SO_4. Yields $C_4H_2BrS.C_6H_4Br$ [1:4] [195°], $C_4H_2(NO_2)S.C_6H_4.NO_2$ [1:4] [178°], a di-sulphonic acid, and a tetrasulphonic acid.

Di-(a)-phenyl-thiophene $S\left<\begin{array}{l}CPh:CH\\CPh:CH\end{array}\right.$. [153°] Formed by heating $C_2H_4Bz_2$ with P_2S_5 at 180° (Paal, *B.* 21, 3058). White plates (from alcohol).

Tri-phenyl-thiophene C_4Ph_3HS. [127°]. Got by heating desyl-acetophenone with P_2S_5 at 150° (A. Smith, *C. J.* 57, 647). Plates, v. sol. benzene. Gives a greenish-yellow colour with H_2SO_4 and isatin or phenanthraquinone.

Tetra-phenyl-thiophene $C_{28}H_{20}S$ *i.e.* $S\left<\begin{array}{l}CPh:CPh\\CPh:CPh\end{array}\right.$. *Thionessal.* [182°].

Formation.—1. By the dry distillation of thiobenzoic aldehyde (Laurent, *A.* 52, 354).—2. By distilling benzyl sulphide or benzyl disulphide (Märcker, *A.* 136, 94).—3. By distilling benzylidene sulphide (Fleischer, *A.* 140, 239; 144, 194).—4. By distilling barium phenyl-acetate with S (Forst, *A.* 178, 376).—5. By heating phenyl-acetic acid with S for 6 hours at 260° (Ziegler, *B.* 23, 2473).—6. By heating phenyl benzyl ketone with S.—7. By heating *s*-di-phenyl-ethylene with S at 250° (Baumann a. Klett, *B.* 24, 3311). Minute needles, sl. sol. alcohol, v. sol. benzene and CS_2. Yields a sulphonic acid, and also the following derivatives: $C_{28}H_{18}Cl_2S$ [219°] (Dorn, *A.* 153, 350), $C_{28}H_{17}Br_3S$ [265°–270°], $C_{28}H_{16}(NO_2)_4S$ [above 250°].

DI-PHENYL-DI-THIO-DI-PHENYL-KETATE $CPh_2(SPh)_2$. *Phenyl-mercaptol of benzophenone.* [139°]. Formed by passing HCl gas into a hot mixture of benzophenone, phenyl-mercaptan, and $ZnCl_2$ (Baumann, *B.* 18, 888). Short prisms, sl. sol. alcohol and ether.

PHENYL THIOPHOSPHATE $PS(OPh)_3$. [49°]. (above 360°). Got by boiling $PSCl_3$ with phenol (Schwarze, *J. pr.* [2] 10, 222) and by heating phenyl phosphate with K_2S (Kreysler, *B.* 18, 1718), or with S at 190° (Anschütz, *A.* 253, 118). Needles (from alcohol), turning red in air and light. Not decomposed by water.

Phenyl tri-thiophosphate $PO(SPh)_3$. [72°]. Got by boiling PhSH with $POCl_3$. Prisms (from alcohol). Decomposed by warm water.

Phenyl tetra-thio-phosphate $PS(SPh)_4$. [86°]. Got from PhSH and $PSCl_3$. Silky white needles, not affected by boiling water.

PHENYL THIOSULPHURIC ACID $C_6H_5.S.SO_2.OH$. *Phenyl hydrogen thiosulphate.* Got by dissolving Ph_2S in H_2SO_4 (Stenhouse, *Pr.* 17, 62; *A.* 149, 254).—BaA'_2 2aq: crystalline.

PHENYL-THIO-URAMIDO-ACETIC ORTHALDEHYDE. *Di-ethyl derivative* $NHPh.CS.NH.CH_2.CH(OEt)_2$. [96°]. Got by mixing phenyl-thiocarbimide with amido-acetal $NH_2.CH_2.CH(OEt)_2$ (Wohl a. Marckwald, *B.* 22, 569). Needles (from dilute alcohol), insol. water and ligroïn, v. sol. ether. Cold conc. H_2SO_4 forms $NHPh.CS.NH.CH_2.CH(OH)(OEt)$ [94°] which yields, by loss of H_2O, the salts $(C_{11}H_{14}N_2SO)_2H_2PtCl_6$ and $C_{11}H_{14}N_2SOC_6H_3N_3O_7$ [190°].

PHENYL-THIO-URAMIDO-BENZOIC ACID *v.* *m*-AMIDO-BENZOIC ACID.

***o*-PHENYL-THIO-URAMIDO-CINNAMIC ACID** $NHPh.CS.NH.C_6H_4.CH:CH.CO_2H$. [237°]. Formed by heating *o*-amido-cinnamic acid with phenyl-thiocarbimide on the water-bath (Rothschild, *B.* 23, 3343).

DI-PHENYL-DI-THIOURAMIDO-TETRA-OXY-DI-PHENYL. *Tetra-methyl derivative* $C_{12}H_4(OMe)_4(NH.CS.NHPh)_2$. [184°]. Formed from $C_6H_2(OMe)_2(NH_2).C_6H_2(OMe)_2(NH_2)$ and phenyl thiocarbimide (Baessler, *B.* 17, 2128). White flakes, sol. hot alcohol and benzene.

PHENYL-THIOURAMIDO-PHENYL-ACETIC ETHER $NHPh.CS.NH.CHPh.CO_2Et$. [162°]. Formed from phenyl-amido-acetic ether and phenyl-thiocarbimide (Kossel, *B.* 24, 4151). White crystals, sol. hot alcohol.

PHENYL-THIO-URAMIDO-THIO-FORMIC ACID *v.* PHENYL-DI-THIO-ALLOPHANIC ACID.

PHENYL-THIOURAMIDO-TOLYL-CARBAMIC ETHER $NHPh.CS.NH.C_6H_3Me.NH.CO_2Et$. [155°]. Formed, together with $CS(NHPh)_2$, by the action of phenyl-thiocarbimide on amido-tolyl-carbamic ether (Schiff, *B.* 23, 1818). Prisms (from alcohol), v. sl. sol. alcohol.

DI-PHENYL-DI-*p*-THIOURAMIDO-DI-TOLYL-*o*-SULPHIDE $C_{28}H_{26}N_4S_3$ *i.e.* $S(C_6H_3Me.NH.CS.NHC_6H_5)_2$. *Thio-p-tolyl-di-phenyl-thiourea.* [134°]. Formed by the action of phenyl-thiocarbimide upon di-*p*-amido-di-tolyl-sulphide (Truhlar, *B.* 20, 670). White prismatic needles. V. sol. alcohol, ether, and benzene.

PHENYL-THIO-UREA $C_7H_8N_2S$ *i.e.* $NHPh.CS.NH_2$. Mol. w. 152. [154°]. S. ·26 at 18°; 5·93 at 100°. S. (alcohol) 5·59 at 16°; 68 at 78°.

Formation.—1. By heating phenyl sulphocyanide with alcoholic NH_3 (Hofmann, *Pr.* 9, 275).—2. By boiling aniline with ammonium sulphocyanide (Schiff, *A.* 148, 338; Rathke, *B.* 18, 3104).—3. By heating aniline sulphocyanide at 190° (Salkowski, *B.* 24, 2728; *cf.* De Clermont, *C. R.* 82, 512).—4. By passing H_2S into a solution of phenyl-cyanamide in benzene (Weith, *B.* 9, 819).

Properties.—Needles, sol. alkalis and reppd. by acids. Tastes bitter.

Reactions.—1. *Heated* in a sealed tube at 180° it yields $CS(NHPh)_2$, ammonium sulphocyanide, NH_3, H_2S, and aniline.—2. *Ammonia* at 140° forms aniline and ammonium sulphocyanide.—3. Boiling *aniline* forms $CS(NHPh)_2$.—4. HClAq at 120° forms aniline, H_2S, NH_3, and CO_2.—5. By boiling with alkaline lead acetate solution it gives phenyl cyanamide $N:C.NHC_6H_5$, which polymerises on heating to tri-phenyl-iso-melamine $(PhN:C)_3(NH)_3$.—6. When boiled for several hours with freshly-precipitated HgO it yields *asymmetrical* tri-phenyl-melamine $PhN{<}\begin{matrix}C(NH).NPh\\C(NH).N\end{matrix}{>}C.NHPh$ (Hofmann, *B.* 18, 3220).—7. $Cl.CO.CO_2Et$ forms oxalyl-di-phenyl-biuret, $NH{<}\begin{matrix}CS.NPh\\CS.NPh\end{matrix}{>}C_2O_2$ (*v.* CHLORO-GLY-OXYLIC ETHER).—8. $ClCO_2Et$ forms phenyl-thio-allophanic ether.—9. *Silicon tetrabromide* gives solid $SiBr_4(C_7H_8N_2S)_4$, sol. hot benzene, but decomposed by boiling alcohol (Reynolds, *C. J.* 53, 856).—10. An alcoholic solution of *allyl bromide* forms a base $C_{10}H_{12}N_2S$ (Werner, *C. J.* 57, 302).—11. *Benzyl chloride* in alcohol forms $CS(N_2H_3Ph)C_7H_7Cl$ [112°] (W.).—12. *Ethylene bromide* forms $C_{16}H_{18}N_4S$ [139°], which gives the salts B″2HBr [214°], B″2HCl [218°], $B''H_2PtCl_6$, and $B''2C_6H_2(NO_2)_3OH$ [196°] (Bertram, *B.* 25, 59).—13. H_2O_2 oxidises it, in alcoholic solution, to di-phenyl-di-amido oiazthiole (Hector, *B.* 22, 1176).

Salts.—$B'_2H_2PtCl_6$.—$B'_6Cu_2Cl_2$ 6aq. [145°] (Rathke, *B.* 17, 305). Trimetric crystals (from alcohol).

Acetyl derivative NHPh.CS.NHAc. [173°]. Formed from acetyl sulphocyanide and aniline (Miguel, *A. Ch.* [5] 11, 318), and by the action of Ac_2O on the product of the action of phenyl thiocarbimide on aldehyde-ammonia (Schiff, *B.* 9, 570). Tables (from dilute alcohol).—B′HBr. [270°]. Prisms, v. e. sol. water.

Benzoyl derivative NHPh.CS.NHBz. [149°]. S. (alcohol) 4 at 78°. Needles, insol. water (Miguel).

o-Oxy-benzoyl derivative $NHPh.CS.NH.CO.C_6H_4OH$. [192°]. Formed from salicyl-thiocarbimide and aniline (M.).

Di-phenyl-thio-urea $C_{13}H_{12}N_2S$ *i.e.* $CS(NHPh)_2$. Mol. w. 228. [151°] (Lellmann, *A.* 221, 21; Losanitsch, *B.* 19, 1821).

Formation.—1. By boiling aniline with CS_2 and alcohol (Hofmann, *A.* 57, 266; 70, 144). 2. By heating aniline with potassium sulphocyanide and H_2SO_4 (Laurent a. Gerhardt, *A. Ch.* [3] 22, 103; 24, 196).—3. From aniline and phenyl-thiocarbimide.—4. From di-phenyl-cyanamide and H_2S (Weith, *B.* 7, 1303).—5. By boiling *s*-di-phenyl-guanidine with CS_2 (Hofmann, *B.* 2, 460).

Properties.—Trimetric crystals (from alcohol), nearly insol. water, v. sol. alcohol and ether. Sol. alkalis and reppd. by acids. Has a very bitter taste.

Reactions.—1. Partially decomposed on *distillation* into tri-phenyl-guanidine, CS_2, and H_2S.—2. P_2O_5, $ZnCl_2$, or HCl split it up into aniline and phenyl-thiocarbimide.—3. Boiling *alcoholic potash* forms di-phenyl-urea.—4. Di-phenyl-urea is formed when the alcoholic solution is boiled with HgO.—5. A cold solution of *nitrous ether* in alcohol forms tri-phenyl-guanidine, phenyl thiocarbimide, and S (Claus, *B.* 4, 143).—6. *Iodine*, added to its boiling alcoholic solution, forms tri-phenyl-guanidine and phenyl thiocarbimide.—7. *Aniline* forms, on heating, tri-phenyl-guanidine and H_2S.—8. *Sodium-amalgam* reduces it to aniline, H_2S, and CH_4 (Merz a. Weith, *Z.* [2] 4, 612).—9. When heated with $HgCl_2$ it yields tri-phenyl-guanidine (Buff, 2, 498).—10. Fuming H_2SO_4 decomposes it on heating, forming aniline, COS, and SO_2 (Fleischer, *B.* 9, 993).—11. $COCl_2$ forms $C_{14}H_{10}N_2SO$ [87°], crystallising in prisms and split up by heat into COS and di-phenyl-cyanamide (Will, *B.* 14, 1486).—12. $CSCl_2$ in benzene forms $C_{14}H_{10}N_2S_3$, crystallising in yellow needles [156°], sl. sol. alcohol. In presence of ether $CSCl_2$ forms $NPh{:}C\left<\begin{matrix}NPh\\ S\end{matrix}\right>CS$ [79°] (Freund a. Wolf, *B.* 25, 1459).—13. H_2S at 170° forms aniline and CS_2 (Weith, *B.* 7, 1304).—14. *Alkyl iodides* form alkyl derivatives, which may perhaps be formulated as derivatives of ψ-thio-urea. Thus, MeI forms $NHPh.C(SMe){:}NPh$ [110°], which is decomposed by heat into MeSH and $C(NPh)_2$, and by alcoholic potash into MeSH and $CO(NHPh)_2$. In like manner EtI forms $C_{15}H_{16}N_2S$ [79°] (*v.* DI-PHENYL-ETHYL-ψ-THIO-UREA), and ethylene bromide gives $C_{15}H_{14}N_2S$ [136°] (Will, *B.* 14, 1490).—15. *Allyl bromide* in alcohol yields $C_{16}H_{17}N_2SBr$, crystallising in trimetric prisms [171°] (Werner, *C. J.* 57, 303).—16. *Benzyl chloride* in alcohol forms $C_{20}H_{19}N_2SCl$, crystallising in prisms [153°] (W.).—17. *Phenyl cyanate* in presence of benzene at 180° forms di-phenyl-urea and phenyl sulphocyanide (Goldschmidt a. Meissler, *B.* 23, 271).—18. Ac_2O yields acetanilide and some phenyl-thiocarbimide (Werner, *C. J.* 59, 398).—19. *Chloro-glyoxylic ether* forms di-phenyl-di-thio-parabanic acid $C_{16}H_{11}N_2S_2O_2$ [215°] and $C_{21}H_{17}N_3S_2O$ [231°], which by boiling with alcohol and $AgNO_3$ is converted into di-phenyl-parabanic acid, aniline, and H_2S, while by boiling alcoholic ammonia it is converted into $C_{14}H_{11}N_4O_2$ [220°], whence fuming HNO_3 forms $C_{13}H_{13}N_5O_6$ [235°]. The compound $C_{21}H_{17}N_3S_2O$ is converted by fuming HNO_3 into $C_{15}H_9N_4SO_4$ [235°] (Stojentin, *J. pr.* [2] 32, 8).

Tri-phenyl-thio-urea $NHPh.CS.NPh_2$. [152°]. Formed by heating phenyl-thiocarbimide with diphenylamine at 280° (Gebhardt, *B.* 17, 2092, 3036). Long white needles, v. sol. hot alcohol.

Tetra-phenyl-thio-urea $CS(NPh_2)_2$. [195°]. Formed by heating tetra-phenyl-guanidine with CS_2 at 270°; the yield being 60 p.c. of the theoretical amount (Bernthsen a. Friese, *B.* 15, 1530). Formed also from $NHPh_2$ and $CSCl_2$ (Bergreen, *B.* 21, 340). Long needles, sol. hot alcohol, insol. alkalis. Yields diphenylamine on heating with diluted (70 p.c.) H_2SO_4.

Di-phenyl-thio-urea *v.* DI-PHENYL-DI-PHENYL-THIO-UREA.

References.—AMIDO-, BROMO-, CHLORO-, IODO-, NITRO-, and OXY- PHENYL-THIO-UREA.

PHENYL-THIO-UREA CARBOXYLIC ACID *v. m*-AMIDO-BENZOIC ACID, *Reaction* 7.

DI-PHENYL-TOLENYL-AMIDINE $C_{20}H_{18}N_2$ *i.e.* $C_6H_4Me.C(NPh).NHPh$. [168°]. Got by warming $C_6H_4Me.C(OEt){:}NH_2Cl$ with aniline and alcohol (Glock, *B.* 21, 2656). Plates (from benzene), v. sol. alcohol.

PHENYL-TOLUENE *v.* METHYL-DIPHENYL.

DI-PHENYL-TOLUIC ALDEHYDE $C_{20}H_{16}O$ *i.e.* $CPh_2H.C_6H_4.CHO$. [–15°]. (190°–195° at 46 mm.). Formed by heating terephthalic aldehyde with benzene and conc. H_2SO_4 at 100° (Oppenheimer, *B.* 19, 2028). Oil. Reduces ammoniacal $AgNO_3$, being itself oxidised to tri-phenyl-methane carboxylic acid. $KMnO_4$ gives tri-phenyl-carbinol *p*-carboxylic acid. Reacts with phenyl-hydrazine. Yields $C_{20}H_{16}ONaHSO_3$, a crystalline pp., sl. sol. water, insol. alcohol.

PHENYL-*o*-TOLUIDINE $C_{13}H_{13}N$ *i.e.* $[1{:}2]C_6H_4Me.NHPh$. [41°]. (305° i.V.) at 728 mm. (Graebe, *A.* 238, 363). Formed, together with $NHPh_2$ and ditolylamine by heating *o*-toluidine with aniline hydrochloride at 280° (Girard a. Willm, *Bl.* [2] 25, 248). Coloured violet-blue by HNO_3.

Phenyl-*m*-toluidine. (300°–305°). Got by heating $[1{:}3{:}5]\ C_6H_3Me(NHPh).OH$ with zinc-dust (Zega a. Buch, *J. pr.* [2] 33, 542). Oil. Coloured green by H_2SO_4 containing HNO_3.

Phenyl-*p*-toluidine $C_7H_7.NHPh$. [87°]. (318° i.V.) at 728 mm. (Graebe, *A.* 238, 363). Formed by distilling tri-tolyl-rosaniline acetate (Hofmann, *A.* 132, 291). Obtained also, together with diphenylamine and ditolylamine by heating *p*-toluidine (1 mol.) with aniline (1 mol.) and HCl (1 mol.) at 230° (De Laire, Girard, a. Chapoteaut, *Bl.* 1867, i. 360; *A.* 140, 347). Prepared by heating phenol with *p*-toluidine and $ZnCl_2$, or *p*-cresol with aniline and $ZnCl_2$ at 200°, or with $SbCl_3$ (Buch, *B.* 17, 2634). Crystals. Coloured blue by HNO_3. With benzoic acid and $ZnCl_2$ at 260° it yields phenyl-methyl-acridine $C_{20}H_{15}N$ (Bonna, *A.* 239, 60). Bromine vapour forms a tetra-bromide [135°], a hepta-bromo-derivative [185°], and a compound $NC_{13}H_{12}Br_7$ or $NC_{13}H_{0}Br_7$ [254°]. Excess of Br at 310° forms $NC_{13}H_2Br_{11}$ [296°] (Bonna). Bromine in HOAc added to an alcoholic solution forms a tetra-bromo-derivative [156°].

Salt.—B'HCl: plates.

Acetyl derivative $C_{13}H_{12}AcN$. [51°]. Yields $C_{13}H_{11}BrAcN$ [72°], crystallising in plates.

Benzoyl derivative $C_{20}H_{17}NO$. Crystals. Yields crystalline $C_7H_6(NO_2).NBz.C_6H_4NO_2$.

Nitrosamine $C_7H_7NPh.NO$. [82°]. Yellow needles (from ligroïn). Br forms $C_{13}H_{11}BrN_2O$ [166°] (Bonna, *A.* 239, 56).

PHENYL-TOLYL-ACETAMIDINE $C_{15}H_{16}N_2$ *i.e.* $CH_3.C(NC_7H_7).NHPh$. [76°]. Formed from acetyl *p*-toluidine by successive treatment with PCl_5 and aniline (Wallach a. Fassbender, *A.* 214, 206).—$B'_2H_2PtCl_6$.

PHENYL-*p*-TOLYL-ACETIC ACID $C_7H_7.CHPh.CO_2H$. [115°]. Formed from *a*-bromo-phenyl-acetic acid, toluene, and zinc-dust (Zincke, *B.* 10, 996; Neure, *A.* 250, 149). Plates (from water), v. sol. alcohol.—KA′ 4aq.—NaA′ 6aq.—CaA'_2 2aq: needles (from dilute alcohol).

Ethyl ether EtA′. [34°]. Plates.

Amide $C_{15}H_{15}NO$. [151°].

Nitrile $C_7H_7CHPh.CN$. [59°].

Phenyl-di-tolyl-acetic acid $C_{22}H_{20}O_2$ [78°–83°]. Got by oxidising $(C_7H_7)_2CPh.CO.C_6H_5$ (Thörner, *A.* 189, 123). Amorphous powder, insol. water, v. sol. alcohol.

PHENYL-TOLYL-AMINE *v.* PHENYL-TOLUIDINE.

PHENYL-*p*-TOLYL-BENZYL-BIURET $NHPh.CO.N(CH_2Ph).CO.NHC_6H_4Me$. [c. 100°]. Formed from *p*-tolyl-benzyl-urea and phenyl cyanate (Kühn a. Henschel, *B.* 21, 505). Needles (from dilute alcohol).

PHENYL-*p*-TOLYL-BENZYL-UREA $C_{21}H_{20}N_2O$. [113°]. Got from *p*-tolyl-benzyl-carbamic chloride and aniline (Hammerich, *B.* 25, 1823). Dimorphous: prisms or plates, sol. ether and alcohol.

PHENYL-DI-*p*-TOLYL-BIURET $C_{22}H_{21}N_3O_2$ *i.e.* $NHPh.CO.N(C_6H_4Me).CO.NHC_6H_4Me$. [140°]. Formed by heating di-*p*-tolyl-urea with phenyl cyanate at 170° (Kühn a. Henschel, *B.* 21, 505). Crystals (from alcohol).

Di-phenyl-tolyl-biuret $NHPh.CO.NPh.CO.NHC_6H_4Me$. [216°]. Got by heating di-phenyl-urea with *p*-tolyl cyanate at 170° (K. a. H.).

PHENYL-*p*-TOLYL-CARBINOL $C_{14}H_{14}O$ *i.e.* $C_6H_4Me.CPhH.OH$. [53°]. Got by reducing phenyl tolyl ketone in alcoholic solution by sodium-amalgam (E. a. O. Fischer, *A.* 194, 265). Stellate groups of needles (from ligroïn).

Di-phenyl-tolyl-carbinol $C_{20}H_{18}O$ *i.e.* $C_6H_4Me.CPh_2.OH$. [150°]. Formed by oxidising di-phenyl-tolyl-methane with CrO_3 and HOAc (F.). Crystals (from ligroïn). May be distilled.

PHENYL-*p*-TOLYL-CARBINOL *o*-CARBOXYLIC ACID. *Lactone v.* TOLYL-PHTHALIDE.

Di-phenyl-tolyl-carbinol carboxylic acid. *Lactone* $\left[5^{2}_{1}\right] C_6H_3Me{<}\begin{matrix}CPh_2\\CO\end{matrix}{>}O$. [147°]. (above 360°). Formed by oxidising di-phenyl-*m*-xylyl-methane with chromic acid mixture (Hemilian, *B.* 16, 2361; 19, 3063). Prisms.

The isomeric $\left[4^{2}_{1}\right] C_6H_3Me{<}\begin{matrix}CPh_2\\CO\end{matrix}{>}O$, [179°], (above 360°), is got by oxidation of di-phenyl-*p*-xylyl-methane, and is accompanied by $[1:2:5]CPh_2(OH).C_6H_3Me.CO_2H$, which yields BaA'_2 and CaA'_2 and does not form a lactone.

PHENYL-*o*-TOLYL-CARBINYLAMINE $[1:2]C_6H_4Me.CHPh.NH_2$. (299°) at 721 mm. Formed by reducing the oxim of phenyl *o*-tolyl ketone dissolved in alcohol by adding sodium-amalgam and HOAc (Goldschmidt a. Stöcker, *B.* 24, 2806). Yields an acetyl derivative [124°].—B′HCl. [249°]. Needles, m. sol. water.

m-**Isomeride.** (299°) at 724 mm. Yields B′HCl [243°] and an acetyl derivative [97°].

p-**Isomeride.** (296°) at 723 mm. Yields an acetyl derivative [131°] and the salts B′HCl [252°], $B'_2H_2PtCl_6$ 2aq [119°], $B'C_4H_6O_6$ [157°], $B'_2C_4H_6O_6$ [73°]. The hydrochloride is converted by potassium sulphocyanide into the compound $C_6H_4Me.CHPh.NH.CS.NH_2$ [101°] and by potassium cyanate into the urea derivative $C_6H_4Me.CHPh.NH.CO.NH_2$ [158°].

PHENYL TOLYL - CARBINYL KETONE CARBOXYLIC ACID $C_{16}H_{14}O_3$ *i.e.* $C_6H_4Me.CH_2.CO.C_6H_4.CO_2H$. [112°]. Formed by heating $C_6H_4{<}\begin{matrix}C(CH.C_6H_4Me)\\CO\text{———}\end{matrix}{>}O$ with KOHAq at 100° (Heilmann, *B.* 23, 3160). Vitreous prisms.—AgA′. Converted by heating with an alcoholic solution of hydroxylamine hydrochloride into $C_6H_4{<}\begin{matrix}C(CH_2.C_6H_4Me)\\CO\text{———}O\end{matrix}{>}N$ [134°].

PHENYL-*o*-TOLYL-CYANAMIDE $NPh:C:NC_6H_4Me$. *Carbophenyltolylimide.* (320°–325° uncor.). Formed by adding HgO to a boiling solution of phenyl-*o*-tolyl-thiourea in dry benzene, the yield being 65 p.c. of the theoretical. Oil. On keeping, it polymerises to a brittle glassy solid [68°–71°]. V. sol. benzene, sl. sol. ether. By boiling with dilute alcohol it is converted into phenyl-*o*-tolyl-urea. H_2S passed into its boiling solution in dry toluene converts it into phenyl-*o*-tolyl-thiourea. Heated with CS_2 at 180°–200° it yields a mixture of phenyl- and *o*-tolyl-thiocarbimides. It combines with *o*-toluidine, forming *u*-phenyl-di-*o*-tolyl-guanidine (Huhn, *B.* 19, 2410).

Phenyl-*p*-tolyl-cyanamide $NPh:C:NC_7H_7$. (325°–330° uncor.). Resembles the preceding isomeride in mode of preparation and properties.

DI-PHENYL-TOLYLENE-TETRA-AMIDO-METHANE $C_{20}H_{20}N_4$ *i.e.* $C_7H_6{<}\begin{matrix}NH\\NH\end{matrix}{>}C(NHPh)_2$(?). [161°]. Formed by heating $C(NPh)_2$ with tolylene-*o*-diamine at 185° (Dahm a. Gasiorowski, *B.* 19, 3057). Needles (from benzene).—$B'_2$3HCl. [174°].—$B'H_2SO_4$.

DI-PHENYL-*m*-TOLYLENE DIAMINE $C_{19}H_{18}N_2$ *i.e.* $[1:3:5]C_6H_3Me(NPhH)_2$. [105°]. Formed by heating orcin (1 pt.) with aniline (4 pts.) and a mixture of $ZnCl_2$ and $CaCl_2$ at 220° (Zega a. Buch, *J. pr.* [2] 33, 542). White needles (from glacial HOAc).

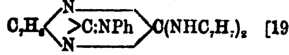
Di-acetyl derivative [160°].

Di-benzoyl derivative [190°].

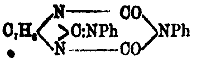
Dinitrosamine $C_{19}H_{16}N_4O_2$. [170°].

Reference. — DI-NITRO-PHENYL-TOLYLENE-DIAMINE.

PHENYL-*o*-TOLYLENE-GUANIDINE $C_7H_6{<}\begin{matrix}NH\\NH\end{matrix}{>}C:NPh$. [167°]. Mol. w. 229 (calc. 223). Formed from *o*-tolylene-diamine and di-phenyl-cyanamide (Keller, *B.* 24, 2514). Needles (from warm alcohol). Di-*p*-tolyl-cyanamide forms



$C_7H_6{<}\begin{matrix}N\text{———}\\{>}C:NPh\\N\text{———}\end{matrix}{>}C(NHC_7H_7)_2$ [193°], while phenyl cyanide gives the compound



$C_7H_6\left\langle\begin{matrix}N\text{——}CO\\ >C:NPh\\ N\text{——}CO\end{matrix}\right\rangle NPh$ [234°].—B'HCl.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$: white needles.

Mono-acetyl derivative. [147°].

Di-benzoyl derivative. [222°]. Prisms.

Nitrosamine $C_{14}H_{12}N_4O$. [125°].

DI-PHENYL-*m*-TOLYLENE-DI-METHYL-DI-AMINE $C_{21}H_{22}N_2$ *i.e.* $C_6H_3Me(NPhMe)_2$. [124°]. Formed from $C_7H_6(NHPh)_2$, NaOH, and MeI (Zega a. Buch, *J. pr.* [2] 33, 546). White laminæ (from HOAc).

DI-PHENYL-*o*-TOLYLENE-DI-THIO-DI-UREA [1:3:4]$C_6H_3Me(NH.CS.NHPh)_2$. [c. 150°]. Formed from tolylene-*o*-diamine and phenyl-thiocarbimide in alcohol (Lellmann, *A.* 221, [illegible]9). Thin plates (from dilute alcohol), v. sol. warm NaOHAq, sl. sol. water.

Di-phenyl-*m*-tolylene-di-thio-di-urea [1:2:4]$C_6H_3Me(NH.CS.NHPh)_2$ [168°]. Formed from tolylene-*m*-diamine and phenyl-thiocarbimide (Lussy, *B.* 8, 670; Gebhardt, *B.* 17, 3046; Billeter a. Steiner, *B.* 18, 3293; 20, 228).

Di-phenyl-*p*-tolylene-di-thio-di-urea [1:2:5]$C_6H_3Me(NH.CS.NHPh)_2$. [181°]. Formed from tolylene-*p*-diamine and phenyl-thiocarbimide in alcohol (Lellmann a. Würthner, *A.* 228, 206). Plates, nearly insol. alcohol.

DI-PHENYL-TOLYLENE-DI-UREA $C_7H_6(NH.CO.NHPh)_2$. [above 300°]. Formed by adding phenyl cyanate to an ethereal solution of tolylene-diamine [99°] (Kuhn, *B.* 18, 1477). White pp. Insol. water, alcohol, ether, and benzene, v. sl. sol. acetic acid. By boiling with aniline it yields *s*-di-phenyl-urea.

PHENYL-*p*-TOLYL-ETHANE $C_{15}H_{16}$, *i.e.* $CH_2Ph.CH_2.C_6H_4Me$. [27°]. (286° uncor.). Formed by reduction of tolyl benzyl ketone by HI and P (Mann, *B.* 14, 1646). White plates.

Phenyl-*p*-tolyl-ethane $CH_3.CHPh.C_6H_4Me$. (279°). Formed from $C_6H_5.C_2H_4Br$, toluene, and zinc-dust (Bandrowski, *B.* 7, 1016). Oil. Yields *p*-benzoyl-benzoic acid on oxidation.

PHENYL-*p*-TOLYL-ETHYLENE $C_{15}H_{14}$, *i.e.* $CHPh:CH.C_6H_4Me$. *Methyl-stilbene.* [120°]. Formed by boiling *p*-tolyl-benzyl-carbinol with dilute H_2SO_4 (Mann, *B.* 14, 1646), and also by distilling *p*-tolyl cinnamate (Anschütz, *C. J.* 47, 898; *B.* 18, 1945). Pearly plates with blue fluorescence, v. sl. sol. alcohol, v. e. sol. ether. Yields $C_{15}H_{14}Br_2$ [187°].

DI-PHENYL-DI-*p*-TOLYL-ETHYLENE OXIDE? $C_{28}H_{24}O$. *Phenyl tolyl* (*a*)*-pinacolin.* [215°]. Formed by the action of zinc and HClAq on phenyl *p*-tolyl ketone in alcohol, and got also by heating a mixture of the ketone with phenyl-tolyl-carbinol, alcohol, and $ZnCl_2$ (Thörner a. Zincke, *B.* 11, 71; *A.* 189, 104). Minute needles, m. sol. hot alcohol. Conc. HClAq at 150° changes it into the isomeric (*β*)-pinacolin $C_6H_5.CO.CPh(C_6H_4Me)_2$ [137°].

PHENYL *p*-TOLYL ETHYLENE DISULPHONE $C_6H_5.SO.C_2H_4.SO_2.C_7H_7$. [162°]. Got by boiling $C_6H_5.SO_2.C_2H_4Cl$ with an alcoholic solution of sodium toluene *p*-sulphinate (Otto, *J. pr.* [2] 30, 199).

PHENYL-TOLYL-ETHYLENE-*ψ*-THIO-UREA $NPh:C\left\langle\begin{matrix}N(C_7H_7)\\ S.CH_2\end{matrix}\right\rangle CH_2$. [128°]. Formed by boiling the methylo-iodide of the ethylene derivative of tolyl-di-thio-carbamic acid with aniline (Will a. Bidschowski, *B.* 15, 1315). Silky plates.

PHENYL-*p*-TOLYL-ETHYL-THIO-UREA $C_{16}H_{18}N_2S$, *i.e.* $NPhEt.CS.NHC_7H_7$. [90°]. Formed from *p*-tolyl-thiocarbimide and ethyl-aniline (Gebhardt, *B.* 17, 2091). Colourless crystals.

***s*-PHENYL-DI-*o*-TOLYL-GUANIDINE** $C_6H_5N:C(NHC_7H_7)_2$. [102°]. Formed by the action of an alcoholic solution of aniline upon di-*o*-tolyl-thiourea in presence of PbO. Got also by the combination of $C_6H_5.N:C:N.C_7H_7$ with aniline (Huhn, *B.* 19, 2412). Felted needles. V. sol. warm alcohol, ether, and benzene.—B'HCl.—$B'_2H_2Cl_2PtCl_4$: orange-yellow tables.

***u*-Phenyl-di-*o*-tolyl-guanidine** $C_7H_7N:C(NHC_6H_5)(NHC_7H_7)$. [112°]. Formed from *o*-toluidine and $C_7H_7N:C:NC_6H_5$ (Huhn). Long needles, v. sol. alcohol. Salts.—B'HCl.—$B'_2H_2PtCl_6$: orange-yellow tables.

***s*-Di-phenyl-*p*-tolyl-guanidine** $C_7H_7N:C:(NHC_6H_5)_2$. [121°]. Formed by the action of an alcoholic solution of *p*-toluidine upon di-phenyl-thiourea in presence of PbO (Hofmann, *B.* 2, 459; Huhn, *B.* 19, 2412). Felted needles. V. sol. alcohol and ether.—B'HCl.—$B'_2H_2Cl_2PtCl_4$: reddish-yellow pp.

***u*-Di-phenyl-*p*-tolyl-guanidine** $C_{20}H_{19}N_3$, *i.e.* $C_6H_5N:C(NHC_6H_5)(NHC_7H_7)$. [127°].

Formation.—1. By heating phenyl-*p*-tolyl-thiourea with an alcoholic solution of aniline in presence of PbO.—2. By the combination of $C_6H_5N:C:NC_7H_7$ with aniline (Huhn, *B.* 19, 2409).—B'HCl.—$B'_2H_2Cl_2PtCl_4$: sparingly soluble pp.

PHENYL TOLYL-IMIDO-BENZYL KETONE $C_6H_5.CO.C(NC_7H_7).C_6H_5$. Formed by heating *o*-toluidine with benzil at 100° (Bandrowski, *M.* 9, 689). Yellow plates (from alcohol).

PHENYL *o*-TOLYL KETONE $C_{14}H_{12}O$ *i.e.* $C_6H_5.CO.C_6H_4Me$ [1:2]. (314°) at 735 mm. (Smith, *B.* 24, 4046); (295°) at 722 mm. (G. a. S.). Formed by the action of $AlCl_3$ on a mixture of *o*-toluic chloride and benzene (Ador a. Rilliet, *B.* 12, 2301; Goldschmidt a. Stöcker, *B.* 24, 2805). Formed also, together with a much larger quantity of the *p*- isomeride, from BzCl, toluene, and $AlCl_3$ (Elbs, *J. pr.* [2] 35, 466). Oil. Yields anthracene on long boiling or on heating with zinc-dust.

syn-Oxim $C_7H_7.\underset{\text{HO.N}}{C}.C_6H_5$. [69°].

anti-Oxim $C_7H_7.\underset{\text{N.OH}}{C}.C_6H_5$. [105°] (S.).

Phenyl-*m*-tolyl ketone $C_6H_5.CO.C_6H_4Me$ [1:3]. (315° i.V.) at 745 mm. S.G. $\frac{17.5}{}$ 1·088. Formed by the action of $AlCl_3$ on a mixture of *m*-toluic chloride, benzene, and $AlCl_3$ (A. a. R.; G. a. S.). Got also by cautious oxidation of phenyl-*m*-tolyl-methane (Senff, *A.* 220, 252). Oil, miscible with alcohol. Reduced by HIAq at 200° to $C_{14}H_{14}$ (269° at 725 mm.).

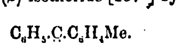
Oxim. [101°]. Reduced by sodium-amalgam in presence of HOAc to *m*-toluic anilide and $C_6H_4Me.CPhH.NH_2$.

Phenyl-*p*-tolyl ketone $C_6H_5.CO.C_6H_4Me$ [1:4]. [60°]. (327° i.V.).

Formation.—1. Together with the *o*-isomeride by heating benzoic acid with toluene and P_2O_5 at 200° (Kollarits a. Merz, *B.* 6, 446; Thörner, *A.* 189, 83).—2. By oxidising $C_6H_4Me.CPhH_2$ (Zincke a. Plascuda, *B.* 7, 982).—3. By distilling a mixture of calcium *p*-toluate and benzoate (Radziszewski, *B.* 6, 810).—4. By heating BzCl with toluene and zinc at 190° (Grucarevic a. Merz, *B.* 6, 1243).—5. By the action of $AlCl_3$ on a mixture of *p*-toluic chloride and benzene (A. a. R.).—6. From BzCl, toluene, and $AlCl_3$.

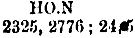
Properties.—Prisms, m. sol. alcohol, v. sol. ether. Dimorphous. Yields *p*-benzoyl-benzoic acid on oxidation. Reduced to $C_6H_4Me.CH_2Ph$ by distillation over zinc-dust. Sodium-amalgam forms phenyl-tolyl-carbinol. Zinc and HClAq acting on the alcoholic solution form two pinacolins $C_{28}H_{24}O$. The (α)-pinacolin [215°] may be converted into the (β)-isomeride [137°] by heating with HOAc.

anti-Oxim



$\underset{HO.N}{C_6H_5.\ddot{C}.C_6H_4Me}$. [154°] (Hantzsch, *B.* 23, 2325, 2776; 24, 58; *cf.* Wegerhoff, *A.* 252, 11). Converted by HOAc and HCl into *p*-toluic anilide. Yields an acetyl derivative [124°] and a benzoyl derivative [85°] (Auwers, *B.* 23, 399).

syn-Oxim



$\underset{N.OH}{C_6H_5.\ddot{C}.C_6H_4Me}$. [116°]. Converted by HOAc and HCl into benzoyl-toluidine and some toluic anilide. Yields an acetyl derivative [118°–122°] and a benzyl derivative [51°].

Phenyl *p*-tolyl diketone $C_6H_5.CO.COC_7H_7$. Formed by heating di-bromo-deoxybenzoïn with water at 183° (Bucher, *B.* 22, 2819). Yellow oil, solidified by cold.

References.—Di-amido-, Nitro-, Oxy-amido-, and Oxy- phenyl-tolyl-ketone.

PHENYL TOLYL KETONE CARBOXYLIC ACID *v.* Toluyl-benzoic acid.

Phenyl *p*-tolyl ketone dicarboxylic acid $C_{16}H_{12}O_5$ ***i.e.*** $C_6H_5.CO.C_6H_2Me(CO_2H)_2$ [1:4:2:6]. *Benzoyl-uvitic acid* [245°]. Formed by oxidising phenyl mesityl ketone with dilute HNO_3 (Elbs, *J. pr.* [2] 35, 489). Needles.—Ag_2A''.

An isomeric acid, got by oxidation of phenyl ψ-cumyl ketone $C_6H_5.CO.C_6H_2Me_3$ [5:1:2:4], yields Ag_2A''.

PHENYL-*o*-TOLYL-METHANE $C_{14}H_{14}$ ***i.e.*** $C_6H_5.CH_2.C_6H_4Me$ [1:2]. *o-Benzyl-toluene.* Mol. w. 182. (284°). Formed, together with the *p*-isomeride, by heating benzyl chloride with toluene and zinc-dust (Zincke, *B.* 6, 906; Senff, *A.* 220, 249). Got also from $C_6H_4Me.CH_2Cl$, benzene, and zinc-dust (Barbier, *B.* 7, 1544). Yields anthracene when passed through a red-hot tube.

Phenyl-*m*-tolyl-methane
$C_6H_5.CH_2.C_6H_4Me$ [1:3]. (275° i.V.). S.G. $\frac{17.5}{}$ ·997. Got by reducing the ketone with HI and P (Ador a. Rilliet, *B.* 12, 2300). Prepared by heating ω-chloro-*m*-xylene (1 pt.) with benzene (7 pts.) and $AlCl_3$ (Senff, *A.* 220, 230; *cf.* Barbier, *C. R.* 79, 660). Oil, sol. alcohol and ether. Gives a di-nitro- derivative [141°].

Phenyl-*p*-tolyl-methane
$C_6H_5.CH_2.C_6H_4Me$ [1:4]. (280° i.V.). Formed, with the *o*- isomeride, by heating benzyl chloride with toluene and zinc-dust (Zincke, *B.* 7, 1153; *A.* 161, 93). Formed also by the action of zinc-dust on benzyl chloride (Prost, *Bl.* [2] 46, 248), and by heating phenyl *p*-tolyl ketone with ammonium sulphide and S at 320° (Willgerodt, *B.* 20, 2470). Oil. Yields *p*-benzoyl-benzoic acid on oxidation. Does not form anthracene when passed through a red-hot tube. Yields a disulphonic acid [38°], which gives $K_2A''\,3\frac{1}{2}aq$, $BaA''\,8\frac{1}{2}aq$, and $CuA''\,4\frac{1}{2}aq$.

Phenyl-di-tolyl-methane $CHPh(C_7H_7)_2$. [56°]. Got by heating $(C_7H_7)_2CPh.CO.C_6H_5$ with soda-lime at 300° (Thörner a. Zincke, *B.* 11, 70).

Di-phenyl-*o*-tolyl-methane $C_{20}H_{18}$ ***i.e.*** $(C_6H_5)_2CH.C_6H_4Me$. [59·5°]. (354°). Formed from leucaniline by diazotising and boiling with alcohol (Fischer, *A.* 194, 282; Rosenstiehl a. Gerber, *A. Ch.* [6] 2, 342). Spherical groups of prisms (from MeOH), v. sol. ether. Oxidised by CrO_3 and HOAc to $(C_6H_5)_2C(OH).C_6H_4Me$ [150°].

Di-phenyl-*m*-tolyl-methane. [62°]. (above 360°). Formed by distilling its carboxylic acid with baryta (Hemilian, *B.* 16, 2368). Long thin needles (from alcohol), v. sol. ether. The crystals emit light when powdered. Its dilute solutions fluoresce blue.

Di-phenyl-*p*-tolyl-methane. [71°]. (above 360°). Formed by distilling its *o*-carboxylic acid, and also by the action of P_2O_5 on a mixture of toluene and di-phenyl-carbinol or of benzene and phenyl-*p*-tolyl-carbinol (Hemilian, *B.* 7, 1209; 19, 3066; Fischer, *A.* 194, 263). Needles or prisms, v. sol. hot alcohol.

References.—Di-amido-, Chloro-, Nitro-, Nitro-amido-, and Oxy- phenyl-tolyl-methane.

PHENYL-*p*-TOLYL-METHANE-*o*-CARBOXYLIC ACID $C_6H_4Me.CH_2.C_6H_4.CO_2H$. [134°]. Formed by warming $C_6H_4Me.CO.C_6H_4.CO_2H$ with NH_3Aq and zinc-dust (Gresly, *A.* 234, 236). Needles (from alcohol), nearly insol. water.—BaA'_2: plates, v. sol. water.

Phenyl-tolyl-methane dicarboxylic acid $CO_2H.C_6H_4.CH(C_7H_7).CO_2H$. [154°]. (above 300°). Got by saponifying the nitrile, which is prepared by treating an alcoholic solution of $CN.C_6H_4.CH_2.CN$ with benzyl chloride and KOH (Eichelbaum, *B.* 21, 2679). Prisms, sol. alcohol.

Amide. [224°]. Small plates.

Imide

$C_6H_4<\begin{smallmatrix}CH(C_7H_7)\\CO.NH\end{smallmatrix}>CO$. [176°]. (above 300°). Got by heating the amide with conc. HClAq. Needles, v. sol. alcohol.

Nitrile. [110°]. (above 300°). Plates.

Di-phenyl-*p*-tolyl-methane carboxylic acid $C_6H_4Me.CHPh.C_6H_4.CO_2H$. [155°]. Formed by warming *p*-tolyl-phthalide with benzene and $AlCl_3$ (Gresly, *A.* 234, 242). Needles (from alcohol).—$BaA'_2\,2\frac{1}{2}aq$: sl. sol. water.

Di-phenyl-*p*-tolyl-methane carboxylic acid $CHPh_2.C_6H_3Me.CO_2H$[4:2:1]. [217°]. Formed from di-phenyl-*p*-tolyl-carbinol carboxylic acid, NaOHAq, and zinc-dust (Hemilian, *B.* 16, 2363). Transparent tables, v. sol. alcohol.—BaA'_2 4aq.—AgA′: minute needles, insol. water.

Di-phenyl-*p*-tolyl-methane carboxylic acid $CHPh_2.C_6H_3Me.CO_2H$[4:1:2]. [203°]. Formed from di-phenyl-methyl-phthalide, NaOHAq, and zinc-dust (Hemilian, *B.* 19, 3064). Needles or tables, sol. hot alcohol.—BaA'_2 3aq.—AgA′.

PHENYL-*p*-TOLYL DI-METHYLENE DI-SULPHONE KETONE $C_{16}H_{16}S_2O_5$ ***i.e.*** $C_6H_5.SO_2.CH_2.CO.CH_2.SO_2.C_6H_4Me$. [112°]. Formed from $CH_2Br.CO.CH_2.SO_2.C_6H_4Me$ by treatment with $C_6H_5SO_2Na$ and obtained also from $C_6H_5.SO_2.CH_2.CO.CH_2Br$ and $C_6H_4Me.SO_2Na$ (Otto, *J. pr.* [2] 36, 427). Plates, m. sol. alcohol, v. sol. $CHCl_3$.

PHENYL-*o*-TOLYL-METHYL-PYRROLE $NC_7H_7<\begin{matrix}CPh{:}CH\\CMe{:}CH\end{matrix}$. [44°]. (327°). Formed by heating its carboxylic acid [199°] (Lederer a. Paal, *B.* 18, 2596). Plates, v. e. sol. alcohol.

Phenyl-*p*-tolyl-methyl-pyrrole. [91°]. (above 350°). Got by heating its carboxylic acid [227°]. Tables (from ligroïn).

PHENYL-*o*-TOLYL-METHYL-PYRROLE CARBOXYLIC ACID $C_6H_4MeN<\begin{matrix}CPh{:}CH\\CMe{:}C.CO_2H\end{matrix}$. [199°]. Got by saponifying its ether, which is formed by boiling acetophenone-acetoacetic ether with *o*-toluidine and HOAc (Lederer a. Paal, *B.* 18, 2596). Small prisms (from alcohol).

p-**Isomeride.** [227°]. Made in like manner from *p*-toluidine. Plates, v. sol. alcohol.

Ethyl ether EtA'. [115°]. Crystals.

PHENYL-*o*-TOLYL-METHYL-THIO-UREA $C_{15}H_{16}N_2S$ *i.e.* $NMePh.CS.NHC_7H_7$. [121°]. Formed from methyl-aniline and *o*-tolyl-thiocarbimide (Gebhardt, *B.* 17, 2091, 3035). Plates.

Phenyl-*p*-tolyl-methyl-thio-urea. [124°]. Formed in like manner from *p*-tolyl-thiocarbimide (G.). Small trimetric tables. By distillation with steam it is resolved into the parent substances, which slowly recombine in the distillate.

PHENYL-TOLYL-NAPHTHYL-GUANIDINE $C_{24}H_{21}N_3$ *i.e.* $CN_3H_2Ph(C_7H_7).C_{10}H_7$. [below 60°]. Formed by boiling an alcoholic solution of phenyl-tolyl-thio-urea and naphthylamine with PbO (Tiemann, *B.* 3, 6). Brittle resin, forming a crystalline hydrochloride.

PHENYL-DI-TOLYL-PHOSPHINE $(C_6H_4Me)_2PC_6H_5$. [57°]. Formed from *p*-bromotoluene (2 mols.), $C_6H_5PCl_2$ (1 mol.), and Na (Dörken, *B.* 21, 1512). Crystals, v. sol. ether.

Di-phenyl-tolyl-phosphine $C_6H_4MeP(C_6H_5)_2$. [68°]. Formed from $(C_6H_5)_2PCl$, *p*-bromotoluene, and sodium (Dörken, *B.* 21, 1511). Small prisms. Yields $(C_6H_5)_2PO(C_6H_4Me)$ [130°] and $(C_6H_5)_2PS(C_6H_4Me)$ [139°].

PHENYL-TOLYL-(*a*)-PINACOLIN $C_{28}H_{24}O$ *v.* DI-PHENYL-DI-*p*-TOLYL-ETHYLENE OXIDE.

Phenyl-tolyl-(β)-pinacolin $C_6H_5.CO.CPh(C_7H_7)_2$. [137°]. Formed by the action of AcCl on phenyl tolyl-(*a*)-pinacolin or on phenyl-tolyl-pinacone (Zincke a. Thörner, *B.* 10, 1477; 11, 65, 1396; *A.* 189, 110). Prepared by boiling phenyl *p*-tolyl ketone with alcohol, HClAq, and zinc. Small dimetric tables, sl. sol. cold alcohol. On heating with soda-lime at 300° it yields phenyl-di-tolyl-methane.

PHENYL-TOLYL-PINACONE $C_{28}H_{26}O_2$ *i.e.* $C_7H_7.CPh(OH).CPh(OH).C_7H_7$. [165°]. Formed by treating an alcoholic solution of phenyl *p*-tolyl ketone with zinc and H_2SO_4 (Zincke a. Thörner, *B.* 10, 1476). Minute needles (from alcohol). Decomposed by fusion and by boiling alcoholic potash into phenyl tolyl ketone and phenyl-tolyl-carbinol. Converted into phenyl-tolyl-(β)-pinacolin by heating with dilute H_2SO_4 at 160°, with HOAc at 190°, with AcCl, or with HClAq. Alcoholic HCl in the cold forms phenyl-tolyl-(*a*)-pinacolin.

PHENYL-TOLYL-PROPANE $C_{16}H_{18}$ *i.e.* $CH_3.CHPh.CH_2.C_6H_4Me$. The *o*- (317°), *m*- (312°), and *p*- (303°) compounds are formed by the action of conc. H_2SO_4 on a mixture of styrene and *o*-, *m*-, and *p*-xylene respectively (Kraemer, Spilker, a. Ebenhardt, *B.* 23, 3271). They are oils, miscible with alcohol and ether.

PHENYL-TOLYL-PROPIONIC ACID $CH_2Ph.CH(C_6H_4Me).CO_2H$. *o*- [95·5°], *m*- [80°], *p*- [105°]. Formed from the corresponding nitriles, which are got from the tolyl-aceto-nitriles by treatment with NaOEt and benzyl chloride (Päpcke, *B.* 21, 1331). The *o*-nitrile is an oil (340°–353°); the *m*-nitrile [53°] (350°–360°), and the *p*-nitrile [79°] are crystalline.

Di-phenyl-*p*-tolyl-propionic acid. *Nitrile* $CH_2Ph.CPh(C_6H_4Me).CN$. [121°]. Formed from phenyl-*p*-tolyl-acetonitrile, NaOEt, and benzyl chloride (Neure, *A.* 250, 150). Needles.

DI-PHENYL-TOLYL-PYRROLE $C_{23}H_{19}N$ *i.e.* $NC_7H_7<\begin{matrix}CPh{:}CH\\CPh{:}CH\end{matrix}$. The *o*- [115°] (above 300°) and *p*- [203°] compounds are formed by distilling the corresponding carboxylic acids with lime (Baümann, *B.* 20, 1492; Paal a. Braikoff, 22, 3089). Both crystallise in white needles.

DI-PHENYL-TOLYL-PYRROLE CARBOXYLIC ACID $N(C_7H_7)<\begin{matrix}CPh{:}C.CO_2H\\CPh{:}CH\end{matrix}$. The *o*-acid [227°] and its *p*- isomeride [206°] are got by saponification of the ethers, which melt at 135° and 145° respectively, and are formed by boiling the corresponding toluidine with phenacyl-benzoyl-acetic ether $CH_2Bz.CHBz.CO_2Et$ and HOAc (Paal a. Braikoff, *B.* 22, 3088). Both acids are crystalline and sl. sol. ether.

Di-phenyl-*p*-tolyl-pyrrole dicarboxylic acid $N(C_7H_7)<\begin{matrix}C(C_6H_4.CO_2H){:}CH\\C(C_6H_4.CO_2H){:}CH\end{matrix}$ [253°]. Formed by heating $C_2H_4(CO.C_6H_4.CO_2H)_2$ with *p*-toluidine on a water-bath (Baumann, *B.* 20, 1489). Yellowish needles, v. sol. alcohol and CS_2.

PHENYL *p*-TOLYL SULPHIDE $Ph.S.C_7H_7$. An oil got by the action of NaSPh on *p*-diazo-toluene chloride (Ziegler, *B.* 23, 2471).

Phenyl *p*-tolyl disulphide $Ph.S_2.C_7H_7$. Formed by adding Br to an ethereal solution of PhSH and C_7H_7SH. Got also, together with Ph_2S_2, by heating toluene *p*-sulphinic acid with PhSH (Otto a. Rössing, *B.* 19, 3133). Thick oil, insol. water, scarcely volatile with steam.

PHENYL *p*-TOLYL SULPHONE $C_{13}H_{12}SO_2$ *i.e.* $C_6H_5.SO_2.C_6H_4Me$. [125°]. S. (alcohol) 1·62 at 20°. Formed by the action of P_2O_5 on a mixture of toluene and benzene sulphonic acid, or of benzene and toluene *p*-sulphonic acid (Michael a. Adair, *B.* 11, 116). Formed also from benzene sulphonic chloride, toluene, and $AlCl_3$ (Beckurts a. Otto, *B.* 11, 2068). Prisms or tablets.

PHENYL-*o*-TOLYL-SEMI-THIOCARBAZIDE $C_{14}H_{15}N_3S$ *i.e.* $NHPh.CS.NH.NH.C_6H_4Me$. [146°]. Formed from phenyl-thiocarbimide and *o*-tolyl-hydrazine (A. E. Dixon, *C. J.* 57, 260). Pearly prisms, v. sl. sol. water, v. sol. hot alcohol.

Isomeride $C_6H_4MeNH.CS.NH.NHPh$. [163°]. Formed from *o*-tolyl-thiocarbimide and phenyl hydrazine. Vitreous prisms, v. sl. sol. water.

PHENYL *o*-TOLYL-THIO-UREA $C_{14}H_{14}N_2S$ *i.e.* $NHPh.CS.NHC_6H_4Me$. [140°]. Formed from *o*-tolyl-thiocarbimide and aniline (Staats, *B.* 13, 137) and by passing H_2S into a boiling solution of phenyl-tolyl-cyanamide $NPh{:}C{:}NC_7H_7$ in dry benzene (Huhn, *B.* 19, 2411). Long needles, sl. sol. water. Boiling HClAq (34 p.c.) splits it up into aniline, *o*-toluidine, phenyl-thiocarbimide, and *o*-tolyl-thiocarbimide (Mainzer, *B.* 15, 1419).

HgO, added to its solution in boiling benzene, forms phenyl-tolyl-cyanamide.

Phenyl-*p*-tolyl-thio-urea NHPh.CS.NHC$_6$H$_4$Me. [137°] (S.); [141°] (F. a. W.). Formed from *p*-tolyl-thiocarbimide and aniline (S.), and from phenyl-*p*-tolyl-cyanamide and H$_2$S (H.). Plates, sl. sol. water. Split up by HClAq in the same way as the *o*- isomeride (M.), and decomposed by HgO in like manner. COCl$_2$ passed into its solution in toluene forms

$NPh{:}C\!\left\langle\begin{matrix}N(C_7H_7)\\S\text{———}\end{matrix}\right\rangle\!CO$

[89°], crystallising in white needles (Freund a. Wolf, *B.* 25, 1466).

Tetra-ω-phenyl-di-*o*-tolyl-thio-urea C$_{39}$H$_{32}$N$_2$S *i.e.* (CHPh$_2$.C$_6$H$_4$.NH)$_2$CS. [123°]. Formed from CHPh$_2$.C$_6$H$_4$.NH$_2$ and CS$_2$ (Fischer a. Fränckel, *A.* 241, 368). White needles, insol. cold alcohol.

References.—NITRO- and OXY- PHENYL-TOLYL-THIO-UREA.

PHENYL-*p*-TOLYL-THIO-UREA-ω-CARBOXYLIC ACID. *Nitrile* NHPh.CS.NH.C$_6$H$_4$.CH$_2$.CN. [141°]. Formed by warming phenyl-thiocarbimide with amido-phenyl-acetonitrile (Freund a. Immerwahr, *B.* 23, 2856). With furfuraldehyde it forms NHPh.CS.NH.C$_6$H$_4$.CCy:CH.C$_4$H$_3$O [160°] crystallising from alcohol.

PHENYL-*o*-TOLYL-UREA C$_{14}$H$_{14}$N$_2$O *i.e.* NHPh.CO.NHC$_6$H$_4$Me. [212°]. Formed by boiling NPh:C:NC$_7$H$_7$ with dilute alcohol (Huhn, *B.* 19, 2410). Slender needles.

Phenyl-*m*-tolyl-urea. [165°]. Formed from phenyl cyanate and *m*-toluidine in ether (Buchka a. Schachtebeck, *B.* 22, 840). Needles.

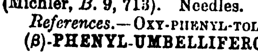
Phenyl-*p*-tolyl-urea. [211°] (H.); [218°] (Freund a. Wolf, *B.* 25, 1467). Formed by boiling phenyl-*p*-tolyl-cyanamide with dilute alcohol (Huhn, *B.* 19, 2408).

Phenyl-di-*p*-tolyl-urea C$_{21}$H$_{20}$N$_2$O. [136°]. Formed from (C$_6$H$_4$Me)$_2$N.COCl and aniline (Hammerich, *B.* 25, 1821). Needles, sol. alcohol.

Di-phenyl-*p*-tolyl-urea NPh$_2$.CO.NHC$_7$H$_7$. [130°]. Formed from NPh$_2$.COCl and *p*-toluidine (Michler, *B.* 9, 713). Needles.

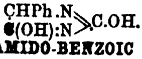
References.—OXY-PHENYL-TOLYL-UREA.

(β)-PHENYL-UMBELLIFERONE C$_{15}$H$_{10}$O$_3$ *i.e.*


$\begin{bmatrix}1\\4\ 2\end{bmatrix}.C_6H_3(OH)\!\left\langle\begin{matrix}CPh{:}CH\\O\text{—}CO\end{matrix}\right.$

[244°]. Prepared by the action of H$_2$SO$_4$ on a mixture of benzoyl-acetic ether and resorcin (Pechmann a. Duisberg, *B*, 16, 2126). Plates (from dilute alcohol).

PHENYL-URAMIDO-ACETO-NITRILE C$_6$H$_5$.CH(CN).NH.CO.NH$_2$. *Phenyl-aceto-nitrile-urea.* [178°] with decomposition. Formed by heating equimolecular quantities of benzaldehyde-cyanhydrin and urea at 100° (Pinner a. Lifschütz, *B.* 20, 2355). Prisms. V. sol. alcohol, m. sol. hot water. By boiling with dilute HCl it is converted into di-oxy-phenyl-glyoxaline


$\left.\begin{matrix}CHPh.N\\C(OH){:}N\end{matrix}\right\rangle C.OH.$

PHENYL-URAMIDO-BENZOIC ACID *v.* vol. i. p. 157.

PHENYL-α-URAMIDO-CROTO-NITRILE C$_6$H$_5$.CH:CH.C(CN)H.NH.CO.NH$_2$. *Phenyl-croto-nitrile-urea.* [160° with decomposition]. Prepared by heating equivalent quantities of cinnamic-aldehyde-cyanhydrin and urea to 96° for several hours; the yield is 40 p.c. of the cyanhydrin (Pinner a. Lifschütz, *B.* 20, 2353). Needles. M. sol. hot alcohol. By boiling with dilute HCl it is converted into di-oxy-styryl-glyoxaline

$CO\!\left\langle\begin{matrix}NH.CH.CH{:}CHPh\\NH.CO\end{matrix}\right.$.

PHENYL-URAMIDO-PHENYL-ACETIC ACID NHPh.CO.NH.CHPh.CO$_2$H. [154°]. Formed by the action of potash on di-phenyl-thiohydantoïn (Kossel, *B.* 24, 4153). Sol. water.

Ethyl ether EtA'. [165°]. Formed from phenyl-amido-acetic ether and phenyl cyanate (K.). Crystalline powder, sol. hot alcohol.

PHENYL-URAMIDO-PROPIONIC ACID C$_{10}$H$_{12}$N$_2$O$_3$ *i.e.* C$_6$H$_5$NH.CO.NH.CH$_2$.CH$_2$.CO$_2$H. [172°]. Formed by heating β-amido-propionic acid with phenyl-urea at 140° (Hoogewerff a. van Dorp, *R. T. C.* 9, 49). Tablets and needles, m. sol. cold alcohol. AcCl forms C$_{10}$H$_{10}$N$_2$O$_2$ [234°] and C$_{10}$H$_9$AcN$_2$O$_2$ [138°]. KOBr and HCl form C$_{10}$H$_{10}$Br$_2$N$_2$O$_3$ [202°] and C$_{10}$H$_9$Br$_3$N$_2$O$_3$ [220°].—KA'.—CaA'$_2$.—AgA'.

Ethyl ether EtA'. [85°]. Needles.

DI-PHENYL-URAZINE C$_{14}$H$_{12}$N$_4$O$_2$ *i.e.*

$NPh\!\left\langle\begin{matrix}NH.CO\\CO.NH\end{matrix}\right\rangle\!NPh.$

[264°]. Formed by heating phenyl semicarbazide at 160° (Pinner, *B.* 21, 2329) or phenyl-carbazic ether at 240° (Heller, *A.* 263, 282). White needles, v. sol. warm HOAc. Yields the acetyl derivatives C$_{14}$H$_{11}$AcN$_4$O$_2$ [173°], C$_{14}$H$_{10}$Ac$_2$N$_4$O$_2$ [153°] and the ether C$_{14}$H$_{11}$EtN$_4$O$_2$ [137°].

PHENYL-URAZOLE *v.* DI-OXY-PHENYL-TRI-AZOLE.

PHENYL-UREA C$_7$H$_8$N$_2$O *i.e.* NHPh.CO.NH$_2$. [147°]. *Formation.*—1. By passing cyanic acid vapour into cooled aniline or from aniline sulphate and potassium cyanate (Hofmann, *A.* 53, 57; 57, 265; 70, 130; 74, 14; Weith, *B.* 9, 810). 2. From aniline and moist cyanogen chloride.—3. From phenyl cyanate and NH$_3$.—4. From mercuric fulminate and aniline (Steiner, *B.* 8, 518). 5. From benzamidoxim, NaOH, and benzene sulphonic chloride (Pinnow, *B.* 24, 4171).

Properties.—Monoclinic needles, v. sol. alcohol and boiling water, sol. ether. Decomposed at 150° into *s*-di-phenyl-urea, CO$_2$, and NH$_3$.

Reactions.—1. Conc. KOHAq yields aniline, NH$_3$, and CO$_2$.—2. *Baryta-water* yields phenyl-biguanide (Emich, *M.* 12, 16).—3. *Aniline* at 190° forms *s*-di-phenyl-urea.—4. Fuming sulphuric acid forms [1:4] C$_6$H$_4$(NH$_2$).SO$_3$H and SO$_3$H.C$_6$H$_4$.NH.CO$_2$H (Hentschel, *B.* 18, 978).—5. ClCO.CO$_2$Et forms phenyl-allophanic ether and phenyl-parabanic acid.

Acetyl derivative NHPh.CO.NHAc. [183°]. Needles (McCreath, *B.* 8, 1181; Kühn, *B.* 17, 2880; Pinnow, *B.* 24, 4171).

Propionyl derivative. [137°]. Prisms.

Benzoyl derivative NHPh.CO.NHBz. [199°]. Silky needles, v. sol. alcohol.

***s*-Di-phenyl-urea** C$_{13}$H$_{12}$N$_2$O, *i.e.* CO(NHPh)$_2$. Mol. w. 212. *Carbanilide.* [235°]. (260°).

Formation.—1. From aniline and phenyl-cyanate (Hofmann, *A.* 57, 266; 74, 15).—2. From aniline and COCl$_2$ (Hofmann, *A.* 70, 138; Hentschel, *J. pr.* [2] 27, 499).—3. By heating di-phenyl-thio-urea with alcoholic potash.—4. By distilling phenyl-urea (H.; Pinnow, *B.* 24, 4172). 5. By dry distillation of aniline oxalate (Hofmann, *Pr.* 15, 335).—6. By heating urea (1 pt.) with aniline (3 pts.) at 160° (Baeyer, *A.* 131, 251) or phenyl-urea (1 mol.) with aniline (1 mol.) at

185° (Weith, *B.* 9, 821).—7. Together with NH_3, benzamide, and benzanilide, by heating di-benzoyl-urea with aniline at 180° (Holleman, *R. T. C.* 10, 72).—8. By the action of an ethereal solution of $ClCO_2CCl_3$ on aniline (Hentschel, *J. pr.* [2] 36, 310).—9. From $NHPh.CO_2Et$ and aniline at 160° or NaOPh at 220°.—10. From $CO(OPh)_2$ and aniline at 150°-180° (Eckenroth, *B.* 18, 516). 11. From $C(OEt)_4$ and aniline at 280° (Bender, *B.* 13, 699).—12. By heating carbamic ether with aniline (3 mols.) at 180°-185° (Smolka, *M.* 11, 200).—13. From benzamidine hydrochloride, phenyl cyanate, and NaOHAq (Pinner, *B.* 22, 1607).

Properties.—Prisms (from alcohol), v. sl. sol. water, v. sol. alcohol and ether. May be distilled.

Reactions.—1. Conc. H_2SO_4 forms CO_2 and $C_6H_4(NH_2)SO_3H$.—2. Alcoholic NH_3 forms urea and aniline (Claus, *B.* 9, 693).—3. PCl_5 forms phenyl cyanate (Weith, *B.* 9, 810). $ClCO_2CCl_3$ also forms phenyl cyanate on heating.—4. P_2O_5 forms phenyl cyanate and aniline.—5. Dry NaOEt at 220° forms aniline and tri-phenyl-guanidine.—6. $ClCO.CO_2Et$ forms di-phenyl-parabanic acid.

Acetyl derivative $NHPh.NPhAc$. [115°]. Laminæ (from water) (McCreath, *B.* 8, 1181).

u-Di-phenyl-urea $NPh_2.CO.NH_2$. [189°]. Formed from $NPh_2.COCl$ [85°] and alcoholic NH_3 at 100° (Michler, *B.* 8, 1665; 9, 396, 715). Needles. Gives a blue colour with H_2SO_4. Split up by distillation into cyanic acid and diphenylamine.

Tri-phenyl-urea $NPh_2.CO.NHPh$. [136°]. Formed by heating a solution of $NPh_2.COCl$, dissolved in chloroform, with aniline at 130° (Michler, *B.* 9, 396, 715). White needles. Resolved by heat into diphenylamine and phenyl cyanate.

Tetra-phenyl-urea $CO(NPh_2)_2$. [183°]. Formed by heating $NPh_2.COCl$ with NPh_2H and zinc-dust (Michler, *B.* 12, 1166). Got also from diphenylamine and $COCl_2$ (Girard a. Willm, *Bl.* [2] 25, 248). Resolved by HClAq at 250° into diphenylamine and CO_2.

References. — Amido-, Bromo-, Chloro-, Chloro-nitro-, Nitro- and Oxy- phenyl-urea.

PHENYL-UREA *m*-CARBOXYLIC ACID $NHPh.CO.NH.C_6H_4.CO_2H$. [270°]. Formed by heating *m*-amido-benzoic acid with phenyl cyanate at 100° (Kühn, *B.* 17, 2882). Prisms, sol. alcohol, sl. sol. ether.

Di-phenyl-urea di-*m*-carboxylic acid $C_{15}H_{12}N_2O_5$, *i.e.* $CO(C_6H_4.NH.CO_2H)_2$.

Formation.—1. By heating *m*-uramido-benzoic acid (Griess, *Z.* 1868, 650; *B.* 9, 796).—2. By heating a mixture of *m*-uramido-benzoic acid with *m*-amido-benzoic acid at 175° (Traube, *B.* 15, 2122).—3. From *m*-amido-benzoic acid and $COCl_2$ (Sarauw, *B.* 15, 44).—4. By boiling $CS(C_6H_4.NH.CO_2H)_2$ with HgO and KOHAq (Griess, *A.* 172, 169).—5. By heating urea with *m*-amido-benzoic acid at 130° (T.).

Properties.—Minute needles, almost insol. water, alcohol, and ether.

Salts.—BaA″ 3aq.—PbA″.—Ag_2A''.

Ethyl ether Et_2A''. [162°]. Needles.

Amide $CO(C_6H_4.NH.CO.NH_2)_2$. Got by heating urea with *m*-amido-benzamide at 140° (Schiff, *A.* 232, 140). White powder, insol. water, decomposing above 270°.

Di-phenyl-urea di-*p*-carboxylic acid. Formed when urea is heated with *p*-amido-benzoic acid (Griess, *J. pr.* [2] 5, 370). Small needles.—BaA″.

TETRA-PHENYL-UVINONE $C_{34}H_{20}O_4$. Formed in small quantity in the preparation of di-phenyl-furfurane by heating di-phenyl-furfurane dicarboxylic acid (Perkin a. Schlosser, *C. J.* 57, 956). Thin yellow needles, not melting at 280°. H_2SO_4 forms a dark-green solution with brick-red fluorescence.

DI-PHENYL-VALERAMIDINE $C_{17}H_{20}N_2$, *i.e.* $C_4H_9.C(NPh).NHPh$. [111°]. Formed by heating isovaleric acid with aniline and PCl_3 at 150° (Hofmann, *J.* 1865, 416). Crystalline, nearly insol. water.

β-PHENYL-*n*-VALERIC ACID $CHPhPr.CO_2H$. [52°]. Formed by heating its nitrile with HClAq at 185° (Rossolymo, *B.* 22, 1235). Needles.

Nitrile $CHPhPr.CN$. (261°). Formed from phenyl-acetonitrile, PrI, and NaOH. Oil.

β-Phenyl-*iso*-valeric acid $C_{11}H_{14}O_2$ *i.e.* $CH_2Ph.CHEt.CO_2H$. (272°). Formed by reduction of phenyl-angelic acid with sodium-amalgam (Baeyer a. Jackson, *B.* 13, 118). Formed also by heating benzyl-ethyl-acetoacetic ether with conc. KOHAq (Anschütz, *A.* 261, 306). Oil.—AgA′.

Chloride (*c.* 147° at 24 mm.). Oil.

Amide $C_{17}H_{19}NO$. [89°]. Monoclinic crystals; *a:b:c* = ·817:1:1·189; β = 70° 28′.

γ-Phenyl-valeric acid $CH_2Ph.CHMe.CH_2.CO_2H$. (176·5° at 15 mm.). Got by potash-fusion from 'diethyl carbobenzonic' acid, which is a product of the action of alcoholic potash on deoxybenzoïn (Anschütz, *A.* 261, 302). Oil, yielding benzoic acid on oxidation.

Ethyl ether $C_{13}H_{18}O_2$. (146° at 15 mm.).

Chloride $C_{11}H_{13}OCl$. (131° at 11 mm.).

Anilide $C_{17}H_{19}NO$. [102°]. Trimetric needles; *a:b:c* = ·685:1: ·608.

δ-Phenyl-valeric acid $CH_2Ph.CH_2.CH_2.CH_2.CO_2H$. [59°]. Formed by reducing $CHPh:CH.CH_2.CH_2.CO_2H$ (Baeyer a. Jackson, *B.* 13, 122). Leaflets, sl. sol. water.

Benzyl ether. (330°-340°). S.G. $\frac{17}{4}$ 1·027. Got by heating benzyl butyrate with Na at 130° (Conrad a. Hodgkinson, *A.* 193, 318). Liquid.

Isomeride *v.* Benzyl-isobutyric acid.

Reference.—Amido-, Di-bromo-, Di-bromo-amido-, Nitro- and Oxy- phenyl-valeric acids.

PHENYL-VINYL- *v.* Styryl-.

DI-PHENYL-VINYL-DIAMINE $C_{14}H_{14}N_2$ *i.e.* $NHPh.CH_2.CH:NPh$. [105°]. Formed by heating $CH_2Cl.CH:NPh$ with aniline (Berlinerblau, *M.* 8, 187). Sol. alcohol and ether.

PHENYL VINYL KETONE CARBOXYLIC ACID *v.* Benzoyl-acrylic acid.

DI-PHENYL-VINYL NITRITE $C_{14}H_{11}NO_2$ *i.e.* $CPh_2:CH.NO_2$. [87°]. Formed by gradually adding HNO_3 (1 pt.) to a hot solution of di-phenyl-ethane (1 pt.) in HOAc (10 pts.) (Anschütz a. Romig, *A.* 233, 327). Needles, v. sol. alcohol and ether.

? **TRI-PHENYL VINYL TRISULPHONE** $C_6H_5.SO_2.CH_2.CH(SO_2C_6H_5)_2$. [86°]. Formed by oxidising the product of the action of NaSPh on $CHCl_2.CH_2Cl$ (Otto, *B.* 24, 1835). Crystalline.

PHENYL-XYLENE *v.* Di-methyl-diphenyl and Phenyl-tolyl-methane.

PHENYL-XYLIDINE $C_{14}H_{15}N$ *i.e.* $C_6H_3Me_2.NHPh$. [52°]. (173° at 15 mm.). Formed by heating xylidine with aniline hydrochloride (Girard a. Vogt, *Bl.* [2] 18, 67). Sol. alcohol.

PHENYL-*o*-XYLYL-CARBINOL $C_{15}H_{16}O$ *i.e.* $C_6H_5.CH(OH).C_6H_3Me_2$ [1:3:4]? [68°]. (336° i.V.) at 744 mm. V.D. 107·7 (for 106). Formed from the ketone, KOH, and zinc-dust (Elbs, *J. pr.* [2] 35, 469). White radiating needles (from alcohol). Somewhat decomposed by distillation.

Phenyl-*m*-xylyl-carbinol $C_6H_5.CH(OH).C_6H_3Me_2$ [1:2:4]? [57°]. (331° i.V.) at 744 mm. V.D. 102·7 (for 106). Formed from the corresponding ketone by reduction (Elbs, *J. pr.* [2] 35, 472).

Phenyl-*p*-xylyl-carbinol $C_6H_5.CH(OH).C_6H_3Me_2$ [1:2:5]. [88°]. Formed from the ketone, KOH, and zinc-dust (Elbs). Prisms (from alcohol); v. sl. sol. water, m. sol. HOAc, v. e. sol. alcohol and ether.

PHENYL-*p*-XYLYL-*p*-CYMYL-METHANE [2:5:1]$Me_2C_6H_3.CHPh.C_6H_3MePr$[1:2:5]. Formed from phenyl-*p*-cymyl-carbinol, *p*-xylene, and P_2O_5 (Elbs, *J. pr.* [2] 35, 498). Oil.

DI-PHENYL-*o*-XYLYLENE-DIAMINE $C_{20}H_{20}N_2$ *i.e.* $C_6H_4(CH_2.NHPh)_2$. [172°]. Formed by boiling di-ω-bromo-*o*-xylene with an alcoholic solution of aniline (Lesser, *B.* 17, 1825). Small plates (from alcohol).

PHENYL *o*-XYLYL KETONE $C_{15}H_{14}O$ *i.e.* $C_6H_5.CO.C_6H_3Me_2$ [1:3:4]? [48°]. (340° i.V.) at 744 mm. V.D. 102·2 (for 105). Formed from BzCl, *o*-xylene, and $AlCl_3$; the yield is 80 p.c. (Elbs, *J. pr.* [2] 35, 467). Groups of snowy needles (from alcohol). Insol. water, sl. sol. cold HOAc, v. sol. alcohol.

Phenyl *m*-xylyl ketone $C_6H_5.CO.C_6H_3Me_2$ [1:2:4]. (321° i.V.) at 744 mm. V.D. 102·3 (for 105). From *m*-xylene, BzCl, and $AlCl_3$ (Söllscher, *B.* 15, 1682; Elbs, *J. pr.* [2] 35, 469). Oil. Partly converted by long boiling into (*B.* 2)-methyl-anthraquinone. In presence of a little of the corresponding phenyl-xylyl-carbinol, (*B.* 2)-methyl-anthracene is formed.

anti-Oxim $\begin{matrix}C_8H_9.C.C_6H_5\\ N.OH\end{matrix}$. [126°]. Converted by PCl_5 into $C_8H_9.CO.NHPh$ (Smith, *B.* 24, 4048). Yields an acetyl derivative [91°], crystallising in flat prisms.

syn-Oxim $\begin{matrix}C_8H_9.C.C_6H_5\\ HO.N\end{matrix}$. [152°]. Formed, as well as the preceding body, by the action of an alcoholic solution of hydroxylamine on the ketone. PCl_5 at −20° forms $C_6H_5.CO.NHC_8H_9$. Yields an acetyl derivative [103°].

Phenyl-*p*-xylyl ketone $C_6H_5.CO.C_6H_3Me_2$ [1:2:5]. [36°]. (317° i.V.) at 744 mm. V.D. 106·2 (for 105). From *p*-xylene, $AlCl_3$, and BzCl (Elbs, *B.* 17, 2847; *J. pr.* [2] 35, 472); the yield is 65 p.c. Transparent prisms (from alcohol), insol. water, m. sol. HOAc, v. e. sol. ether and alcohol. Very slightly volatile with steam. Yields methyl-anthracene when boiled for a long time.

Reaction.—1. H_2SO_4 has no action in the cold, but on warming HOBz is split off.—2. $H_2S_2O_7$ forms a disulphonic acid $C_6H_2Me_2.CO.C_6H_3(SO_3H)_2$, whose salt BaA″2aq is v. e. sol. water.—3. HNO_3 (S.G. 1·15) at 180° forms benzophenone dicarboxylic acid $C_6H_5.CO.C_6H_3(CO_2H)_2$ [1:2:5].

PHENYL-*o*-XYLYL-KETONE *o*-CARBOXYLIC ACID [4:3:1] $C_6H_3Me_2.CO.C_6H_4.CO_2H$ [2:1]. *Xylene-phthaloylic acid.* [162°]. Formed by the action of $AlCl_3$ on a mixture of phthalic anhydride and *o*-xylene (F. Meyer, *B.* 15, 636). Minute prisms (containing aq). Yields benzoic and (4,3,1)-di-methyl-benzoic acids when fused with potash.

Phenyl-*m*-xylyl-ketone *o*-carboxylic acid [4:2:1] $C_6H_3Me_2.CO.C_6H_4.CO_2H$. Formed in like manner from *m*-xylene (M.). Needles, sl. sol. water, sol. alcohol.

Phenyl-*p*-xylyl-ketone *o*-carboxylic acid [5:2:1] $C_6H_3Me_2.CO.C_6H_4.CO_2H$ [1:2]. Formed in like manner from *p*-xylene. Amorphous solid, insol. water, sol. alcohol and benzene.

Phenyl-*m*-xylyl-ketone (α)-carboxylic acid $C_6H_5.CO.C_6H_2Me_2.CO_2H$ [4:5:3:1]. [160°]. Formed, together with the following isomeride, by oxidising benzoyl-mesitylene with chromic acid mixture (Louise, *Bl.* [2] 44, 418; *A. Ch.* [6] 6, 218). Needles, v. sol. ether, insol. cold water.—BaA'_2 2aq.—MgA'_2 6aq.—AgA′: needles.

Phenyl-*m*-xylyl-ketone (β)-carboxylic acid $C_6H_5.CO.C_6H_2Me_2.CO_2H$[2:5:3:1]. [185°]. Formed as above. The Mg salt is more soluble than that of the isomeric acid. Efflorescent needles, v. sl. sol. hot water. Converted by P_2O_5 into di-methyl-anthraquinone [158°].—AgA′: needles.

Phenyl-xylyl-ketone dicarboxylic acid $C_6H_5.CO.C_6HMe_2(CO_2H)_2$. *Benzoyl-cumidic acid.* [85°]. Formed by oxidation of phenyl duryl ketone (F. Meyer a. Ador, *J.* 1879, 562). Melts at 85°, becomes solid, and melts again at 173°.—$BaA'_2 2\frac{1}{2}aq$: long silky needles.

PHENYL-DI-*p*-XYLYL-METHANE $C_6H_5.CH(C_6H_3Me_2)_2$ $[1:2:5]_2$. [93°]. (above 360°). From phenyl *p*-xylyl carbinol and *p*-xylene (Elbs, *J. pr.* [2] 35, 476). Or from di-*p*-xylyl carbinol, benzene, and P_2O_5. Prisms (from ligroïn). Its solutions show blue fluorescence.

Di-phenyl-*o*-xylyl-methane $C_{21}H_{20}$ *i.e.* $(C_6H_5)_2CH.C_6H_3Me_2$[1:3:4]. [68·5°]. (above 360°). Formed from di-phenyl-carbinol, *o*-xylene, and P_2O_5 (Hemilian, *B.* 19, 3070). Needles, v. sol. alcohol and ether.

Di-phenyl-*m*-xylyl-methane $(C_6H_5)_2CH.C_6H_3Me_2$ [1:2:4]. [61·5°]. (above 360°). Formed by boiling di-phenyl-carbinol with *m*-xylene and P_2O_5 (Hemilian, *B.* 19, 3061). Prisms, v. sol. alcohol and ether. Oxidised by chromic acid mixture to methyl-di-phenyl-phthalide and di-phenyl-phthalide carboxylic acid.

Di-phenyl-*p*-xylyl-methane. [92°]. (above 360°). Formed by digesting di-phenyl-carbinol with *p*-xylene and P_2O_5 (Hemilian, *B.* 16, 2360; *Bl.* [2] 34, 326; Petrieff, *Bl.* [2] 41, 316). Monoclinic crystals, v. sol. alcohol and ether. Oxidised by chromic acid mixture to di-phenyl-methyl-phthalide [179°], di-phenyl-tolyl-carbinol *m*-carboxylic acid [c. 253°] and di-phenyl-phthalide carboxylic acid [245°].

Reference.—NITRO-DI-AMIDO-PHENYL-DI-XYLYL-METHANE.

PHENYL-DI-XYLYL-METHANE *o*-CARBOXYLIC ACID [4:2:1] $C_6H_3Me_2.CH_2.C_6H_4.CO_2H$. [158°]. Formed by reducing phenyl-*m*-xylyl-ketone carboxylic acid with zinc-dust and NH_3Aq (Gresly, *A.* 234, 237). Small needles (from alcohol).—BaA'_2aq: plates (from dilute alcohol).

PHENYL-*p*-XYLYL-(β)-PINACOLIN $C_{30}H_{28}O$ *i.e.* $C_6H_5.C(C_6H_3Me_2)_2.CO.C_6H_5$. [146°]. Formed by the action of zinc and HClAq on phenyl *p*-xylyl ketone (Elbs, *J. pr.* [2] 35, 477). Clumps of prisms (from ligroïn), m. sol. alcohol and ether. Soda-lime at 320° splits it up into benzoic acid and phenyl-di-xylyl-methane.

PHENYL-XYLYL-PROPANE $C_{17}H_{20}$ *i.e.* $C_6H_5.CHMe.CH_2.C_6H_3Me_2$. (324°). Formed from ψ-cumene, styrene, and conc. H_2SO_4 (Kraemer, Spilker a. Ebenhardt, *A.* 23, 3273).

PHENYL-XYLYL-PROPIONIC ACID $C_6H_3Me_2.CHPh.CH_2.CO_2H$. Formed from cinnamic acid, *m*-xylene, and H_2SO_4 (Liebermann a. Hartmann, *B.* 25, 959). Amorphous, v. sol. warm benzene. When allocinnamic acid is used it is accompanied by another acid [220°].

DI-PHENYL-XYLYL-PYRROLE CARBOXYLIC ACID $C_8H_9N{<}\begin{smallmatrix}CPh:C.CO_2H\\ CPh:CH\end{smallmatrix}$. [254°]. Formed by saponifying its oily ether, which is got from phenacyl-benzoyl-acetic ether and (4,2,1)-*m*-xylidine (Paal a. Braikoff, *B.* 22, 3090). Small needles, m. sol. hot alcohol and benzene.

PHENYL-XYLYL SULPHONE $C_{14}H_{14}SO_2$, *i.e.* $C_6H_5.SO_2.C_6H_3Me_2$. [80°]. Formed from benzene sulphonic chloride, *m*-xylene, and $AlCl_3$ (Beckurts a. Otto, *B.* 11, 2069). Yellowish needles.

PHENYL *m*-XYLYL-UREA $C_{15}H_{16}N_2O$ *i.e.* $C_8H_9NH.CO.NHPh$. [131°]. Formed by mixing *m*-xylidine with phenyl cyanate (Brömme, *B.* 21, 2703). White matted needles, sol. alcohol.

PHENYTHRONIC ACID *v.* PHENYL-METHYL-FURFURANE DICARBOXYLIC ACID.

PHILLYRIN $C_{27}H_{34}O_{11}$ 1½aq. [160°]. S. ·08 at 9°; S. (alcohol) 2·5 at 9°. A glucoside in the bark of *Phillyrea latifolia* (Bertagnini, *A.* 92, 109; 118, 124). Crystalline, insol. ether. Split up by dilute acids into glucose and crystalline phillygenin $C_{21}H_{24}O_6$, v. sol. ether. A glucoside $C_{26}H_{32}O_{11}$ ([184°]; S. ·05 in the cold, 12·5 at 100°) in *Olea fragrans* is perhaps identical with phillyrin. It is split up by acids into glucose and $C_{20}H_{22}O_6$ [70°] (Eykman, *R. T. C.* 5, 127).

PHLEIN $C_{36}H_{62}O_{31}$. [215°]. S.G. 1·48. S. 3·26 at 10°. $[\alpha]_D = -48·5$. Occurs in the bulbs of cat's-tail grass (*Phleum pratense*) and in the roots of *Baldigera arundinacea* (Ekstrand a. Johanson, *B.* 20, 3310; 21, 597). Carbohydrate resembling starch, but not coloured blue by iodine. Reduces $AgNO_3$, but not Fehling's solution.

PHLOBAPHENE $C_{38}H_{20}O_{17}$. Named from φλοιός, bark, and βαφή, colour. Occurs in oak bark, and formed by boiling quercitannic acid with dilute acids (Hofstetter, *A.* 51, 63; Grabowski, *A.* 145, 8; Oser, *J.* 1876, 903; Böttinger, *A.* 202, 270; 240, 338). Reddish-brown powder, insol. water, ether, and cold alcohol. Alkalis form a reddish-brown solution, which absorbs oxygen from the air. Turned black by $FeCl_3$. Potash-fusion yields protocatechuic acid (Procter, *C. J.* 36, 979). Yields $C_{38}H_{19}Ac_7O_{17}$, $C_{38}H_{19}Bz_7O_{17}$, and $C_{38}H_{20}K_6O_{17}$, which is insol. alcohol, v. sol. water. Bromine yields $C_{38}H_{16}Br_{10}O_{17}$ and $C_{38}H_{20}Br_6O_{17}$, which forms $C_{38}H_{13}Br_6Ac_7O_{17}$. A substance $C_{50}H_{46}O_{25}$ resembling phlobaphene occurs in hops (Etti, *A.* 180, 223; *D. P. J.* 228, 354).

PHLOGISTIC THEORY *v.* COMBUSTION, vol. ii. pp. 241–2.

PHLORAMINE $C_6H_7NO_2$, *i.e.* $C_6H_3(OH)_2(NH_2)$. *Amido-resorcin?* Formed by passing NH_3 over phloroglucin (Hlasiwetz a. Pfaundler, *A.* 119, 202). Thin plates (from water), sl. sol. cold water, v. sol. alcohol, insol. ether. Turns brown in air. Decomposed by alkalis. Its solutions are not coloured by $FeCl_3$. —B'HCl.— $B'_2H_2SO_4$ 2aq: long yellowish needles.

PHLOREÏN $C_{18}H_{11}NO_7$. Formed by passing nitrous acid gas into an ethereal solution of phloroglucin (4 g.) containing HNO_3 (4 c.c. of S.G. 1·25) (Benedikt, *B.* 7, 445; *A.* 178, 93). Lustrous dark-green powder, insol. water, v. sol. alcohol and ether, forming a dark-brown solution. Alkalis form a purple solution. Yields phloroglucin when fused with potash. Zinc and dilute H_2SO_4 form a colourless body, re-oxidised to phloreïn by air.

PHLORETIC ACID *v.* *p*-OXY-α-PHENYL-PROPIONIC ACID. It yields a crystalline di-bromo-derivative (Hlasiwetz, *A.* 102, 145).

PHLORETIN $C_{15}H_{14}O_5$. [255°]. Formed by boiling phlorizin or glycyphyllin with dilute acids (Stas, *A.* 30, 200; G. Roser, *A.* 74, 178; Hlasiwetz, *A.* 96, 118; Schiff, *A.* 156, 2; 172, 357; 229, 374; Rennie, *C. J.* 49, 860). Small laminæ, with sweet taste, v. sl. sol. hot water and ether, v. e. sol. alcohol. Inactive to light. Bromine forms $C_{15}H_{10}Br_4O_5$ [205°–210°] (Schmidt a. Hesse, *A.* 119, 103). Alkaline solutions absorb oxygen and turn orange in air; boiling conc. KOHAq splits it up into phloretic acid and phloroglucin. Aniline at 170° forms $C_{21}H_{19}NO_4$, a scarlet powder. AcCl gives amorphous $C_{15}H_{12}Ac_2O_5$ aq.

Salts.—$C_{15}H_{11}(NH_4)_3O_5$: amorphous. Gives off NH_3 in air.—$C_{30}H_{18}Pb_5O_{10}$ 5aq.—$C_{15}H_{13}AgO_5$: unstable pp.

PHLORIZIN $C_{21}H_{24}O_{10}$ 2aq. Named from φλοιός, bark, and ῥίζα, root. [109°] (when anhydrous). S.G. ^{19} 1·43. S. ·1 in the cold. $[\alpha]_D = -49$ at 15°. Occurs in the root-bark of the apple, pear, plum, and cherry tree, from which it may be extracted by dilute alcohol (Stas a. De Koninck, *A.* 15, 75; 30, 193; *A. Ch.* [2] 69, 367; Mulder, *Rev. Scient.* 3, 50; Roser, *A.* 74, 178; Strecker, *A.* 74, 184; Rennie, *C. J.* 51, 635). Silky needles with slightly bitter taste, sl. sol. cold water, v. e. sol. hot water and alcohol, insol. ether. Melts at 109°, becomes solid, and melts again at 171°. Lævogyrate. Decomposed by dilute acids into glucose and phloretin. Gives pps. with baryta and MeOH, with lime-water, and with lead subacetate. Air and ammonia form reddish-brown amorphous phlorizeïn $C_{21}H_{30}N_2O_{13}$. Gives a violet colour on boiling with $ZnSO_4$ and KNO_2 (Nickel, *Fr.* 28, 248). $FeCl_3$ gives a brownish-red colour. Aniline at 180° forms $C_{33}H_{34}N_2O_8$, a yellow powder, yielding a mono- and a tri- acetyl derivative.

Acetyl derivatives $C_{21}H_{23}AcO_{10}$ 2aq: needles (from water). — $C_{21}H_{21}Ac_3O_{10}$. — $C_{21}H_{19}Ac_5O_{10}$ aq: amorphous solid.

Tri-benzoyl derivative. Powder.

Isophlorizin $C_{21}H_{24}O_{10}$. [105°]. Occurs in the leaves of the apple-tree (Rochleder, *Z.* [2] 4, 741). Silvery needles. Its ammoniacal solution turns brown in air. Its solution is ppd. by lead subacetate. Dilute H_2SO_4 splits it up into glucose and isophloretin $C_{15}H_{14}O_5$, which is v. sol. ether, and yields phloroglucin when heated with conc. KOHAq.

PHLOROBROMIN C_6Br_5HO. [152°]. Formed by the action of excess of bromine on a very dilute aqueous solution of phloroglucin (Benedikt, *A.* 189, 165; *C. J.* 34, 499). Dimetric prisms; $a:b = 1:1·2$. Insol. water. Not attacked by potash or HNO_3. Warm alcohol decomposes it, forming penta-bromo-acetone [76°]. NH_3Aq forms CBr_3H and $C_5Br_6H_4N_2$, crystallising from water in colourless laminæ [124°].

PHLOROGLUCIN $C_6H_6O_3$ *i.e.* $C_6H_3(OH)_3$ [1:3:5]. Mol. w. 126. [219°] (Baeyer, *B.* 19, 2186). H.F. 153,348 (Stohmann, *J. pr.* [2] 33, 471).

Formation.—1. By boiling phloretin with conc. KOHAq (Hlasiwetz, *A.* 96, 118).—2. By potash-fusion from quercetin, maclurin, catechin, scoparin, gamboge, dragon's blood, limettin, and bergaptene (Hlasiwetz, *A.* 112, 96; 119, 199; 127, 357; 134, 118, 283; 138, 190; Zwenger, *A.* 123, 154; Gautier, *Bl.* [2] 33, 583; Tilden a. Beck, *C. J.* 57, 323; Pomeranz, *M.* 12, 387).—3. By fusing resorcin with a large excess of NaOH, the yield being 65 p.c. (Barth a. Schreder, *B.* 12, 503).—4. By soda-fusion from phenol, benzene, trisulphonic acid, orcin, and naringenin (Barth a. Schreder, *B.* 12, 422; *M.* 3, 649; Will, *B.* 20, 297).—5. By fusing its tricarboxylic ether with potash (Baeyer, *B.* 19, 3458).—6. By fusing *s*-di-bromo-phenol with potash (Blau, *M.* 7, 632).

Preparation.—By soda-fusion from resorcin (Tiemann a. Will, *B.* 14, 954; 18, 1323).

Properties.—Trimetric crystals (containing 2aq); $a:b:c = ·825:1:3·417$. Melts at 200°-209° when slowly heated. V. sol. water, alcohol, and ether; sl. sol. NaClAq. Tastes sweeter than sugar. May be sublimed. Its solution is ppd. by lead subacetate. $FeCl_3$ gives a bluish-violet colour. Reduces Fehling's solution and ammoniacal $AgNO_3$. Its alkaline solution absorbs oxygen and turns brown in air. Colours acidified pine-wood red. An alcoholic solution gives a red colour with HClAq and vanillin (Lindt, *Fr.* 26, 260), oil of cloves, or oil of pimento (Ihl, *Chem. Zeit.* 13, 204).

Reactions.—1. *Bromine* forms crystalline tri-bromo-phloroglucin and finally phlorobromin. 2. *Chlorine* passed into its aqueous solution forms tri-chloro-phloroglucin $C_6Cl_3(OH)_3 3aq$ [136°], which soon decomposes into tetra-chloro-acetone hydrate, and di-chloro-acetic acid (Webster, *C. J.* 47, 423; Zincke a. Kegel, *B.* 22, 1476). Chlorine passed into its solution in HOAc forms $CHCl_2.CO.CHCl_2 4aq$ [49°]. Chlorine passed into a cooled solution of dry phloroglucin in chloroform forms $CO\Big\langle\begin{smallmatrix}CCl_2.CO\\CCl_2.CO\end{smallmatrix}\Big\rangle CCl_2$ [48°], (269°), decomposed by water into CO_2, di-chloro-acetic acid, and $CO(CHCl_2)_2$.—3. Dilute HNO_3 forms nitro-phloroglucin.—4. *Ammonia* produces phloramine.—5. *Nitrous acid* in its ethereal solution forms phloreïn. In acetic acid solution it gives tri-nitroso-phloroglucin (vol. iii. p. 619).—6. Aqueous HI at 140° forms nearly tasteless scales of phloroglucide $C_{12}H_{10}O_5 2aq$, sl. sol. warm water. Phloroglucide is also got by heating phloroglucin alone or with $POCl_3$.—7. Heated with *salicylic acid* it forms two compounds of the form $C_6H_4\Big\langle\begin{smallmatrix}O\\CO\end{smallmatrix}\Big\rangle C_6H(OH)\Big\langle\begin{smallmatrix}O\\CO\end{smallmatrix}\Big\rangle C_6H_4$, one of these (described by Kostanecki and Nessler) which yields an acetyl derivative $C_{20}H_9O_4(OAc)$ [218°]; the other isomeride [326°] crystallises from HOAc in green-yellow tables.—8. With *o-amido-benzoic aldehyde* and NaOHAq it forms red $C_{13}H_9NO_3$, possibly di-oxy-acridine $C_6H_2(OH)_2\Big\langle\begin{smallmatrix}N\\CH\end{smallmatrix}\Big\rangle C_6H_4$, which forms $B'_2H_2PtCl_6$ and $C_{13}H_7Bz_2NO_3$ (Eliasberg a. Friedländer, *B.* 25, 1752).—9. *Phenyl cyanate* unites, forming $C_6H_3(O.CO.NHPh)_3$, a yellowish powder [128°] (Goldschmidt a. Meissler, *B.* 23, 269).—10. *Benzene sulphonic chloride* added to the slightly alkaline solution forms $C_6H_3(O.SO_2C_6H_5)_3$ [117°] (Georgesen, *B.* 24, 418).—11. *Aniline* at 210° forms tri-phenyl-tri-amido-benzene [193°] (Minunni, *B.* 21, 1984).—12. *Phloretic acid* at 170° forms $C_{33}H_{28}O_{14}$, crystallising from water in laminæ (Hlasiwetz, *A.* 119, 199).

Tri-oxim $C_6H_6(NOH)_3$. Formed from phloroglucin and aqueous hydroxylamine (Baeyer, *B.* 19, 159). Colourless crystals, v. sl. sol. water and alcohol, sol. alkalis and acids. Explodes at 155°.

Phenyl-hydrazine derivatives. The salt $C_6H_6O_3N_2H_3Ph$ [78°-83°] is got from phloroglucin (1 mol.) and phenyl-hydrazine (3 mols.) in alcoholic solution (Baeyer a. Kochendörfer, *B.* 22, 2190). Nodules, sol. alcohol and ether. Cold NaOHAq sets free phenyl-hydrazine. In alcoholic solution it changes on keeping to $C_6H_3(OH)(N_2H_2Ph)_2$ [144°], which crystallises from toluene in needles, and yields a penta-benzoyl derivative [176°].

Tri-acetyl derivative $C_6H_3(OAc)_3$. [106°]. Got by heating phloroglucin with AcCl.

Di-benzoyl derivatives $C_6H_3(OH)(OBz)_2$. Two isomerides [165°] and [191°-195°] are got from phloroglucin with BzCl. The compound [165°] is more sol. benzene than the other (Skraup, *M.* 10, 391, 722).

Tri-benzoyl derivative $C_6H_3(OBz)_3$. [174°]. Formed, together with $C_{12}H_6(OBz)_4$ [199°], by warming phloroglucin with BzCl and NaOH (S.). Plates, sol. benzene.

Tri-methyl ether $C_6H_3(OMe)_3$. [52°]. (256°). Formed by passing HCl into a solution of phloroglucin in MeOH, the resulting $C_6H_3(OH)(OMe)_2$ being treated with MeI and KOH (Will, *B.* 21, 603). Crystals, insol. water and alkalis, v. sol. alcohol and ether. Conc. HNO_3 forms a blue solution. Bromine gives $C_6Br_3(OMe)_3$ [145°]. When phloroglucin is treated with KOH and MeI the products are $C_6H_3Me_3O_3$ [184°], $C_6H_2Me_4O_3$ [114°], and $C_6Me_6O_3$ [80°] (Margulies, *M.* 9, 1052; 10, 459). When tetra-methyl-phloroglucin is heated in sealed tubes with HClAq it yields isopropyl ketone, isobutyric acid, HOAc, and CO_2. Hence it would appear to be $CMe_2\Big\langle\begin{smallmatrix}CO.CH\\CO.CMe_2\end{smallmatrix}\Big\rangle C.OH$ (Spitzer, *M.* 11, 104, 287). Hexamethyl-phloroglucin heated with HIAq at 200° produces isobutyric acid and C_7H_{14}, and, on oxidation, yields di-isopropyl ketone. Hence it would appear to be $CMe_2\Big\langle\begin{smallmatrix}CO.CMe_2\\CO.CMe_2\end{smallmatrix}\Big\rangle CO$.

Di-ethyl ether $C_6H_3(OEt)_2(OH)$. [[illegible]°]. Made by passing HCl into an alcoholic solution of phloroglucin or its carboxylic acid (Will a. Albrecht, *B.* 17, 2106). Long white needles. May be distilled.

Tri-ethyl ether $C_6H_3(OEt)_3$. [43°]. Got by heating the di-ethyl ether with EtI and alcoholic potash (W. a. A.).

Penta-ethyl derivative *v.* vol. ii. p. 505.

Tri-phenyl ether $C_6H_3(OPh)_3$? [175°]. A product of the action of Na on phenyl acetate (Hodgkinson, *C. J. Proc.* **2**, 188). V. sl. sol. Aq.

References.—TRI-BROMO-, BROMO-DI-IODO-, TRI-CHLORO-, NITROSO-, and NITRO- PHLOROGLUCIN.

PHLOROGLUCIN CARBOXYLIC ACID *v.* TRI-OXY-BENZOIC ACID.

Phloroglucin tricarboxylic ether $C_{15}H_{18}O_9$ *i.e.* $C_6(OH)_3(CO_2Et)_3$. [106°]. Formed from malonic ether and $ZnEt_2$ (Lang, *B.* 19, 2937). Prepared by dissolving Na (14·4 g.) in malonic ether (200 g.) at 100° and heating the product for six hours at 145° (Baeyer, *B.* 18, 3457; Bally, *B.* 21, 1766). In this preparation an anhydride $C_6(OH)_2(CO_2Et)_2{<}\begin{smallmatrix}O\\CO\end{smallmatrix}$ [170°] is also formed. Needles (from dilute alcohol), insol. water. Does not react with nitrous acid gas.

Reactions.—1. *Potash-fusion* yields phloroglucin.—2. *Bromine* in CS_2 ppts. bromo-phloroglucin dicarboxylic ether [128°].—3. *Chlorine* gives tri-chloro-acetamide.—4. *Phenyl cyanate* and C_6H_6 at 200° form $C_6(O.CO.NHPh)_3(CO_2Et)_3$ [195°] (Goldschmidt a. Meissler, *B.* 23, 270).

Tri-acetyl derivative $C_6(OAc)_3(CO_2Et)_3$. [76°]. Needles (from alcohol or ether).

Oxim $C_6H_3(NOH)_3(CO_2Et)_3$. [171°].

PHLOROGLUCIN-PHTHALEÏN $C_{20}H_{12}O_7$. Formed by heating phloroglucin with phthalic anhydride at 170° (Link, *B.* 13, 1652). Minute orange needles, sl. sol. water. Its alkaline solutions are orange-red, without fluorescence. Zinc-dust and NaOHAq reduce it to phloroglucin-phthalin $C_{20}H_{14}O_7$, an amorphous reddish-yellow mass.

PHLOROGLUCIN SULPHONIC ACID $C_6H_6SO_6$ *i.e.* $C_6H_2(OH)_3.SO_3H$. Formed by mixing phloroglucin with $H_2S_2O_7$ (Schiff, *B.* 6, 26; *A.* 178, 191). Yields a crystalline K salt. $POCl_3$ converts it into the anhydrides $C_{12}H_{10}S_2O_{11}$, v. e. sol. water, and $C_{12}H_8S_2O_{10}$, sl. sol. water, and $C_{24}H_{16}S_2O_{15}$.

PHLOROL *v.* *o*-ETHYL-PHENOL.

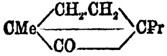
PHLORONE *v.* XYLOQUINONE.

PHORONE $C_9H_{14}O$ *i.e.* $CO(CH:CMe_2)_2$. Mol. w. 138. [28°]. (197°) at 743 mm. S.G. $\frac{20}{4}$ ·885. $\mu_D = 1{\cdot}500$ at 20° (Brühl, *A.* 235, 15). R_∞ 70·93 in a 14·5 p.c. benzene solution. Formed, together with mesityl oxide, by leaving acetone in contact with quicklime (Fittig, *A.* 110, 32). Formed also by the action of conc. HClAq on acetone (Baeyer, *A.* 140, 301), and by heating nitroso-triacetonamine with potash (Heintz, *A.* 187, 250). Yellowish prisms. Yields acetone, oxalic acid, and CO_2 on oxidation with $KMnO_4$ (Pinner, *B.* 15, 591). Slowly combines with $NaHSO_3$, forming di-isobutyl ketone di-sulphonic acid. Yields ψ-cumene on heating with P_2O_5 and mesitylene on heating with conc. H_2SO_4. Yields mesityl oxide on distilling with dilute H_2SO_4 (Claisen, *A.* 180, 18). Bromine in CS_2 forms $C_9H_{14}Br_4O$ [88°]. Zinc and H_2SO_4 reduce it, in alcoholic solution, to deoxyphorone $C_{18}H_{28}O$ [108°]. HI forms $C_9H_{16}I_2O$ [13°] (Kasaneff, *B.* 8, 435). Phorone does not react with benzoic aldehyde (Claisen, *B.* 14, 352).

Oxim C_9H_{14}:NOH. [48°]. (218°). Tables, v. sol. alcohol (Nägeli, *B.* 16, 496).

Isophorone. The substance to which this name has been given is a mixture (Laycock, *A.* 258, 230).

Camphor-phorone $C_9H_{14}O$ *i.e.*



$$CMe{<}\begin{matrix}CH_2.CH_2\\ \hline CO\end{matrix}{>}CPr$$

(Königs a. Eppens, *B.* 25, 260). (208°) (Kachler, *A.* 164, 79). Got by distilling calcium camphorate (Laurent, *A. Ch.* [2] 65, 329; Gerhardt a. Liès-Bodart, *A.* 72, 293) and by heating camphor (1 pt.) with H_2SO_4 (4 pts.) at 100° (Schwanert, *A.* 123, 298). Colourless oil with aromatic odour. Inactive to light. PCl_5 yields $C_9H_{13}Cl$ (205°). Yields α-methyl-glutaric and acetic acids on oxidation. Na followed by MeI yields $C_9H_{13}MeO$ (225°–230°). Na followed by AcCl yields $C_{18}H_{27}AcO_2$ (230°–240°). Bromine in CS_2 forms $C_9H_{13}Br_3O$ [52°].

PHORONIC ACID $C_{11}H_{18}O_5$. [184°]. Formed by saponification of its nitrile, which is got by boiling the product of the action of gaseous HCl on acetone with alcoholic potash (Pinner, *B.* 14, 1071; 15, 585). Large prisms (from dilute alcohol), sl. sol. water.—KHA″ 1½aq: needles, v. sol. water.—CaA″ 3aq: prisms.—Ag_2A'' aq: pp.

Ethyl ether Et_2A''. [125°].

Amide. [above 300°]. Prisms.

Anhydride $C_{11}H_{16}O_4$. [138°]. Got by heating the acid at 190°.

Imide $C_{11}H_{16}O_3(NH)$. [205°]. Formed from the anhydride and alcoholic NH_3.

Nitrile $C_{11}H_{18}N_2O_2$. [above 320°].

PHOSENE *v.* SYNANTHRENE.

PHOSGENE GAS. Another name for $COCl_2$; *v.* CARBON OXYCHLORIDE, vol. i. p. 692.

PHOSPHAM. (?)PN_2H. When dry NH_3 is passed into well-cooled PCl_3, a solid colourless mass is obtained, said by H. Rose to contain PCl_3 and NH_3 in the ratio PCl_3:$5NH_3$ (*P.* 24, 308; 28, 529). This substance is probably a mixture of various compounds; other substances are formed if the PCl_3 is not cooled. If PCl_5 is treated with NH_3 at the ordinary temperature, $5NH_3$ are absorbed by PCl_5 (H. Rose, *l.c.*); from this product ether dissolves out $N_3P_3Cl_6$ (*v.* NITROGEN PHOSPHOCHLORIDE, vol. iii. p. 570); if the product is heated, HCl and NH_4Cl are evolved, and a white, loose powder remains, to which Gerhardt (*A. Ch.* [3] 18, 188; 20, 225) gave the composition PN_2H and the name *phospham*. Liebig a. Wöhler (*A.* 11, 139) obtained this compound by passing PCl_3 or PCl_5 over heated NH_4Cl, and washing and heating the product; they supposed it to be PN_2. The same substance was obtained by Pauli (*A.* 101, 41) by heating an intimate mixture of P_2S_5 and NH_4Cl, also by heating red P with S and NH_4Cl, and by heating powdered Ca phosphide with S and NH_4Cl, and washing the residue with an acid. Pauli's analyses showed less N than is required by the formula PN_2H. By treating PCl_5 with NH_3, washing for a long time with water, digesting with HClAq, then with KOHAq, washing with water and then with ether, Salzmann (*B.* 7, 494) obtained a substance resembling phospham and approximately agreeing with the composition $P_3N_5H_4$; Salzmann regarded this substance as probably a mixture of several very similar compounds of P, N, and H. Besson (*C. R.* 114, 1264) says that PCl_5 absorbs $8HN_3$, and that on heating PN_2H is formed.

Phospham is a white, loose powder; insoluble in ordinary solvents; melts and vaporises when heated in absence of air; oxidised by heating in air; yields HPO_3 and HN_3 when moistened with water and heated (Gerhardt, *l.c.*); fused with KOH or BaO_2H_2 forms NH_3 and orthophosphate, with incandescence.

Phospham may be regarded as one of the nitriles of H_3PO_4: thus $PO.OH.(ONH_4)_2 - 4H_2O = PN_2H$; the other nitriles would be PON, which is known (*v.* PHOSPHORUS OXYNITRIDE, p. 144) [$PO(OH)_2ONH_4 - 3H_2O = PON$], and PN_3H_4, which has not been isolated [$PO(ONH_4)_3 - 4H_2O = PN_3H_4$]. Mendelejeff (*B.* 23, 3472 *note*) thinks it likely that phospham is a polymeride of PN_2H, inasmuch as it is analogous to N_3H (*hydrazoic acid*, vol. iii. p. 559) and both P and P compounds show a greater readiness to polymerise than N and compounds of N. M. M. P. M.

PHOSPHAMIC ACIDS AND ALLIED COMPOUNDS. Two amic acids may be derived theoretically from $PO(OH)_3$, viz. $PONH_2(OH)_2$ and $PO(NH_2)_2OH$; both acids have been isolated. The compound $PO(NH_2)_3$ is described as PHOSPHAMIDE, and $PO.NH.NH_2$ as PHOSPHAMIDO-IMIDE (*infra*). The two thiophosphamic acids, $PS.NH_2.(OH)_2$ and $PS(NH_2)_2OH$ are probably formed by the action of NH_3 on $PSCl_3$ (*v.* THIOPHOSPHORYL CHLORIDE, *Reaction* 7, p. 148). The three amic acids (or salts of these) derivable from $H_4P_2O_7$ are known: $P_2O_3NH_2(OH)_3$, $P_2O_3(NH_2)_2(OH)_2$, and $P_2O_3(NH_2)_3OH$. By heating $P_2O_3(NH_2)_3OH$ the NH_4 salt of the acid $P_2O_3(OH)N$ is obtained. There are also several acids (or their salts) known, which may be derived from hypothetical $P_4O_7(OH)_6[2P_2O_3(OH)_4 - H_2O = P_4O_7(OH)_6]$ by replacing OH by NH_2 or NH. Imidophosphoric acid, PO.NH.OH, perhaps exists.

PHOSPHAMIC ACID $PO.NH_2(OH)_2$. (*Amidophosphoric acid.*) Obtained by Stokes (*Am.* 15, 198 [1893]) by suspending the lead salt in a little ice-water, decomposing by excess of H_2S, and filtering into alcohol. White microscopic crystals; easily sol. water; does not give NH_3 with caustic alkalis; heated to 100° is slowly changed to an NH_4 salt, perhaps $NH_4.PO_3$; aqueous solution soon changes to $NH_4H_2PO_4$. Acid and normal salts have been prepared. The lead salt is formed by adding lead acetate to a solution of $PO.NH_2.OH.OK$, which salt is produced by adding alcoholic NH_3 to an alcoholic solution of $PO.Cl(OPh)_2$, and saponifying the $PO.NH_2(OPh)_2$ thus formed by KOHAq.

PHOSPHODIAMIC ACID $PO.(NH_2)_2OH$. (*Diamidophosphoric acid.*) Stokes (*B.* 27, 565 [1894]) prepared this acid by saponifying the product of the action of NH_3Aq on $POCl_2(OPh)$. The acid gives salts $PO(NH_2)_2OM$, and also salts of an acid $P(NH_2)_2(OH)_3$ (*Abstract* in *C. J.* 66 [11], 188 [1894]).

PYROPHOSPHAMIC ACID $P_2O_3(NH_2)(OH)_3$. This is said by Gladstone (*C. J.* 17, 229) to be the chief product of the action of NH_3 on P_2O_5; Schiff (*A.* 103, 168) formulated this product as PO.NH.OH, *imido-phosphoric acid*; Stokes (*l.c.*) says the product is a mixture. For details *v.* G. (*l.c.*; also *C. J.* 3, 135; 21 64); also G. a. Helmes (*C. J.* 17, 225).

PYROPHOSPHODIAMIC ACID $P_2O_3(NH_2)_2(OH)_2$ (G., *C. J.* 19, 290; G. a. H., *l.c.*). Formed by action of water or alkalis on $N_3P_3Cl_6$, by treating $POCl_3$ with conc. NH_3Aq, and in many other ways. A white amorphous solid, easily soluble in water and alcohol. The acid is dibasic. The salts are difficult to obtain pure, as they easily change into pyrophosphamates; salts of Ba, Ag, and Zn are described.

PYROPHOSPHOTRIAMIC ACID $P_2O_3(NH_2)_3OH$ (G., *C. J.* 19, 1; 21, 64). Dry NH_3 is passed into $POCl_3$ until saturated, the product is heated to 220° and boiled for a short time with water, the residue is washed with cold water, and then with a little dilute alcohol. A white, amorphous, tasteless powder, nearly insoluble in water; slowly acted on by cold water, more quickly by hot water, yielding $P_2O_3(NH_2)_2(OH)_2Aq$ and NH_3Aq; boiled with HClAq gives H_3PO_4 and NH_3. *Pyrophosphotriamates* of NH_4, Ba, Cd, Co, Cu, Cr, Fe, Pb, Mg, Mn, Hg, Ni, Pt, K, Ag, Tl, and Zn are described; the acid is said to be tetrabasic.

PYROPHOSPHONITRILIC ACID $P_2O_3(OH)N$. The NH_4 salt of this acid is said to be formed by heating $P_2O_3(NH_2)_3OH$, and the K salt by heating $P_2O_3(NH_2)_3OK$ (G., *C. J.* 22, 19).

TETRAPHOSPHAMIC ACIDS AND ALLIED COMPOUNDS. By the reaction of NH_3 with $POCl_3$ under different conditions, Gladstone (*C. J.* 21, 261; 22, 15), obtained various compounds which may be regarded as (1) *tetraphosphodiamic acid* $P_4O_7(NH_2)_2(OH)_4$, (2) $P_4O_7(NH_2)_4(OH)_2$ *tetraphosphotetramic acid*, (3) ? *tetraphospho-imido-tetramide* $P_4O_7(NH_2)_4NH$ (called by G. *tetraphosphopentazotic acid*), (4) ? *tetraphosphodiimido-diamide* $P_4O_7(NH_2)_2(NH)_2$ (called by G. *tetraphosphotetrimic acid*). Some of the above acids are regarded by Mente (*A.* 248, 232) as imido-acids. M. M. P. M.

PHOSPHAMIDES. I. PHOSPHORIC TRIAMIDE $O.P(NH_2)_3$ (*Phosphoryl triamide*) [derived from $O.P(OH)_3 = H_3PO_4$]. This compound is said by Schiff (*A.* 101, 300) to be obtained by passing NH_3 gas into $POCl_3$, and treating the product with water. It is described as a snow-white, amorphous solid; heated out of air gives NH_3 and PON; fused with KOH gives NH_3 and K phosphate; scarcely acted on by boiling water, KOHAq, or dilute acids; soluble in hot conc. H_2SO_4; slowly attacked by boiling conc. HNO_3 or HClAq. Gladstone (*C. J.* 22, 18) could not obtain this compound.

II. PHOSPHOROUS DIAMIDE $OH.P.(NH_2)_2$ [derived from $OH.P(OH)_2 = H_3PO_3$]. The white powder produced by passing NH_3 into P_4O_6 in benzene or ether has probably this composition (Thorpe a. Tutton, *C. J.* 59, 1027). It dissolves in water with incandescence; HClAq reacts violently, forming non-inflammable PH_3, P, NH_4Cl, H_3PO_3Aq, and H_3PO_4Aq.

THIOPHOSPHAMIDE is described under THIOPHOSPHORYL CHLORIDE, *Reactions*, No. 7, p. 148.

M. M. P. M.

PHOSPHAMIDO-IMIDE $PO.NH.NH_2$ (*Phosphoryl imido-amide.* Formerly called *Phosphodiamide*) (Gerhardt, *A. Ch.* [3] 18, 188; Schiff, *A.* 101, 300). Obtained by saturating PCl_5 with NH_3, boiling the product with water as long as HCl passes into solution, then boiling with potash, then with HNO_3Aq or H_2SO_4Aq, washing, and drying over H_2SO_4. A white powder, insoluble in alcohol, water, or turpentine; heated out of air gives NH_3 and PON; heated in moist air gives NH_3 and HPO_3; fused with KOH gives K phosphate and NH_3; slowly oxidised by fusion with KNO_3, but resists action of most oxidisers. M. M. P. M.

PHOSPHATES. *Salts of the phosphoric acids.* Besides the salts directly derived from the three phosphoric acids HPO_3, H_3PO_4, and $H_4P_2O_7$ (*v.* PHOSPHORIC ACIDS, p. 124), phosphates exist which are probably derived from hypothetical di-, tri-, or meta- phosphoric acid $nHPO_3$; and a few salts have been isolated which are perhaps derived from the hypothetical acids $P_4O_7(OH)_6$ and $P_{10}O_{19}(OH)_{12}$.

Composition.—*Orthophosphates* are derived from H_3PO_4; they may be divided into classes according to the replacing powers of the metals: (1) monovalent metals form MH_2PO_4, M_2HPO_4, and M_3PO_4; (2) divalent metals form $MH_4P_2O_8$, $MHPO_4$, and $M_3P_2O_8$; (3) trivalent metals form $MH_3P_2O_8$ and $M_2P_2O_8$; (4) tetravalent metals form $MH_2P_2O_8$ and $M_3P_4O_{16}$.

Pyrophosphates are derived from $H_4P_2O_7$: (1) salts of monovalent metals $M_2H_2P_2O_7$ and $M_4P_2O_7$; (2) salts of divalent metals $MH_2P_2O_7$ and $M_2P_2O_7$, &c.

Metaphosphates are derived from HPO_3: (1) salts of monovalent metals MPO_3; (2) salts of divalent metals MP_2O_6, &c. Various modifications of Na (and other) metaphosphates are known, all having the empirical formula MPO_3, but differing both in physical and chemical properties from one another; these salts were classified by Fleitmann a. Hanneberg (*A.* 65, 304; F., *P.* 78, 233, 338) as: (1) *dimetaphosphates*, salts of $H_2P_2O_6$; (2) *trimetaphosphates*, salts of $H_3P_3O_9$; (3) *tetrametaphosphates*, salts of $H_4P_4O_{12}$; and (4) *hexametaphosphates*, salts of $H_6P_6O_{18}$. Tammann (*Z. P. C.* 6, 122) has examined the electrical conductivities, and the depressions of freezing-points, of aqueous solutions of several di-, tri-, and hexa- metaphosphates; he comes to the conclusion that Fleitmann's dimetaphosphates should be represented in solution as $M_3(PO_3)_3$ (*i.e.* as trimetaphosphates), and [illegible]is tri- salts when in solution are really $M_2(PO_3)_2$ (*i.e.* dimetaphosphates). Tammann's results point to the existence in aqueous solution of 3 isomeric hexametaphosphates which may be represented as (i.) $M_2.M_4(PO_3)_6$ *e.g.* $Na_2.Na_4(PO_3)_6$, $K_2.Na_4(PO_3)_6$; (ii.) $M_4.M_2(PO_3)_6$ *e.g.* $Na_4.Na_2(PO_3)_6$, $Ag_4.Na_2(PO_3)_6$; (iii.) $M_5.M(PO_3)_6$ *e.g.* $Na_5.Na(PO_3)_6$, $(NH_4)_5.Na(PO_3)_6$. There are also, according to Tammann, three different Na metaphosphates insoluble in water (*v.* also T., *J. pr.* [2] 45, 417).

Tetra-* and *deka-phosphates. Salts of the compositions $Na_6P_4O_{13}$ and $Na_{12}P_{10}O_{31}$ are obtained by fusing together $Na_4P_2O_7$ and $Na_6(PO_3)_6$; these salts may be regarded as derived from the hypothetical condensed acids $H_6P_4O_{13}$ ($=3H_4P_2O_7-H_2O$), and $H_{12}P_{10}O_{31}$ ($=5H_4P_2O_7-4H_2O$), respectively.

The composition of all the phosphates may be represented empirically by the expression $nMO.mP_2O_5.xH_2O$, where MO stands for a basic oxide.

Occurrence.—Phosphates of Al and Ca occur in large quantitie[illegible] rocks; phosphates of Fe, Pb, Mg, NH_4, &c. are also widely distributed minerals. Coprolites (the fossilised excrements of former land-animals), and guano (the excrement of certain birds) consist very largely of Ca phosphate. Phosphates occur in some kinds of coal, in the ashes of plants, and in the bones of animals.

Formation.—Some of the *orthophosphates* are obtained by reacting on H_3PO_4Aq with metallic oxides or carbonates; others are formed by double decomposition from the alkali phosphates; when a metaphosphate is fused with a metallic oxide or hydroxide a normal orthophosphate is generally formed. Many *pyrophosphates* are obtained by double decomposition from $Na_4P_2O_7$, which is formed by strongly heating Na_2HPO_4; other pyrophosphates are found by neutralising $H_4P_2O_7Aq$ by basic oxides or hydroxides. *Metaphosphates* are generally formed by strongly heating orthophosphates MH_2PO_4 or $MRHPO_4$, when M or R is a metal whose oxide is volatile; many are produced by double decomposition from $NaPO_3$; some are formed by heating $Cu_2(PO_3)_4$ with a metallic sulphide and filtering from CuS.

The processes by which any one of the three classes of phosphates is formed from another is perhaps best understood by representing the phosphates thus:

meta	*pyro*	*ortho*
$P_2O_5.M_2O$	$P_2O_5.2M_2O$	$P_2O_5.3M_2O$

Metaphosphate becomes pyro- by gaining M_2O, and becomes ortho- by gaining $2M_2O$, and so on. Metaphosphate fused with metallic oxide, hydroxide, or carbonate yields pyrophosphate or orthophosphate, according to the quantities used; thus (1) $2NaPO_3+Na_2CO_3=Na_4P_2O_7+CO_2$; (2) $2NaPO_3+2Na_2CO_3=2Na_3PO_4+2CO_2$. The metaphosphate of a heavy metal yields an orthophosphate and H_3PO_4 by boiling with water; thus $3AgPO_3+3H_2O=Ag_3PO_4+2H_3PO_4$. The change from a pyro- to an ortho- phosphate is often effected by boiling with water, the product being an acid salt, thus $Na_4P_2O_7+H_2O=2Na_2HPO_4$; or the pyrophosphate is fused with hydroxide or carbonate, thus

$$Ba_2P_2O_7+BaO_2H_2=Ba_3(PO_4)_2+H_2O.$$

Acid orthophosphates with one atom of H yield pyro-phosphates when strongly heated, *e.g.* $2Na_2HPO_4-H_2O=Na_4P_2O_7$; and those with two atoms of H yield metaphosphates, *e.g.*

$$NaH_2PO_4-H_2O=NaPO_3.$$

Similarly a double orthophosphate of the form M_2RPO_4 yields a pyrophosphate on heating if R forms a volatile oxide, *e.g.* $2Na_2(NH_4)PO_4=Na_4P_2O_7+H_2O+2NH_3$. The removal of M_2O from a normal orthophosphate with formation of a metaphosphate is often effected by fusing with SiO_2 or B_2O_3 or other anhydride which forms a salt with M_2O, *e.g.* $Na_3PO_4+SiO_2=NaPO_3+Na_2SiO_3$.

The metaphosphates formed by the processes sketched above belong to several series of salts all of which have the empirical formula $nMPO_3$. According to Fleitmann a. Henneberg (*A.* 65, 304; F., *P.* 78, 233, 338), these salts belong to five series.

Monometaphosphates MPO_3. Not many of these have been obtained with certainty; they are produced by heating alkaline oxides with equivalent quantities of H_3PO_4 to redness until the residue ceases to give an acid reaction (the temperature not being high enough to melt the mass), and washing the residue with cold water; some of the salts—*e.g.* $NaPO_3$ and KPO_3—are formed by heating MH_2PO_4 or $M_2H_2P_2O_7$ to redness (*c.* 315°) till the residue is almost wholly insoluble in cold water (Maddrell, *C. S. Mem.* 3, 273).

Dimetaphosphates $M_2P_2O_6$. The salts of Cu, Zn, and Mn are prepared by heating equivalent quantities of MO and H_3PO_4 to redness. The Na and NH_4 salts are obtained by decomposing the Cu salt by Na_2SAq or NH_4 sulphide solution, filtering, and ppg. by alcohol. These salts yield others of the series by double decomposition. The salts of this series are soluble in water and crystallisable. Tammann (*Z. P. C.* 6, 122) thinks these salts are really trimetaphosphates (*v. Properties and Reactions*).

Trimetaphosphates $M_3P_3O_9$. The salts of this series are crystalline. The Na salt is prepared by slowly heating $NaNH_4HPO_4$ with frequent stirring, till the residue has a faintly acid reaction, treating with cold water, filtering, and allowing the filtrate to crystallise. The salt is also formed by heating $NaNH_4HPO_4$ till a glassy mass remains, and cooling very slowly. The other salts are obtained from the Na salt by double decomposition. Tammann (*l.c.*) regards these salts as dimetaphosphates (*v. Properties and Reactions*).

Tetrametaphosphates $M_4P_4O_{12}$. PbO is heated with H_3PO_4 to redness, as in making the Cu, Zn, and Mn dimetaphosphates (*v. supra*); the crystalline salt which is formed is insoluble in water, and much more easily decomposed by acids than the Pb salt got from $Na_2P_2O_6$. The Na salt is obtained by decomposing the Pb salt by Na_2SAq; and other salts are obtained from the Pb salt by double decomposition. Salts of Bi and Cd are obtained similarly to the Pb salt. These phosphates are uncrystallisable. Tammann (*J. pr.* [2] 45, 417) says that $CuNa_2P_4O_{12}$ is the only salt which certainly belongs to this series.

Hexametaphosphates $M_6P_6O_{18}$. $NaNH_4HPO_4$ is heated till a glassy mass remains, which is cooled rapidly (Graham, *T.* 1833. 253). The Na salt yields others by double decomposition. These salts are non-crystallisable, and dry to resinous-like masses. Tammann's experiments (*l.c.*) seem to show that $Na_6P_6O_{18}$ is a mixture of several isomeric salts (*v.* p. 118).

Tammann (*l.c.*) describes salts belonging to the series of *penta-*, *okto-*, *deka-*, and *tetrakaideka- metaphosphates.*

Tetraphosphates $M_6P_4O_{13}$. A few of these salts have been prepared, *e.g.* $Na_6P_4O_{13}$ by fusing $2NaPO_3 + Na_4P_2O_7$, and $Ba_3P_4O_{13}$ by fusing the Na salt with $BaCl_2$ (F. a. H., *A.* 65, 304; Uelsmann, *A.* 118, 99).

Dekaphosphates $M_{12}P_{10}O_{31}$. The Na salt was obtained by fusing $Na_4P_2O_7 + 8NaPO_3$ (F. a. H., *l.c.*); some other salts were obtained from the Na salt by double decomposition (U., *l.c.*).

Properties and Reactions.—The *orthophosphates* MH_2PO_4 dissolve in water, forming acid solutions; the dimetallic salts M_2HPO_4 dissolve in water when M is an alkali metal, the solutions are feebly alkaline. Of the normal salts M_3PO_4, only those of the alkali metals are soluble in water; the solutions have an alkaline reaction, and are decomposed very easily, even by CO_2, forming M_2HPO_4Aq. Most of the heavy metals form only M_3PO_4. Solutions of alkali orthophosphates give a yellow pp. (Ag_3PO_4) with $AgNO_3Aq$, and a yellow pp. on warming with NH_4 molybdate solution. The orthophosphates M_3PO_4 are not decomposed by heating strongly, unless they are salts of volatile bases; M_2HPO_4 give $M_4P_2O_7$ and H_2O, and MH_2PO_4 give MPO_3 and H_2O when strongly heated. M_3PO_4, M = alkali or alkaline earth metal, are not changed by heating with charcoal, but M_2HPO_4 and MH_2PO_4 give M_3PO_4 and P. When M is a heavy metal, the salts M_3PO_4 generally give metallic phosphides by heating with C. Orthophosphates heated with K or Na yield alkali phosphide. Many insoluble orthophosphates are decomposed by fusion with alkali carbonate, but those of the alkaline earths are only partially decomposed. H_2SO_4 decomposes all orthophosphates. When the salts M_3PO_4 are heated with SO_2Aq under pressure, M_2HPO_4 or MH_2PO_4 are formed (Pitter, *Chem. Indust.* 1878. 398; Gerland, *J. pr.* [2] 4, 97).

Of the *pyrophosphates*, the normal alkali salts are soluble in water, with feebly alkaline reactions; the others are generally insoluble but dissolve in $Na_4P_2O_7Aq$, forming double salts (H. Rose, *P.* 76; 13; Schwarzenberg, *A.* 65, 183; Persoz, *A.* 65, 163). Solution of pyrophosphates give orthophosphates when boiled with the stronger acids, or heated with water to 280° (Reynoso). $M_4P_2O_7$ are not changed by heat unless they are salts of bases decomposed by heat; $M_2H_2P_2O_7$ give MPO_3 and H_2O when strongly heated. All the pyrophosphates are changed to orthophosphates by heating strongly with sufficient alkali or alkali carbonate. Pyrophosphates of metals whose oxides are not reduced by H give orthophosphates and P_2O_5 when heated in H; those which contain metals whose oxides are reduced by H, but not by heat alone, give metallic phosphide when heated in H; and those containing metals the oxides of which are reduced by heat alone, yield metal, H_2O, H_3PO_4, &c., when heated in H (Struve, *J. pr.* 79, 345). Pyrophosphates in solution give a white pp. with $AgNO_3Aq$; they do not give an immediate pp. with warm NH_4 molybdate, and they do not coagulate albumen when acidified by acetic acid.

Some *metaphosphates* are soluble, others are insoluble, in water; some are crystalline, others are amorphous (*v. supra*: *Formation of different classes of metaphosphates*). Solutions of these salts in water are changed to orthophosphates on long-continued boiling; they give a white pp. with $AgNO_3Aq$, no immediate pp. with NH_4 molybdate, and they coagulate albumen after acidification by acetic acid.

Tammann (*Z. P. C.* 6, 123) has examined the electrical conductivities of solutions of Fleitmann's di- and tri- metaphosphates of Na; his results indicate that the ions of the salts in solution are Na_x and $(PO_3)_x$. He has also measured the depression produced in the freezing-point of water by dissolving these salts therein; and, taking the results along with the electrical conductivities, he concludes that Fleitmann's di-salts are tri- salts, and F.'s tri- salts are really di- salts. By the reaction of $AgNO_3Aq$ on the $Na_6P_6O_{18}$ of Graham and Fleitmann, Tammann obtained a crystalline salt $Ag_6P_6O_{18}$, and two salts $Ag_4Na_2P_6O_{18}$ and $Ag_5NaP_6O_{18}$, and from these he formed three Na salts which he formulates as $Na_6P_6O_{18}$, $Na_4.Na_2.P_6O_{18}$, and $Na_5.Na.P_6O_{18}$. Measurements of the electrical conductivities of these salts confirm the above formulæ, and they tend to show that the ions of the salts in solution are Na_4 and $Na_2P_6O_{18}$, and Na_5 and NaP_6O_{18} respectively. A fuller examination of Graham's salt led T. to conclude that it contains another isomeric hexametaphosphate $Na_2.Na_4.P_6O_{18}$.

For *detection and estimation* of phosphates a manual of analysis must be consulted.

ORTHOPHOSPHATES. *Salts derived from* H_3PO_4. (For *thioxyorthophosphates v.* PHOSPHORIC SULPHIDE, p. 147.)

Aluminium orthophosphates. Many occur in minerals, *e.g. angelite, fischerite, wavellite, turquois.* The pps. obtained by adding Na_2HPO_4Aq to alum solutions vary in composition. They may be represented as xAl_2O_3, yP_2O_5, x being chiefly 1, 2, 3, and y being 1 and 2 (Munroe, *A.* 159, 638; Wittstein, *J. B.* 27, 167; Fuchs, *S.* 24, 121; Millot, *C. R.* 82, 89).

The *normal salt*, $AlPO_4.xH_2O$, is obtained by gradually pouring neutral alum solution into excess of Na_2HPO_4Aq; a white loose powder; soluble mineral acids, soluble organic acids, soluble NH_4 citrate solution (Erlenmeyer, *B.* 14, 1869), soluble Al salt solution (Fleischer, *Fr.* 6, 28), soluble in potash; infusible at red heat, fused with Fe and SiO_2 gives Fe phosphide (Schlösing, *C. R.* 67, 1247); partially decomposed by fusing with K_2CO_3 (Rammelsberg, *P.* 64, 405; *cf.* Vauquelin, *A. Ch.* [2] 21, 138). When air-dried $x = 4$ to 5; dried over H_2SO_4, $x = 8$ (Rammelsberg, Millot, Wittstein). For other phosphates of Al *v.* Rammelsberg (*l.c.*), Schweitzer (*B.* 3, 310; 6, 28), Ludwig (*Ar. Ph.* [2] 59, 19), Hautefeuille a. Margottet (*C. R.* 106, 135), Erlenmeyer (*Z.* 3, 572).

Double salts with phosphates of Ca, Li, and Mg have been described (*v. Gm.-K.*, i. 2, 670).

Ammonium orthophosphates. The *normal salt*, $Am_3PO_4.3H_2O$, crystallises in short pyramids, obtained by treating Am_2HPO_4 with conc. NH_3Aq (Berzelius, *Gm.-K.* i. 2, 527). Loses two-thirds NH_3 by boiling water (Kraut, *C. C.* 1855. 894). Sestini (*B.* 11, 1927) obtained a salt with $5H_2O$. The *di-ammonium salt*, Am_2HPO_4, is formed in monoclinic prisms by allowing NH_3 or $(NH_4)_2CO_3$ in H_3PO_4Aq to evaporate; soluble four parts cold water, solution is alkaline; on boiling NH_3 is evolved; S.G. 1·62–1·67 (Rammelsberg, *B.* 3, 278; Schiff, *A.* 112, 88; Buignot, *J.* 1861. 15; Proust a. Brooke, *Gm.-K.* i. 2, 528). The *mon-ammonium salt*, AmH_2PO_4, crystallises in quadratic forms, isomorphous with KH_2PO_4, by adding NH_3Aq to H_3PO_4Aq till $BaCl_2Aq$ ceases to give a pp. S.G. 1·758 (Schiff, *l.c.*; Mitscherlich, *P.* 19, 385).

Barium orthophosphates. The *normal salt*, $Ba_3P_2O_8$, is a heavy white solid, obtained by ppg. $BaCl_2Aq$ by Na_3PO_4Aq (Graham; Rotondi, *B.* 15, 1441). Two *acid salts* have been obtained: (1) $BaHPO_4$, by boiling the normal salt with H_3PO_4Aq, or by ppg. $BaCl_2Aq$ by Na_2HPO_4Aq soluble in 10,000 to 20,000 parts water, easily soluble if NH_4 salts, $BaCl_2$, or NaCl is present; soluble in H_3PO_4Aq or dilute HNO_3Aq (Berzelius, Ludwig, Rose, Brett, Wittstein, Bischoff, Malaguti, *Gm.-K.* i. 2, 272; Skey, *C. N.* 22, 61; Erlenmeyer, *J.* 1857. 145; Setschenoff, *C. C.* 1875. 97; Gerland, *J. pr.* [2] 4, 125); (2) $BaH_4P_2O_8$, from a solution of $BaHPO_4$ in H_3PO_4; white triclinic crystals; decomposed by much water to H_3PO_4Aq and $BaHPO_4$ (Berzelius).

Double salts.—(1) $3Ba_3P_2O_8.BaCl_2$ (Rose, *P.* 8, 211; Ludwig, *Ar. Ph.* [2] 56, 265; Deville a. Caron, *A. Ch.* [3] 67, 451);
(2) $4BaHPO_4.BaCl_2$ (Erlenmeyer, *J.* 1857. 145);
(3) $BaNaPO_4.10H_2O$ (Rose, Guyton, Berzelius, *Gm.-K.* i. 2, 313; de Schulten, *Bl.* [2] 39, 500; Joly, *C. R.* 104, 1702); (4) $BaKPO_4.10H_2O$ (de S., *l.c.*).

Beryllium orthophosphates. The *normal salt*, $Be_3P_2O_8$, is a white pp., obtained by adding Na_2HPO_4Aq to solution of a salt of Be. An *acid salt* is obtained by dissolving the normal salt in H_3PO_4Aq (Vauquelin, *Gm.-K.* i. 2, 269).

Double salts. $Be.NH_4$ and Be.K phosphates are known (Rössler, *Fr.* 1878. 148; Ouvrard, *C. R.* 110, 1333).

Bismuth orthophosphate $BiPO_4$. White powder, obtained by adding $Bi_2O_3.xH_2O$ to H_3PO_4Aq; little known (Wenzel, *Gm.-K.* i. 2, 832; Chancel, *C. R.* 50, 416).

Cadmium orthophosphates. The *normal salt*, $Cd_3P_2O_8$, is obtained as an amorphous pp. by adding Na_3PO_4Aq to a Cd salt solution (de Schulten, *Bl.* [3] 1, 473).

Acid salts (de S., *l.c.*): (1) $Cd_5H_2P_4O_{16}.4H_2O$, by ppg. hot $CdCl_2Aq$ by Na_2HPO_4Aq.
(2) $CdH_4P_2O_8.2H_2O$, by dissolving the foregoing salt in cold dilute H_3PO_4Aq and allowing to evaporate at ordinary temperature.

Double salt $3Cd_3P_2O_8.CdCl_2$ (de S., *l.c.*).

Calcium orthophosphates. Ca phosphates are widely distributed minerals.

Normal salt $Ca_3P_2O_8$. Obtained, as a white amorphous powder, by adding NH_3Aq to solution of bone-ash in HClAq or HNO_3Aq; by adding Na_3PO_4Aq, or a mixture of Na_2HPO_4Aq and NH_3Aq, to $CaCl_2Aq$. For details of preparation from *phosphorite*, or bone-ash, &c. *v.* DICTIONARY OF APPLIED CHEMISTRY. The pp. from $CaCl_2Aq$ in presence of NH_3 contains $5H_2O$ according to Wittstein (*J.* 1866. 168; *v.* also Ludwig, *Ar. Ph.* [2] 69, 286). Slightly soluble in water; one litre cold water dissolved 79 mgm. freshly ppd., and 31 mgm. strongly heated, $Ca_3P_2O_8$ (Völcker, *J.* 1862. 131). Decomposed slowly by boiling water into $CaH_4P_2O_8$ and $2Ca_3P_2O_8.CaO_2H_2$ (Warington, *C. J.* [2] 11, 983). Solubility in water is increased by small quantities of alkali salts (*v.* Wöhler, *P.* 4, 166; Liebig, *A.* 61, 128; Lassaigne, *J.* 1847. 341; Thomson, *Ann. Philos.* 17, 12; Völcker, *J.* 1862. 131; Fresenius, *Fr.* 10, 133; Hünefeld, Delkeskampf, Morveau, *Gm.-K.* i. 2, 367; Terreil, *Bl.* [2] 35, 548; Erlenmeyer, *B.* 14, 1253). Presence of starch and various organic substances increases solubility in water (*v.* Wöhler, *A.* 98, 143; Hayes, *N. Ed. P. J.* 5, 378). Soluble in CO_2Aq; $CaCO_3$ and $CaHPO_4$ separate on standing (Liebig, *A.* 106, 196; Warington, *C. J.* [2] 4, 296; Dusart a. Pelouze, *C. R.* 66, 1327; von Georgievics, *M.* 12, 566).

Partially decomposed by boiling with NaOHAq, or by fusing with Na_2CO_3 (Wöhler, *A.* 51, 437; Rose, *P.* 95, 437; Fresenius, *Fr.* 10, 133). Easily changed to CaC_2O_4 by boiling with $(NH_4)_2C_2O_4Aq$ (Fresenius, *l.c.*).

Strongly heated with C and SiO_2, gives Ca silicate, P, and CO; heated in CO, all P is set free (Schlösing, *C. R.* 59, 384; Anderson, *B.* 5, 1065). Heated with Na, K, or Mg, metallic phosphide is formed (*v. Gm.-K.* i. 2, 366).

Dissolved by SO_2Aq; on standing, $CaHPO_4$ and $CaSO_3$ separate (*v.* Gerland, *C. N.* 20, 268; Aldred, *C. N.* 42, 177; Rotondi, *B.* 15, 1441). Dilute H_2SO_4Aq forms $CaHPO_4$, or $CaH_4P_2O_8$, or $CaSO_4$ and H_3PO_4, according to the quantities of H_2SO_4 and $Ca_3P_2O_8$, the temperature, and the time of action (*v. Gm.-K.* i. 2, 369; Kolb, *C. R.* 78, 825; Joulie, *C. R.* 76, 1288; Crum, *A.* 63, 394). For the (similar) reactions with HClAq and HNO_3Aq *v.* Crum, *l.c.*; Piccard (*J.* 1886. 468); Bischof (*S.* 67, 39); Birnbaum a. Packard (*Z.* [2] 7, 137); Tissier (*C. R.* 38, 192); Warington (*C. J.* [2] 4, 302).

Double salts. (1) $Ca_3P_2O_8.Ca_2SiO_4$ (Carnot a. Richard, *C. R.* 97, 316). (2) $3Ca_3P_2O_8.CaCl_2$ by fusing $Ca_3P_2O_8$ with NaCl, or heating to 250° with $CaCl_2Aq$, or passing PCl_3 vapour over glowing lime (Forchhammer, *P.* 91, 568; Debray, *A. Ch.* [3] 61, 424; Daubrée, *Ann. M.* (4) 19, 684; Deville a. Caron, *A. Ch.* [3] 67, 451). (3) $3Ca_3P_2O_8.CaF_2$; occurs native as *apatite* (with varying quantities of $CaCl_2$); obtained by fusing Na_2HPO_4, CaF_2, and $CaCl_2$ (D. a. C., *l.c.*; Briegler, *A.* 97, 95). (4) $Ca(NH_4)PO_4.xH_2O$ (Herzfeld a. Feuerlein, *Fr.* 1881. 191). (5) $CaKPO_4$ (Rose, *P.* 77, 291). (6) $CaLiPO_4$ (Rose, *P.* 77, 298). (7) $CaNaPO_4$ (Rose, *P.* 77, 291; Bunge, *A.* 172, 18).

Acid salts. I. *Dicalcium phosphate* $Ca_2H_2P_2O_8$. Obtained by adding Na_2HPO_4Aq, or $NaNH_4HPO_4Aq$, to excess of $CaCl_2Aq$; pp. contains a little $Ca_3P_2O_8$: also by the action of CO_2Aq on $CaCO_3$ and $(NH_4)_2HPO_4Aq$ (Becquerel, *C. R.* 34, 573); and by acting on powdered $CaCO_3$ with H_3PO_4Aq (Debray, *A. Ch.* [3] 61, 424); by passing CO_2 into H_2O, holding freshly ppd. $Ca_3P_2O_8$ in suspension (Percy, *P. M.* [3] 26, 194; Reichardt, *Ar. Ph.* [3] 2, 236). Obtained in crystals by allowing solutions of $(NH_4)_2HPO_4$ and $CaCl_2$ to mix slowly through a porous cell (Vohl, *A.* 88, 114), or through a layer of water (Drevermann, *A.* 87, 120); also by allowing a solution of amorphous $CaHPO_4$ in a weak acid to evaporate (Bödeker, *A.* 69, 206; Baer, *P.* 75, 152; Vorbringer, *Fr.* 9, 457; *v.* also Causse, *J. Ph.* [5] 21, 544). $CaHPO_4$ ppd. at low temperatures and dried quickly at 100° contains $2H_2O$, which is lost by long drying at 100° in a stream of dry air. Forms $Ca_2P_2O_7$ when strongly heated; decomposed to $Ca_3P_2O_8$ and $CaH_4P_2O_8$ by long boiling with water. For description of various hydrates $xCaHPO_4.yH_2O$ *v.* Vorbringer (*Fr.* 9, 457), Gerland (*J. pr.* [2] 4, 104), Millot (*Bl.* [2] 33, 194), Skey (*C. N.* 22, 61), Dusart a. Pelouze (*C. R.* 66, 1327), Davies (*C. N.* 64, 287). Soluble in boiling NH_4ClAq (Kraut, *Ar. Ph.* [2] 111, 102); soluble SO_2Aq (Gerland, *J. pr.* [2] 4, 123), in HClAq and HNO_3Aq (Berzelius, Baer, *Gm.-K.* i. 2, 372). Decomposed by boiling alkali carbonate solutions (Malaguti, *Gm.-K.* i. 2, 373).

II. *Monocalcium phosphate* $CaH_4P_2O_8.H_2O$. This salt is the chief constituent of artificial '*superphosphate of lime*' prepared by treating crushed bones, *phosphorite*, &c., with H_2SO_4 (*v.* DICTIONARY OF APPLIED CHEMISTRY). Prepared by dissolving $Ca_2H_2P_2O_8$ in 81 p.c. H_3PO_4Aq, crystallising, washing with absolute alcohol, then with ether, and drying (Stoklasa, *Listy Chem.*, 13, 203, 240, 273; abstract in *C. J.* 58, 695). This salt is also formed by evaporating $Ca_2H_2P_2O_8$ with $HNO_3Aq + H_2SO_4Aq$. Also by leaving a solution of the commercial honey-like monocalcium phosphate in contact with $Ca_3P_2O_8$ for some time, and evaporating the solution formed at a gentle heat; the salt is thus obtained in crystals (Pointet, *Bl.* [3] 5, 254). Not hygroscopic; the hygroscopic nature of the preparation made by Birnbaum and others is said by Stoklasa (*l.c.*) to be due to traces of H_3PO_4. Thin rhombic plates (*v.* Haushofer, *Z. K.* 7, 263); S.G. 2·02 (Schröder, *B.* 11, 126). Loses H_2O at 100°, decomposes at 200° to mixture of CaP_2O_6 and $Ca_2P_2O_7$ (Birnbaum, *B.* 6, 898). Decomposed by H_2O. Stoklasa (*l.c.*) represents the decomposing action of water as

$$xCaH_4P_2O_8.H_2O + H_2O$$
$$= (x-1)CaH_4P_2O_8.H_2O + CaHPO_4 + 2H_2O + H_3PO_4;$$

the greater the quantity of water the more salt is dissolved without decomposition; with 200 parts H_2O to 1 part salt a clear solution is formed without any free H_3PO_4; above this limit $CaH_4P_2O_8$ is re-formed from the products of its decomposition (for older observations *v.* Birnbaum, *l.c.*; Erlenmeyer, *N. J. P.* 7, 225; Warington, *Fr.* 1880. 243). According to Reynoso (*C. R.* 34, 795), water at 280° decomposes the salt, forming H_3PO_4 and crystalline $Ca_3P_2O_8$. Various salts produce $Ca_2H_2P_2O_8$ from solutions of $CaH_4P_2O_8$ (*v.* Debray, *A. Ch.* [3] 61, 424; Dusart a. Pelouze, *C. R.* 66, 1327; Vorbringer, *Fr.* 9, 457; Erlenmeyer, *l.c.*; Birnbaum, *l.c.*).

Cerium orthophosphate $CePO_4$. By fusing Ce_2O_3 with KPO_3; also by digesting $Ce_2K_3(PO_4)_3$ with KClAq. Monoclinic prisms; S.G. 3·8 (Ouvrard, *C. R.* 107, 37). The *double salt* $Ce_2K_3(PO_4)_3$ is formed by fusing K_3PO_4 or $K_4P_2O_7$ with Ce_2O_3.

Chromium orthophosphates. The *normal chromic salt*, $Cr_2P_2O_8$, is known in two forms, green and violet. *Violet form*, $Cr_2P_2O_8.12H_2O$, a violet crystalline pp. by adding Na_2HPO_4Aq to excess of Cr alum solution; loses $7H_2O$ at 100°, becoming green; changed to green by conc. HNO_3Aq, H_2SO_4, or PCl_3 (Rammelsberg, *P.* 68, 383; Etard, *C. R.* 84, 1091). *Green form*, $Cr_2P_2O_8.6H_2O$, by adding excess of Na_2HPO_4Aq to Cr alum; also by ppg. a slightly acid solution of a Cr salt by Na_2HPO_4 and Na acetate (Rose, *P.* 77, 291, 298; Carnot, *Bl.* [2] 37, 482; Vauquelin, *Gm.-K.* i. 2, 304). Soluble mineral acids, also KOHAq (*v.* Dowling a. Plunkett, *Chem. Gazette*, 1858. 220; Kämmerer, *Fr.* 12, 375). Gives alkali chromates by fusion with alkali sulphates (Grandeau, *C. R.* 95, 921). Forms a *double salt* with Ca (Dingler, *D. P. J.* 212, 532; Plessy, *Rép. Chim. app.* 1862. 453; Köthe, *D. P. J.* 214, 59). The *acid salt* $CrH_4P_2O_8.8H_2O$ is probably formed by dissolving $Cr_2O_3.xH_2O$ in H_3PO_4Aq (Vauquelin, *Gm.-K.* i. 2, 304; Haushofer, *Z. K.* 7, 263).

Chromous orthophosphate $Cr_3P_2O_8.H_2O$, a blue pp. by adding Na_2HPO_4Aq to $CrCl_2Aq$;

quickly becomes green in air (Moissan, *A. Ch.* [5] 25, 401).

Cobalt orthophosphates. The *normal salt* $Co_3P_2O_8.xH_2O$ is formed by heating $CoHPO_4.3H_2O$ with water, or with $Co(NO_3)_2Aq$, to 250° in a sealed tube (Debray, *A. Ch.* [3] 61, 438); also by treating $Co(NH_4)PO_4.6H_2O$ with boiling water (Chancel, *Précis d'analyse* [Paris, 1862] 1, 263). In this salt $x = 2$. A salt with $x = 8$ is said to be formed by ppg. $CoH_4P_2O_8Aq$ by alcohol (Reynoso, *C. R.* 34, 795; Reitler, *Vierteljahr. Pharm.* 7, 246). Two *acid salts* are known: (1) $CoHPO_4.3H_2O$, by boiling $CoCO_3$ with H_3PO_4Aq, or boiling solution of a Co salt with $CaH_4P_2O_8$ (Debray, *J. Ph.* [3] 46, 121); a salt with $5H_2O$ was obtained by Bödeker (*A.* 94, 357). (2) $CoH_4P_2O_8$, by heating Co pyrophosphate with water to 280° (Reynoso, *C. R.* 34, 795). *Double salts*: NH_4 salts *v.* Dirvell, *C. R.* 89, 903; Popp, *Z.* [2] 6, 305. For luteo- and roseo- cobaltamine phosphates *v.* Gibbs a. Genth, *Am. S.* [2] 21, 86; 23, 234, 319; Braun, *Gm.-K.* i. 3, 463; Porumbaru, *C. R.* 93, 342. For K and Na double salts *v.* Ouvrard, *C. R.* 106, 1729.

Copper orthophosphates. *Normal salt* $Cu_3P_2O_8.3H_2O$, obtained by adding a little Na_2HPO_4Aq to excess of a Cu salt solution (Mitscherlich, *Gm.-K.* i. 3, 614); also by heating $CuCO_3$ with H_3PO_4Aq to 70° (Debray, *A. Ch.* [3] 61, 437). A blue-green powder; decomposed by hot water under pressure (Debray; *v.* also Reynoso, *C. R.* 34, 1795; Jörgensen, *Gm.-K.* i. 3, 615). *Basic salts* and *acid salts* are known; composition doubtful (*v.* Rammelsberg, *P.* 68, 383; Metzner, *A.* 149, 67). For *double salts* with NH_4 *v.* Metzner, *l.c.*, and Schiff, *A.* 123, 41; with Na, *v.* Weineck, *A.* 156, 57; with K, also with Na, *v.* Ouvrard, *C. R.* 111, 177. For an account of the salts produced by the reaction of Na_2HPO_4Aq with $CuSO_4Aq$ and $Cu(NO_3)_2Aq$ *v.* Steinschneider, *C. C.* 1891, ii. 51 (abstract in *C. J.* 60, 1423).

Didymium orthophosphate $DiPO_4$: also double salts with alkali metals (Ouvrard, *C. R.* 107, 37).

Iron orthophosphates. Ferrous salts. The *normal salt* $Fe_3P_2O_8.8H_2O$ occurs native as *vivianite*; it is obtained by ppg. $FeSO_4Aq$ with excess of Na_2HPO_4Aq, and digesting at 60°-80° for eight days. Small monoclinic crystals (Rammelsberg, *P.* 64, 251, 405), nearly colourless but becoming blue in air (Debray, *C. R.* 59, 40). A salt with one H_2O is obtained by heating $Fe_2H_2P_2O_8.4H_2O$ with water at 250° (Debray, *A. Ch.* [3] 61, 437). Various *acid salts* are obtained by dissolving Fe in H_3PO_4Aq; if the materials are air-free, and evaporation is effected in CO_2, the salt $Fe_2H_2P_2O_8.4H_2O$ is formed (Erlenmeyer, Debray, Rammelsberg, *l.c.*). For *double salts* with NH_4, *v.* Otto, *J. pr.* 2, 409; and Debray, *C. R.* 59, 40.

Ferric salts. The *normal salt* $FePO_4$ is obtained by ppg. $FeCl_3Aq$ by Na_2HPO_4Aq; dried at 50° contains $8H_2O$, at 100° contains $4H_2O$, dehydrated by heating strongly; also formed by oxidation in air of $Fe_3P_2O_8$ (Debray, Rammelsberg, Wittstein, *l.c.*). Whether the salt ppd. from $FeCl_3Aq$ in presence of acetic acid is the normal or a basic salt is undecided (*v.* Winkler, *J. prakt. Pharm.* 5, 337; Heydenrich, *C. N.* 4, 158; Struve, *N. Peters. Acad. Bull.* 1, 465; Wackenroder a. Ludwig, *Ar. Ph.* [2] 53, 1; Mohr *Fr.* 2, 520). $FePO_4.xH_2O$ is sol. c. 1500 parts boiling water; but is decomposed (Lachowicz, *M.* 13, 357). *Acid salts* are obtained by dissolving $Fe_2O_3.xH_2O$ in H_3PO_4Aq: Erlenmeyer got $FeH_6P_3O_{12}$ by evaporating quickly (*v.* also Waine, *C. N.* 36, 132; Wagner, *Chem. Zeitung*, 1881. 247). Hautefeuille a. Margottet (*C. R.* 106, 1357) obtained various ferric phosphates by dissolving $Fe_2O_3.xH_2O$ in glacial phosphoric acid.

Lanthanum orthophosphate $LaPO_4$: also double salts with K and Na (*v.* Ouvrard, *C. R.* 107, 37).

Lead orthophosphates. The *normal salt*, $Pb_3P_2O_8$, is ppd. as a white powder by adding Na_2HPO_4Aq to Pb acetate solution (Berzelius; Mitscherlich, *Gm.* 3; *v.* also Heintz, *P.* 73, 119; Gerhardt, *A. Ch.* [3] 22, 505; Haushofer, *Z. K.* 7, 264). A *double salt* with $PbCl_2$ is obtained by action of Na_2HPO_4Aq on $PbCl_2$ (Debray, *A. Ch.* [3] 61, 419; Manross, *A.* 82, 348; Deville a. Caron, *A. Ch.* [3] 67, 451). By ppg. boiling $Pb2NO_3Aq$ by H_3PO_4Aq, Heintz (*P.* 73, 119) obtained the *acid salt* $Pb_2H_2P_2O_8$.

Lithium orthophosphates. The *normal salt*, $Li_3PO_4.H_2O(?2Li_3PO_4.H_2O)$. By heating Na_2HPO_4Aq with solution of a salt of Li (Mayer, *A.* 98, 183; *v.* also Berzelius, *P.* 4, 245; Rammelsberg, *C. N.* 38, 240, also *B.* 15, 283; Fresenius, *Fr.* 1, 42; Kraut, *A.* 182, 165). Loses H_2O at 100°. Obtained in rhomboidal tables, S.G. 2·41 at 15°, by dissolving in fused LiCl (de Schulten, *Bl.* [3] 1, 479). Soluble in c. 2,540 parts water. *Acid salts*: LiH_2PO_4 and $LiH_5P_2O_8.H_2O$, by dissolving normal salt in H_3PO_4Aq (Rammelsberg, *l.c.*).

Magnesium orthophosphates. The *normal salt*, $Mg_3P_2O_8.xH_2O$, is obtained with $4H_2O$ by ppg. Mg salts by alkali phosphate and drying at 100° (Graham; Rose, *P.* 76, 84; Gregory, *A.* 54, 98; Stein a. Tollens, *A.* 187, 79; Fresenius). Forms monoclinic crystals (Haushofer, *Z. K.* 6, 137). Very slightly soluble water (Völker, *J.* 1862. 131). For solubility in salt solutions *v.* Liebig (*A.* 106, 185), and in citric acid *v.* Erlenmeyer (*B.* 14, 1253). Soluble SO_2Aq (Gerland, *J. pr.* [2] 4, 126; Rotondi, *B.* 15, 141). Crystals with $6H_2O$ separate from $MgSO_4Aq + Na_2HPO_4Aq$ at 36° and upwards; and at lower temperatures a salt with $14H_2O$ is obtained (*v.* Percy, *P. M.* [3] 26, 194; Reischauer, *N. R. P.* 12, 43; 14, 57).

Acid salts. 1. $MgHPO_4.xH_2O$ ($x = 6,7,8,9$); by dissolving *magnesia alba* in H_3PO_4Aq (Bergmann, Fourcroy, *Gm.-K.* i. 2, 446; Debray, *J. pr.* 97, 116; Haushofer, *Z. K.* 7, 257).—2. $MgH_4P_2O_8$; by boiling the foregoing acid salt with water (Schaffner; Rotondi, *B.* 15, 141).

Double salts. Magnesium-ammonium orthophosphate $MgNH_4PO_4.6H_2O$. By adding Na_2HPO_4Aq to a Mg salt to which NH_4ClAq and excess of NH_3Aq have been added; or by adding a mixture of H_3PO_4Aq and excess of NH_3Aq to a Mg salt. For experiments on different conditions of formation *v.* Graham (*A.* 29, 25); Riffault (*A. Ch.* [2] 19, 90); Mohr (*Fr.* 12, 36); Gibbs (*C. N.* 28, 51); Lesieur (*C. R.* 59, 191); Stein a. Tollens (*Gm.-K.* 1, 2, 476); Kubel (*Fr.* 8, 125); Kissel (*Fr.* 8, 164); Brunner (*Fr.* 11, 30); Berzelius (*P.* 4, 275); Heintz (*Fr.* 9, 16). Obtained in large crystals by separating the reacting liquids by a membrane (Vohl, *A.* 88, 114; Nonier, *C. R.* 78, 800; Millot, *Bl.* [2] 18, 20; Millot a. Maquenne, *Bl.* [2] 23, 238). Loses NH_3 in air; strongly heated gives $Mg_2P_2O_7$. For solubility in various solutions *v.* Fresenius (*A.* 55, 109); Ebermayer (*J. pr.* 60, 41); Liebig (*A.* 106, 196); Völcker (*J.* 1862. 131); Kissel (*Fr.* 8, 173); Gerland (*J. pr.* [2] 4, 127); Millot (*Bl.* [2] 18, 20); Ville (*C. R.* 75, 344). Another Mg-NH_4 phosphate is described by Gawalovski (*C. C.* 1885. 721). For other double salts: with $MgCl_2$, *v.* Deville a. Caron (*A. Ch.* [3] 67, 456); with $MgCl_2$ and MgF_2, *v.* Bischof (*D. P. J.* 237, 51, 136); with $MgCl_2$ and CaF_2, *v.* D. a. C. (*l.c.*); with K, *v.* Haushofer (*Z. K.* 7, 257), Ouvrard (*C. R.* 106, 1729); with Na, *v.* Rose, Berzelius, &c. (*Gm.-K.* i. 2, 476), Ouvrard (*l.c.*).

Manganese orthophosphates. *Normal manganic orthophosphate*, $MnPO_4.H_2O$, a greenish grey pp. by adding conc. $Mn(NO_3)_2Aq$ to H_3PO_4 and a little boiling water (Christensen, *J. pr.* [2] 28, 1). For properties of products of reaction of H_3PO_4 on manganates and permanganates *v.* Laspeyeres (*J. pr.* [2] 15, 320); Hermann (*P.* 74, 303); Rose (*P.* 105, 289); Barreswill (*C. R.* 44, 677); Hoppe-Seyler (*J. pr.* 90, 303).

Normal manganous orthophosphate, $Mn_3P_2O_8.xH_2O$. Obtained with $14H_2O$ by ppg. $MnSO_4Aq$ by Na_2HPO_4Aq; loses $7H_2O$ over H_2SO_4, and one more H_2O at 100° (Erlenmeyer, *A.* 190, 208). Salts with 9 to 11 H_2O, $7H_2O$, and $3H_2O$ are obtained by decomposing $MnHPO_4.xH_2O$ by water, and drying under different conditions (E., *l.c.*). The salt without H_2O is formed by strongly heating the hydrates, also by heating $Mn_2P_2O_7$ in H (Struve, *J.* 1860. 73). A white amorphous pp., soluble mineral acids and acetic acid, and various salt solutions (*v.* Berzelius, *Gm.-K.* i. 2, 472; Heintz, *P.* 74, 449; Joulin, *A. Ch.* [4] 30, 272; Gerland, *J. pr.* [2] 4, 97; Wittstein, *Gm.-K.* 2, 472; Braun, *Fr.* 7, 340; Erlenmeyer, *B.* 14, 1253).

Various *acid salts* have been described:—1. $MnHPO_4.3H_2O$ (Bödeker, *A.* 69, 206; Heintz, *P.* 74, 449; Erlenmeyer, *A.* 190, 208).—2. $MnH_4P_2O_8.2H_2O$ (Heintz, Erlenmeyer, *l.c.*).—3. $Mn_3P_2O_8.MnHPO_4.xH_2O$ (Erlenmeyer, *l.c.*; Haushofer, *Z. K.* 7, 257). *Double salts*: with $MnCl_2$ (Deville a. Caron, *A. Ch.* [3] 67, 459); with $Fe_3P_2O_8$ and $MnCl_2$, and with $Fe_3P_2O_8$ and MnF_2 (D. a. C., *l.c.*); with NH_4 (Otto, *S.* 66, 288; Heintz, *l.c.*); with K and with Na (Ouvrard, *C. R.* 106, 1729).

Mercury orthophosphates. *Normal mercurous orthophosphate*, Hg_3PO_4, by ppg. excess of Na_2HPO_4Aq by $HgNO_3Aq$ (Gerhardt, *J.* 1849. 283). Brooks (*P.* 66, 63) describes a *basic salt*. A *double salt* with $HgNO_3$ is described by Gerhardt (*l.c.*; *v.* also *Gm.-K.* 3, 918). *Normal mercuric orthophosphate*, $Hg_3P_2O_8$, is obtained by heating Hg_3PO_4 to low redness, also by adding strongly acidified $Hg(NO_3)_2Aq$ to Na_2HPO_4Aq (*v. Gm.-K.* 3, 754, 918; also Haack, *C. C.* 1890. [2] 736). For a *double salt* $Hg.NH_2Hg_2O.PO_4$ *v.* Hirzel (*Gm.-K.* 3, 820).

Nickel orthophosphates. The *normal salt* $Ni_3P_2O_8.7H_2O$ is obtained as a green flocculent pp. by adding Na_2HPO_4Aq to a Ni salt; heated strongly loses $7H_2O$ (Rammelsberg, *P.* 68, 383; Struve, *Gm.-K.* 3, 543). *Double salts*: with NH_4 (Debray, *C. R.* 59, 40); with Mg (Rose, *Gm.-K.* 3, 568); with Na and with K (Debray, *l.c.*; Ouvrard, *C. R.* 106, 1729).

Potassium orthophosphates. *Normal salt* K_3PO_4. A white solid, obtained by adding excess of K_2CO_3 to H_3PO_4Aq, and evaporating; slightly soluble cold water, more soluble hot water. *Acid salts*: 1. K_2HPO_4 (Graham, Funke, *Gm.-K.* 2, 30). 2. KH_2PO_4; by dissolving K_2CO_3 in so much H_3PO_4Aq that blue litmus paper is turned red but goes blue again on drying. Colourless tetragonal crystals; very soluble water; at red heat gives KPO_3; S.G. 2·29 to 2·4 (*v. Gm.-K.* 2, 30; also Senarmont, *A. Ch.* [3] 33, 391; Schiff, *A.* 112, 88; Buignet, *J.* 1861. 15).

Silver orthophosphates. *Normal salt* Ag_3PO_4, a yellow solid, obtained by adding an alkali phosphate to $AgNO_3Aq$ (Wetzlar, *Gm.-K.* 3, 918; Skey, *C. N.* 22, 61; Lassaigne, *J. Ph.* [3] 16, 289; Joly, *C. R.* 103, 1071). The *acid salt* Ag_2HPO_4 forms, in white hexagonal crystals, from a solution of the normal salt in H_3PO_4Aq (Berzelius, *P.* 2, 163; Hurtzig a. Geuther, *A.* 111, 160; Schwarzenberg, *A.* 65, 162; Joly, *C. R.* 103, 1071).

Sodium orthophosphates. The *normal salt*, $Na_3PO_4.12H_2O$, is obtained by adding excess of NaOHAq to Na_2HPO_4Aq and evaporating. Six-sided pyramids; melt at 77°; S.G. 1·618 (Schiff, *A.* 112, 18); soluble in 2 pts. water at 15°; solution absorbs CO_2 from air, giving Na_2HPO_4Aq. The anhydrous salt, Na_3PO_4, is obtained by heating the salt with $12H_2O$, or by heating $Na_2HPO_4.12H_2O$ with NaOH in equal molecular proportions (Graham, Mitscherlich, *Gm.-K.* 2, 163). S.G. 2·511 at 12°, 2·536 at 17·5° (Clarke's *Table of Specific Gravities*). For experiments on diffusion of the different Na orthophosphates *v.* van Bemmelen, *B.* 11, 1675; Hinteregger, *B.* 11, 1619; Tobias, *B.* 15, 2452.

Disodium hydrogen orthophosphate $Na_2HPO_4.12H_2O$. (*Ordinary sodium phosphate.*) Occurs in urine of carnivorous animals. Prepared by adding a slight excess of Na_2CO_3 to H_3PO_4Aq, and crystallising. (For preparation from bone-ash &c. *v.* DICTIONARY OF APPLIED CHEMISTRY.)

Colourless, rhombic, prisms; for measurements *v.* Senarmont, *A. Ch.* [3] 33, 391. S.G. 1·5235 at 16° (*v. Gm.-K.* 2, 165); melts at 35° (Kopp, *A.* 93, 129; *v.* also *Gm.-K.* 2, 165); effloresces in air, losing $5H_2O$.

Solubility in water (Mulder, *Gm.-K.* 2, 165).
100 pts. water dissolve Na_2HPO_4,

at 0°	2·5 pts.
5	2·8
10	3·9
15	5·8
20	9·3
25	15·4
30	24·1
35	39·3
40	63·9
45	74·8
50	82·5
at 55°	87·7 pts.
60	91·6
65	93·8
70	95·0
75	95·8
80	96·6
85	97·2
90	97·8
95	98·4
99	98·8
100	99·4

Saturated Na_2HPO_4Aq boils at 105°, and freezes at −·45° (Rüdorff). S.G. of Na_2HPO_4Aq at 19° (Schiff, *A.* 110, 70); 2 p.c. = 1·0083, 4 p.c. = 1·0166, 6 p.c. = 1·025, 8 p.c. = 1·0332, 10 p.c. = 1·0418, 12 p.c. = 1·0503 (p.c. of $Na_2HPO_4.12H_2O$). S.G. solution saturated at 15° = 1·0469, at 16° = 1·0511

(Michel **a. Kraft, Stolba,** *Gm.-K.* 2, 166). **Loses** $12H_2O$ ***in vacuo*** **over** H_2SO_4, **or by heating to** 100°; **a** salt with $7H_2O$ crystallises from Na_2HPO_4Aq at 33° (Blücher, Mulder, Clark, *Gm.-K.* 2, 166). For vapour-pressure of water-gas when the salt is warmed *v.* Debray (*C. R.* 66, 195), Horstmann (*A. Suppl.* 8, 125), Pfaundler (*B.* 4, 773). For change of volume on melting *v.* Wiedemann (*W.* 17, 561).

Absorbs HCl, probably forming NaH_2PO_4 and NaCl (Thomas, *C. J.* 33, 27). Na_2HPO_4Aq absorbs CO_2 (Pagenstecher, *J. B.* 21, 124; Liebig, *A.* 64, 349; 79, 112; Heidenhain a. L. Meyer, *A. Suppl.* 2, 157; Marchand, *J. pr.* 37, 321). The solution decomposes NH_4Cl (Rose, *Gm.-K.* 2, 166); boiled with S forms Na_3PO_4Aq with $Na_2S_2O_3$Aq and Na polysulphides (Filhol a. Senderens, *C. R.* 94, 649; 95, 343; 96, 1057). For remarks on character of reactions of Na_2HPO_4Aq with solutions of metallic salts *v.* Joly, *C. R.* 103, 1129.

Trisodium diphosphate $Na_3H_3P_2O_8.xH_2O$; by exactly neutralising H_3PO_4Aq by NaOHAq, and evaporating *in vacuo* (Filhol a. Senderens, *l.c.*).

Sodium dihydrogen phosphate $NaH_2PO_4.H_2O$; by adding H_3PO_4 to solution of $Na_3H_3P_2O_8$ till $BaCl_2$Aq is no longer ppd. (Mitscherlich, Berzelius, *Gm.-K.* 2, 167). A salt with $4H_2O$ was obtained by Joly a. Duffet (*C. R.* 102, 1391) by cooling a very conc. solution.

Double salts. 1. *Sodium ammonium hydrogen orthophosphate* $Na(NH_4)HPO_4.4H_2O$ (*Microcosmic salt*). Occurs in guano. Obtained by dissolving 5 pts. $Na_2HPO_4.12H_2O$ and 2 pts. $(NH_4)_2HPO_4$ in water, adding a little NH_3Aq, and allowing to crystallise in the cold (Berzelius). Large, clear, monoclinic crystals; S.G. 1·554 (Schiff); very soluble water, solution loses NH_3. The solid effloresces in air, losing all NH_3 and $4H_2O$, and leaving NaH_2PO_4; when strongly heated leaves $Na_6(PO_3)_6$. For double salts formed by fusing with metallic oxides *v.* Wallroth, *B.* 16, 3059.—2. $NaKHPO_4.7H_2O$ (Mitscherlich, Liebig, Schiff, *Gm.-K.* 2, 167). – **3.** $Na(NH_4)_2PO_4.4H_2O$ (*v. Gm.-K.* 2, 220). – **4.** $Na_2(NH_4)PO_4.12H_2O$ *(Herzfeld a. Feuerlein, Fr. 1881. 191). — 5.* $Na_4K_3H_5(PO_4)_4.22H_2O$, and $Na_3(NH_4)_3H_6(PO_4)_4.3H_2O$ (Filhol a. Senderens, *C. R.* 94, 649; 95, 343; 96, 1057).— 6. $2Na_3PO_4.NaF.xH_2O$; $x=19$ and 22 (Baumgarten, *J.* 1865. 219; Thorpe, *C. J.* [2] 10, 660).

Strontium orthophosphates. *Normal salt* $Sr_3P_2O_8$, is ppd. by adding Na_3PO_4Aq or Na_2HPO_4Aq + NH_3Aq to excess of $SrCl_2$Aq; also by adding cold ammoniacal solution of 90 pts. $Na_2HPO_4.12H_2O$ to 100 pts. $SrCl_2$ in Aq (Barthe, *C. R.* 114, 1267). By pouring $SrCl_2$Aq into Na_3PO_4Aq at c. 10° gelatinous $Sr_3P_2O_8$ is formed, but rapidly changes to crystalline $SrNaPO_4.9H_2O$ (Joly, *C. R.* 104, 1702.)—*Acid salt* $SrHPO_4$; by adding Na_2HPO_4Aq to $SrCl_2$Aq (Skey, *C. N.* 22, 61; Berzelius, Brett, Wittstein, *Gm.-K.* 2, 324; Malaguti, *A. Ch.* [3] 51, 346; Barthe, *l.c.*). Barthe (*l.c.*) describes another *acid salt*, $SrH_4P_2O_8.2H_2O$.

Double salts. 1. $3Sr_3P_2O_8.SrCl_2$ (Deville a. Caron, *A. Ch.* [3] 67, 452).—2. $SrKPO_4$ (Rose, Weber, *Gm.-K.* 2, 324).—3. $SrNaPO_4.9H_2O$ (R. W., *l.c.*; Joly, *C. R.* 104, 905, 1702).

Thallium orthophosphates. *Normal thallous orthophosphate* Tl_3PO_4; by adding H_3PO_4Aq and NH_3Aq to $TlNO_3$Aq, or mixing Tl_2SO_4Aq and Na_2HPO_4Aq with a little NH_3Aq (Crookes, *C. N.* 3, 193, 303; 7, 290; 8, 159; Lamy, *Bl.* [2] 4, 193). While silky mass, or needles; insoluble alcohol, easily soluble NH_4 salts (Carstanjen, *J. pr.* 102, 65, 129). *Acid salts.*—TlH_2PO_4 and $Tl_2HPO_4.xH_2O$ (Lamy, *l.c.*); according to Rammelsberg (*B.* 15, 283) the second of these does not exist. *Normal thallic orthophosphate* $TlPO_4.2H_2O$, by adding H_3PO_4Aq to $Tl(NO_3)_3$Aq (Willm, *Bl.* [2] 2, 89; 5, 354; Strecker, *J. pr.* 102, 65, 129).

Thorium orthophosphates. Various *double salts* of Th and K, and Th and Na, are described by Troost and Ouvrard (*C. R.* 102, 1422; 105, 30).

Tin orthophosphates. The compositions of the *stannous salt*, obtained by adding Na_2HPO_4Aq to $SnCl_2$ in dilute acetic acid, and the *stannic salt*, by digesting SnO_2 with H_3PO_4Aq, are somewhat doubtful (*v.* Lenssen, *A.* 114, 113; Reynoso, *J. pr.* 54, 261; Reissig, *A.* 98, 339; Girard, *C. R.* 54, 468). Ouvrard (*C. R.* 111, 177) describes various double Sn-K and Sn-Na phosphates.

Titanium orthophosphates. Various *double salts* of Ti and K, and Ti and Na, are described by Ouvrard (*C. R.* 111, 177).

Uranium orthophosphates. For *double* U-K and U-Na *salts*, *v.* Ouvrard (*C. R.* 110, 1333). Johnson (*B.* 22, 976) describes a salt $UO_3.2P_2O_5$.

Zinc orthophosphates. *Normal salt* $Zn_3P_2O_8.4H_2O$; by ppg. solution of a Zn salt by Na_2HPO_4Aq; pp. is gelatinous, but becomes crystalline. Insoluble water, easily soluble in acids, NH_3Aq, and NH_4 salts (*v.* Mitscherlich, *Gm.-K.* 3, 16; Schindler, *Mag. Pharm.* 26, 62; Debray, *Bl.* [2] 2, 14; Heintz, *A.* 143, 356; Graham, *A.* 29, 23). The *acid salt* $ZnH_4P_2O_8.2H_2O$ is obtained in large, triclinic crystals by dissolving ZnO in H_3PO_4Aq (Demel, *B.* 11, 1171).

Double salts. 1. With NH_4, *v.* Debray (*C. R.* 59, 40), Bette (*A.* 15, 129), Heintz (*A.* 143, 156), Schweikert (*A.* 145, 57), Rother (*A.* 143, 356).—2. *With Na, v. Scheffer (A. 145, 53), Ouvrard (C. R. 106, 1729).*—3. With K, *v.* Ouvrard (*l.c.*).

Zirconium orthophosphates. For *double salts* with K and Na, *v.* Ouvrard, *C. R.* 102, 1422; 105, 30.

PYROPHOSPHATES. *Salts derived from* $H_4P_2O_7$. (For *Thiopyrophosphates v.* PHOSPHORIC SULPHIDE, *Reactions*, No. 7, p. 147; and for *Selenopyrophosphates*, *v.* PHOSPHORIC SELENIDE, p. 145.)

Aluminium pyrophosphate $Al_4(P_2O_7)_3$. White amorphous pp. by adding $AlCl_3$Aq to $Na_4P_2O_7$Aq; soluble NH_3Aq, $Na_4P_2O_7$Aq, and mineral acids (Schwarzenberg, *A.* 65, 147; Rose, *A.* 76, 16; Wittstein, *Repert.* 63, 224). Forms a *double salt* with Na (Persoz, *A.* 65, 170; Pahl, *Bl.* [2] 22, 122).

Ammonium pyrophosphates. *Normal salt* $(NH_4)_4P_2O_7$; by adding excess NH_3Aq to $H_4P_2O_7$Aq and recrystallising from alcohol. Solution boiled gives the *acid salt* $(NH_4)_2H_2P_2O_7$ (Schwarzenberg, *A.* 65, 141).

Barium pyrophosphate $Ba_2P_2O_7.xH_2O$. White amorphous solid; by adding $Na_4P_2O_7$Aq to $BaCl_2$Aq, or $H_4P_2O_7$Aq to BaOAq. Heated in

steam gives off PH_3; gives orthophosphate by heating with alkali carbonates (Hesse, *P.* 80, 71; Schwarzenberg, *l.c.*; Birnbaum, *Z.* [2] 7, 139; Struve, *J. pr.* 79, 348; Rose, *P.* 76, 20). Forms a *double salt* with Na (Baer, *P.* 75, 166).

Bismuth pyrophosphate $Bi_4(P_2O_7)_3$ (Chancel, *C. R.* 50, 416).

Cadmium pyrophosphate $Cd_2P_2O_7.2H_2O$ (at 100°) (Schwarzenberg, *A.* 65, 153).

Calcium pyrophosphates *Normal salt* $Ca_2P_2O_7.4H_2O$, by adding $Na_4P_2O_7Aq$ to $CaCl_2Aq$, or CaOAq to $H_4P_2O_7Aq$; sol. in much $Na_4P_2O_7Aq$. Amorphous, but crystallises from solution in acetic acid or SO_2Aq (Schwarzenberg, *A.* 65, 145; Rose, *P.* 76, 16, 20, 230). For action of heat, *v.* Baer (*P.* 75, 155). Decomposed by water at 280° to H_3PO_4Aq and $Ca_3P_2O_8$ (Reynoso, *C. R.* 34, 795). Partially decomposed by boiling with NaOHAq or fusing with alkali carbonate (Rose). The *acid salt* $CaH_2P_2O_7.2H_2O$ is said to be obtained by decomposing the normal salt by a little $H_2C_2O_4Aq$ (Pahl, *Bl.* [2] 22, 122). Von Knorre a. Oppelt (*B.* 21, 769) failed to obtain this salt, but prepared the salt $2CaH_2P_2O_7.Ca_2P_2O_7.6H_2O$ by adding $CaCl_2Aq$ to $Na_2H_2P_2O_7Aq$.

Double salt $CaNa_2P_2O_7.4H_2O$ (Baer, *P.* 75, 159).

Chromium pyrophosphate $Cr_4(P_2O_7)_3$. A reddish green pp. by adding $Na_4P_2O_7Aq$ to Cr alum solution; soluble $Na_4P_2O_7Aq$, KOHAq, SO_2Aq, and mineral acids (Schwarzenberg, *A.* 65, 149).

Cobalt pyrophosphates. Salts having the composition $Co_3P_4O_{13}$ and $Co_6P_{10}O_{31}$ are said to be formed by strongly heating luteo-cobalt phosphate (Braun, *Fr.* 3, 468; *Gm.-K.* 3, 463).

Copper pyrophosphates. The *normal salt* $Cu_2P_2O_7.2H_2O$, by adding $Na_4P_2O_7Aq$ (not excess) to Cu salt solutions and drying at 100°; greenish-white amorphous pp., becoming crystalline by boiling in SO_2Aq; soluble $Na_4P_2O_7Aq$, NH_3Aq, and mineral acids (Schwarzenberg, *A.* 65, 156; Stromeyer a. Gladstone, *Gm.-K.* 3, 615). Forms *double salts* with NH_4, K, and Na (*v.* Schwarzenberg, *l.c.*; Schiff, *A.* 123, 1; Persoz, *A. Ch.* [3] 20, 315; Fletimann a. Henneberg, *A.* 65, 387).

Iron pyrophosphates. The *ferrous salt* is obtained by ppg. $FeSO_4Aq$ by $Na_4P_2O_7Aq$; composition not decided (*v.* Schwarzenberg, *A.* 65, 153; Struve, *J. pr.* 79, 318). The *ferric salt* $Fe_4(P_2O_7)_3.9H_2O$ is a yellowish pp., formed by adding neutral $FeCl_3Aq$ to $Na_4P_2O_7Aq$ (acidified $FeCl_3Aq$ gives $FePO_4$; Schwarzenberg). Gladstone (*C. J.* [2] 5, 435) obtained an allotropic form by heating the ordinary salt in dilute H_2SO_4Aq.

Double salts, with Na (Gladstone, *l.c.*; Persoz, *A. Ch.* [3] 20, 315; Fleitmann a. Henneberg, *A.* 65, 390; Rieckher, *N. J. P.* 23, 1; Milck, *J.* 1865. 263).

Lead pyrophosphate $Pb_2P_2O_7$. A white amorphous powder; by ppg. $Pb(NO_3)_2Aq$ by $Na_4P_2O_7Aq$. Obtained in colourless, transparent, rhombic prisms by dissolving PbO in molten KPO_3 (Ouvrard, *C. R.* 110, 1333). Soluble excess of $Na_4P_2O_7Aq$, insoluble acetic acid or NH_3Aq; decomposed by boiling water (Stromeyer, Schwarzenberg, *Gm.-K.* 3, 121; Gerhardt, *A. Ch.* [3] 22, 5[illegible]6). Forms a *double salt* with Na (Gerhardt, *l.c.*; Ouvrard, *l.c.*).

Lithium pyrophosphate $Li_4P_2O_7.2H_2O$; by adding $Na_4P_2O_7Aq$ to LiClAq, dissolving in acetic acid, and ppg. by alcohol (Rammelsberg, *B. B.* 1883. 18; Merling, *J.* 1879. 1043). A *double salt*, $Li_3NaP_2O_7$, is formed in prismatic crystals by dissolving Li_2CO_3 in molten $NaPO_3$ (Ouvrard, *C. R.* 110, 1333).

Magnesium pyrophosphates. The *normal salt* $Mg_2P_2O_7.3H_2O$ is formed by adding $MgSO_4Aq$ to $Na_4P_2O_7Aq$ (Rose, *P.* 76, 16, 20), or by dissolving MgO in $Na_2H_2P_2O_7Aq$ and heating (Schwarzenberg, *Gm.-K.* 2, 448). Pp. becomes crystalline by remaining under liquid from which it has been ppd. (Popp, *Z.* [2] 6, 305), also by boiling with SO_2Aq (Schwarzenberg, *l.c.*). The salt is obtained, without H_2O, by strongly heating $MgNH_4PO_4$. Loses $3H_2O$ at 100°; fused with soda or heated with conc. H_2SO_4 gives $Mg_3P_2O_8$ (Rose; Weber, *P.* 73, 137). Easily soluble HClAq and HNO_3Aq; ppd. incompletely by NH_3Aq (Fresenius; Weber). An *acid salt*, $MgH_2P_2O_7$, combined with NO_2, is said to be formed by evaporating to dryness with HNO_3Aq (Luck, *Fr.* 13, 255; Campbell, *P. M.* [4] 21, 380). Forms a *double salt* with Na (Persoz, *A.* 65, 169; Schwarzenberg, *A.* 65, 146; Beer, *P.* 75, 168).

Manganese pyrophosphates. The *normal manganous salt* $Mn_2P_2O_7.3H_2O$ is a white amorphous powder; by ppg. a salt of Mn by $Na_4P_2O_7Aq$ (Schwarzenberg, *A.* 65, 133). Soluble $Na_4P_2O_7Aq$ (Pahl, *Bl.* [2] 22, 122). Loses one H_2O at 120° (S., *l.c.*). The salt without H_2O is formed by strongly heating the hydrated salt, or $MnHPO_4.3H_2O$, or $MnNH_4PO_4.H_2O$ (S., *l.c.*; Heintz, &c., *Gm.-K.* 2, 475); white powder, S.G. 3·5847 at 20° (Lewis, *Am. S.* [3] 14, 281); heated to whiteness in H gives $Mn_3P_2O_8$; reduced by charcoal to Mn phosphide (Struve, *J.* 1860. 78). The *acid salt* $MnH_2P_2O_7.4H_2O$ is said to be formed by action of oxalic acid on the normal salt (Pahl, *l.c.*). Various *double salts* are described with K (Pahl, *l.c.*; Schjerning, *J. pr.* [2] 45, 515); with Na (Pahl, Rose; Christensen, *J. pr.* [2] 34, 41); with Na and NH_4 (*v.* Otto, *J. pr.* 2, 418). The *acid manganic salt* $MnHP_2O_7$ is said to be formed by heating $MnPO_4$ with H_3PO_4Aq to 170°-190° (Christensen, *J. pr.* [2] 28, 1).

Mercury pyrophosphates. The *normal mercurous salt* $Hg_4P_2O_7.H_2O$ is a heavy white powder obtained by adding $Na_4P_2O_7Aq$ to $HgNO_3Aq$ (Rose, *Gm.-K.* 3, 754; Schwarzenberg, *A.* 65, 133). The *normal mercuric salt*, $Hg_2P_2O_7$, is obtained by adding $Na_4P_2O_7Aq$ to $Hg(NO_3)_2Aq$ (S., *l.c.*; Reynoso, *C. R.* 34, 795).

Nickel pyrophosphate $Ni_2P_2O_7$. A green pp. by adding $Na_4P_2O_7Aq$ to $NiSO_4Aq$; soluble excess $Na_4P_2O_7Aq$, NH_3Aq, and acids; obtained crystalline by boiling with SO_2Aq; decomposed by water at 280°-300° (S., *l.c.*; Reynoso, *l.c.*).

Potassium pyrophosphates. The *normal salt*, $K_4P_2O_7.xH_2O$, is obtained by strongly heating K_2HPO_4; also formed by reaction of $POCl_3$ with KOHAq (Gladstone, *C. J.* [2] 5, 435). Loses one H_2O at 100°, and is dehydrated at 300°. Solution in water does not change to K_2HPO_4 on boiling (Schwarzenberg), nor on evaporation (Gladstone), but change is effected by heating to 280° (Reynoso, *C. R.* 34, 795); boiling with KOHAq produces the ortho- salt. The *acid salt*, $K_2H_2P_2O_7$, *is obtained by treating the normal with acetic* acid and alcohol, and evaporating over H_2SO_4 (Schwarzenberg, *A.* 65, 137). Forms a *double salt* with $2K_2(NH_4)HP_2O_7.H_2O$ (S., *l.c.*); also with $Cr_2H_4(P_2O_7)_2$ (Schjerning, *J. pr.* [2] 45, 515).

Silver pyrophosphates. *Normal salt*, $Ag_4P_2O_7$; a white pp. from $AgNO_3Aq$ and $Na_4P_2O_7Aq$ (Clark, Stromeyer, *Gm.-K.* 3, 919). S.G. 5·306 at 7·5°; soluble NH_3Aq, reppd. by HNO_3Aq; boiled with Na_2HPO_4Aq gives Ag_3PO_4. Heated with H_3PO_4Aq at 180° gives the *acid salt* $Ag_2H_2P_2O_7$ (Hurtzig a. Geuther, *A.* 111, 160).

Sodium pyrophosphates. The *normal salt*, $Na_4P_2O_7$, is formed by strongly heating Na_2HPO_4; a glass-like solid, becoming opaque on cooling (Clark, *N. Ed. P. J.* 7, 298); gives Na_3PO_4 and PH_3 when heated in H (Struve, *J. pr.* 79, 350); heated with NH_4Cl gives NaCl, $NaPO_3$, and PCl_3 (Rose). The hydrated salt, $Na_4P_2O_7.10H_2O$, crystallises from $Na_4P_2O_7Aq$ (Clark, *l.c.*; von Blücher, *P.* 50, 542) in monoclinic crystals (Rammelsberg; Haidinger, *P.* 16, 510; Handl, *W. A. B.* 32, 250; Schacchi, *P.* 109, 365; Duffet, *C. R.* 102, 1327). Crystallises unchanged from Aq with NH_3 or NH_4Cl added. Solution boiled with acids gives Na_3PO_4Aq. Poggiale (*J. Ph.* [3] 44, 273) gives solubility; 100 parts water dissolve—

	$Na_4P_2O_7$	$Na_4P_2O_7.10H_2O$
at 0°	3·0	5·41
10	3·95	6·81
20	6·23	10·92
30	9·96	18·11
40	13·5	24·97
50	17·45	33·25
60	21·83	44·07
70	25·62	52·11
80	30·04	63·40
90	35·11	77·47
100	40·26	93·11

The *acid salt* $Na_2H_2P_2O_7$; by heating NaH_2PO_4 to 190°–204° (Graham, *Gm.-K.* 2, 169), or by addition of alcohol to an acetic acid solution of $Na_4P_2O_7$ (Schwarzenberg, *A.* 65, 139). Crystallises from aqueous solution with $6H_2O$ (Bayer, *J. pr.* 106, 501; Rammelsberg, *B.* 16, 21; Duffet, *C. R.* 102, 1327). When strongly heated gives $Na_4H_2P_4O_{13}$ (Fleitmann a. Henneberg, *A.* 65, 328).

Double salts.—1. $Na_2(NH_4)_2P_2O_7.xH_2O$, $x=5$ or 6 (Schwarzenberg, *A.* 65, 140, 142; Rammelsberg). — 2. $Na_2K_2P_2O_7.12H_2O$, and $Na_4P_2O_7.Na_2H_2P_2O_7.2H_2O$ (S., *l.c.*; R., *l.c.*). Wallroth (*Bl.* [2] 39, 316) has described double salts with pyrophosphates of Al, Be, Bi, Cd, Ca, Ce, Cr, Co, Cu, Di, Er, La, Mn, Mg, Ni, Th, Yb, Y, Zn, and Zr. For double salts with pyrophosphates of Sn and Ti *v.* Wunder, *J.* 1870. 359; 1871. 323. $Na_4P_2O_7$ seems to combine with B_2O_3 by fusing $Na_4P_2O_7$ with boric acid (Prinvault, *C. R.* 74, 1219).

Strontium pyrophosphate, $Sr_2P_2O_7$. A crystalline powder; from $Sr(NO_3)_2Aq$ and $Na_4P_2O_7Aq$; also by heating $SrHPO_4$ (S., *l.c.*). Forms *acid salts* (von Knorre a. Oppelt, *B.* 21, 769); also a *double salt* with Na (Baer, *P.* 75, 166).

Thallium pyrophosphates. *Normal thallous salt*, $Tl_4P_2O_7$; by heating Tl_2HPO_4 (Descloizeaux, *A. Ch.* [4] 17, 329). S.G. 6·786. Crystallises from aqueous solution with $2H_2O$ (D., *l.c.*). The *acid salt* $Tl_2H_2P_2O_7.H_2O$ is formed by heating TlH_2PO_4 to 250°–275° (Lamy, Rammelsberg, *Gm.-K.* 3, 177).

Thorium pyrophosphates. *Double salts* with K and Na are described by Ouvrard (*C. R.* 105, 30).

Uranium pyrophosphates. *Double salts* with K and Na are described by Ouvrard (*C. R.* 110, 1333).

Yttrium pyrophosphate. Johnson describes $Y_4(P_2O_7)_3$, formed by heating Y_23SO_4 with HPO_3 to 316° (*B.* 22, 976).

Zinc pyrophosphate, $Zn_2P_2O_7$. By ppg. Zn salts by $Na_4P_2O_7$ (Stromeyer, *Gm.-K.* 2, 832; Gladstone, *ibid.* 3, 16; Schwarzenberg). Forms a *double salt* with NH_4 (Bette, *A.* 15, 129).

Zirconium pyrophosphates. *Double salts* with K and Na are described by Ouvrard (*C. R.* 105, 30).

METAPHOSPHATES. *Salts derived from* HPO_3. The general methods of preparation, properties, and reactions of the metaphosphates are described at the beginning of this article (p. 106); the divisions into *mono-*, *di-*, *tri-*, *tetra-*, and *hexa- metaphosphates*, with the processes by which typical salts of each division are prepared, have also been described already (p. 107). It will suffice here to enumerate the salts, with an indication in each case to which division the salt is assigned by Maddrell, Fleitmann a. Henneberg (*cf.* Tammann's results regarding Na, di-, and tri- metaphosphates p. 107). T.'s paper in *J. pr.* [2] 45, 417 should also be consulted.

Aluminium dimetaphosphate, $Al_2P_6O_{18}$. By dissolving $Al_2O_3.xH_2O$ in H_3PO_4Aq, evaporating, and heating to 316° (Maddrell, *C. S. Mem.* 3, 373; Johnson, *B.* 22, 976). For *hexa- salt v.* T., *J. pr.* [2] 45, 417.

Ammonium metaphosphates. $(NH_4)_2P_2O_6$, from Cu salt by $(NH_4)_2SAq$; at 200°–250° becomes *mono- salt* $(NH_4)PO_3$ (Fleitmann, *A.* 72, 236). For *deca-* and *penta- salts* v. T., *l.c.*

Barium metaphosphates. (1) ? *Mono- salt* BaP_2O_6; by heating $BaCO_3$ with H_3PO_4 to 316° (M., *l.c.*; F., *l.c.*; Rose, *P.* 76, 5; Birnbaum, *Z.* [2] 7, 139). (2) *Di- salt*, $Ba_2P_4O_{12}.xH_2O$; from Na or NH_4 salt and $BaCl_2Aq$ (F., *l.c.*). (3) *Tri- salt*, $Ba_3P_6O_{18}.xH_2O$; from Na salt and $BaCl_2Aq$ (F. a. Henneberg, *A.* 65, 313). (4) *Hexa- salt*; from Na salt and $BaCl_2Aq$ (Rose; Graham, *P.* 32, 68).

Bismuth metaphosphate. ? *Tetra- salt*; by fusing H_3PO_4 with $Bi_2O_3.xH_2O$ (F., *l.c.*); HPO_3Aq, $Bi3NO_3$ solution and NH_3Aq give a pp. (Persoz, *Gm.-K.* 2, 832).

Cadmium metaphosphate. ? *Tetra- salt* (F., *l.c.*; Persoz, *Gm.-K.* 3, 54). *Double salts* with Na and K (Ouvrard, *C. R.* 106, 1729).

Calcium metaphosphates. A salt is obtained by heating $CaHPO_4$; for action of HPO_3 on $CaCO_3$ *v.* Rose (*P.* 76, 5), Liebig (*A.* 11, 262). *Di- salt*, $Ca_2P_4O_{12}.xH_2O$; from Na salt and $CaCl_2Aq$ (M., *l.c.*; F., *l.c.*). *Double salts.*— $CaAm_2P_4O_{12}.2H_2O$ (F., *l.c.*); $CaNaP_3O_9$ (F. a. H., *l.c.*).

Chromium dimetaphosphate, $Cr_2P_6O_{18}$. By heating CrO_3H_3 with H_3PO_4 to 316° (M., *l.c.*; Hautefeuille a. Margottet, *C. R.* 96, 849, 1042; Johnson, *B.* 22, 976).

Cobalt metaphosphates. ? *Mono- salt* CoP_2O_6; by evaporating $CoSO_4$ with H_3PO_4Aq, and heating to 316° (M., *l.c.*; H. a. M., *l.c.*). *Di- salt* $Co_2P_4O_{12}$; by heating roseo-cobaltic phosphate (Braun, *Ammon. Kobaltverbindungen* [Göttingen, 1862]). ? *Hexa- salt* $Co_6P_{12}O_{36}$; by $CoCl_2$Aq and the Na salt (Rose). *Okto- salt* (T., *l.c.*). *Double salt* with Na (M., *l.c.*).

Copper metaphosphates. *Di- salt* $Cu_2P_4O_{12}$; by heating CuO or $Cu(NO_3)_2$ with H_3PO_4 to 316° (M., *l.c.*; F., *l.c.*); obtained with $8H_2O$ by evaporating $CuSO_4$Aq mixed with $Na_2P_2O_6$ (F. *l.c.*). ? *Hexa- salt*; by ppg. $CuCl_2$Aq (*not* $CuSO_4$Aq) by the Na salt (Rose). *Double salts* with NH_4 and Na (F., *l.c.*; T., *l.c.*).

Iron metaphosphate. *Di-ferric salt* $Fe_2P_6O_{18}$; by heating $FeCl_3$ with H_3PO_4 to 316° (M., *l.c.*; H. a. M., *l.c.*; Johnson, *B.* 22, 976).

Lithium hexametaphosphate. A *double salt* $Li_2Na_4P_6O_{18}$, is described by Tammann (*l.c.*).

Lead metaphosphates. *Di- salt* $Pb_2P_4O_{12}$; from $Pb(NO_3)_2$Aq and the Na salt; also by heating H_3PO_4 and PbO (F., *l.c.*). *Tri- salt* $Pb_3P_6O_{18}$; from the Na salt and $Pb(NO_3)_2$Aq (F. a. H., *l.c.*). *Deka-salt*, T. (*l.c.*). *Double salt* $PbAm_2P_4O_{12}$ (F., *l.c.*).

Magnesium metaphosphates. ? *Mono- salt* MgP_2O_6, by heating MgO with H_3PO_4 (M., *l.c.*). *Di- salt* $Mg_2P_4O_{12}.xH_2O$; and *tri- salt* $Mg_3P_6O_{18}.xH_2O$; from the corresponding Na salt and $MgCl_2$Aq (F., *l.c.*). *Hexa- salt* $Mg_6P_{12}O_{36}$ (Graham, *Gm.-K.* 2, 214). *Double salts*, with NH_4 and Na, *v.* F. (*l.c.*); F. a. H. (*l.c.*); M. (*l.c.*); Graham (*l.c.*); Ouvrard (*C. R.* 106, 1729); Tammann (*l.c.*).

Manganese metaphosphates. *Di- salt* $Mn_2P_4O_{12}$; by heating a Mn salt with H_3PO_4 to 316° (M., *l.c.*; F., *l.c.*); with $8H_2O$ by ppg. $(NH_4)_2P_2O_6$Aq by excess of $MnCl_2$Aq (F., *l.c.*). *Tri- salt* $Mn_3P_6O_{18}.11H_2O$; from $MnCl_2$Aq (*not* $MnSO_4$) and $Na_3P_3O_9$. *Hexa- salt* $Mn_6P_{12}O_{36}$; by using $Na_6P_6O_{18}$ (Otto, Rose, *Gm.-K.* 2, 490; Braun, *l.c.*). *Deka- salt* $Mn_{10}P_{20}O_{60}$ (Tammann, *J. pr.* [2] 45, 417). *Double salts*, with NH_4 and Na (*v.* F., *l.c.*; Rose, *l.c.*; T., *l.c.*).

Mercury metaphosphates. White pps. are formed by adding Na tri- and hexa- metaphosphate to $Hg(NO_3)_2$Aq (F. a. H., *l.c.*; Rose, *Gm.-K.* 2, 754).

Nickel metaphosphates. *Di- salt* $Ni_2P_4O_{12}$; by heating Ni_2O_3 with H_3PO_4 to 316° (M., *l.c.*; H. a. M., *l.c.*). *Hexa- salt* $Ni_6P_{12}O_{36}$; by adding $NiCl_2$Aq to $Na_6P_6O_{18}$ (Rose). *Double salt* with Na (M., *l.c.*).

Potassium metaphosphates. *Mono- salt* KPO_3; by heating KH_2PO_4 to full redness (M., *l.c.*; Graham, Darracq, *Gm.-K.* 2, 32). S.G. 2·2639 at 14·5° (Clarke, *Am. S.* [3] 14, 281). *Di- salt* $K_2P_2O_6$; by treating the Cu salt with K_2SAq (F., *l.c.*). *Hexa- salt* $K_6P_6O_{18}$ (T., *l.c.*). *Double salt* with NH_4 (F., *l.c.*). *Compound with* B_2O_3 (Prinvault, *C. R.* 74, 1249).

Silver metaphosphates. *Di- salt* $Ag_2P_2O_6$; and *tri- salt* $Ag_3P_3O_9$; from $AgNO_3$Aq and the corresponding Na salts (F., *l.c.*; F. a. H., *l.c.*). *Hexa- salt* $Ag_6P_6O_{18}$; from $AgNO_3$ heated with H_3PO_4 to 316°, or by adding $Na_6P_6O_{18}$Aq to $AgNO_3$Aq (Graham; F., *l.c.*; T., *l.c.*; Rose, Berzelius). *Double salts* with Al, Cr, and Fe (H. a. M., *l.c.*).

Sodium metaphosphates. For conditions of formation and general reactions *v.* p. 106. The following salts have been described: *Mono- salt* $NaPO_3$ (F., *l.c.*; M., *l.c.*; F. a. H., *l.c.*; Graham, *Gm.-K.* 2, 170; Jamieson, *A.* 59, 350; Müller, *P.* 127, 428); *di- salt* $Na_2P_2O_6.2H_2O$ (F., *l.c.*); *tri- salt* $Na_3P_3O_9.6H_2O$ (F. a. H., *l.c.*); *tetra- salt* $Na_4P_4O_{12}$ (F., *l.c.*); *hexa- salt* $Na_6P_6O_{18}$ (F., *l.c.*; T., *l.c.*; G., *l.c.*). For *double salts* with Na and NH_4, *v.* F. (*l.c.*).

Strontium metaphosphates. ? *Mono- salt* SrP_2O_6; by heating $SrCO_3$ with H_3PO_4 (M., *l.c.*; *cf.* Rose, *P.* 76, 8; Scheerer, *J. pr.* 75, 113). For a *deka- salt*, *v.* T. (*l.c.*).

Thallium metaphosphate. $TlPO_3$ said to exist in two forms, one insoluble in water (? di-salt), and the other soluble (Lamy, *Gm.-K.* 2, 177).

Thorium metaphosphate ThP_4O_{12} (? di- salt, $Th_2P_8O_{24}$); by heating $Th(SO_4)_2$ with H_3PO_4 to redness (Johnson, *B.* 22, 976). For *double salts* with K and Na, *v.* Troost a. Ouvrard (*C. R.* 105, 30).

Uranium metaphosphate. *Di- salt* $U_2P_8O_{18}$ (H. a. M., *l.c.*).

Zinc metaphosphates. *Di- salt* $Zn_2P_4O_{12}$; by heating ZnO with H_3PO_4 to 350° (F., *l.c.*); with $4H_2O$ by adding $ZnCl_2$Aq to $(NH_4)_2P_2O_6$Aq. For *double salts* with NH_4 and Na, *v.* F. a. H. (*l.c.*); Bette (*A.* 15, 129).

TETRAPHOSPHATES and DEKAPHOSPHATES. *Salts of the hypothetical acids* $H_6P_4O_{13}$ and $H_{12}P_{10}O_{31}$ (*v.* pp. 106, 107).

Barium tetraphosphate $Ba_3P_4O_{13}$. A heavy crystalline powder; by fusing $Na_6P_4O_{13}$ with $BaCl_2$ (F. a. H., *A.* 65, 313).

Magnesium tetraphosphate $Mg_3P_4O_{13}$. Prepared similarly to the Ba salt (F. a. H., *l.c.*).

Silver tetraphosphate $Ag_6P_4O_{13}$. From the Na salt and $AgNO_3$Aq (Berzelius, *P.* 19, 331).

Sodium tetraphosphate $Na_6P_4O_{13}$. By fusing $Na_6P_6O_{18}$ with $Na_4P_2O_7$ or Na_3PO_4 (F. a. H., *l.c.*; Uelsmann, *A.* 118, 101).

Silver dekaphosphate $Ag_{12}P_{10}O_{31}$. From the Na salt and $AgNO_3$Aq (F. a. H., *l.c.*; U., *l.c.*).

Sodium dekaphosphate $Na_{12}P_{10}O_{31}$. A glassy mass; by fusing $Na_6P_6O_{18}$ and $Na_4P_2O_7$ (F. a. H., *l.c.*).

M. M. P. M.

PHOSPHENYL CHLORIDE *v.* PHENYL-*di-chloro*-PHOSPHINE.

PHOSPHENYLIC ACID *v.* PHENYL PHOSPHITES.

PHOSPHENYLOUS ACID $C_6H_5PHO.OH$. *Benzene phosphinic acid.* [70°]. S. 7·23 in the cold; 211 at 100°. Formed by adding water to $C_6H_5PCl_2$, and boiling (Michaelis, *A.* 181, 303; *B.* 10, 816). Leaflets, v. sol. alcohol. Decomposed by heat into phenyl-phosphine, benzene, and HPO_3. PCl_5 forms $C_6H_5PCl_2$.—KA′ 2aq.—NH_4A'. BaA′₂ 4aq.—PbA′₂: amorphous pp.

Ethyl ether EtA′. Oil.

Di-ethyl ether $C_6H_5P(OEt)_2$ (235°). Formed from $C_6H_5PCl_2$ and NaOEt. Liquid with very powerful odour.

PHOSPHIDES. *Compounds of P with one other more positive element.* The chief phosphides are those of Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cu, Cr, Au, H, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Pt, Ag, Na, Th, Sn, Tl, W, Zn, Zr. (Phosphides of H are described as *Phosphorus hydrides* under PHOSPHORUS.) Many phosphides are formed by heating together P and the more positive element in an atmosphere of CO_2 or N; phosphides are also produced by heating P with several metallic oxides or with salts in solution; also by heating metals or their oxides in PH_3. Phosphides are generally brittle solids; many react with water or dilute acids, evolving P hydrides; some yield basic phosphates when heated in air. For descriptions of the different phosphides *v.* the individual elements.

M. M. P. M.

PHOSPHINE. PH_3 is sometimes known by this name, *v.* PHOSPHORUS, HYDRIDES OF, p. 135.

PHOSPHINES are the phosphorus analogues of amines, and result from the replacement of hydrogen in phosphuretted hydrogen by alkyl radicles. They may be classified, like the amines, into primary, secondary, and tertiary bases, and, in addition, quaternary compounds are known analogous to the salts of compound ammoniums.

Methods of preparation. 1. *Action of the haloid derivatives of hydrocarbon radicles on metallic phosphides.* It was by this reaction that Paul Thénard (*C. R.* 21, 141; 25, 892) discovered the first members of the phosphine group in 1843-47. He experimented with methyl chloride and calcium phosphide, and apparently isolated trimethyl-phosphine, $(CH_3)_2P_4$ as an inert solid, and a substance $(CH_3)_4P_2$ analogous to cacodyl as a spontaneously inflammable liquid, boiling at 250°, very explosive, poisonous, and unstable. Thénard recognised the relationship of trimethyl-phosphine to ammonia, and predicted the existence of the then undiscovered organic compounds of nitrogen and antimony.

In 1855 Hofmann a. Cahours (*T.* 1857; *A. Ch.* [3] 61, 5) investigated the action of methyl iodide on sodium phosphide, and obtained tetramethyl-phosphonium iodide in addition to trimethyl-phosphine and the phosphorised cacodyl of Thénard. They found that the method was dangerous, and furnished mixtures the separation of which presented enormous difficulties.

Berlé (*J. pr.* 66, 73) about the same time obtained very small quantities of triethyl-phosphine by the action at a very high temperature of ethyl iodide on sodium phosphide obtained by heating sodium and phosphorus together in rock oil.

Cahours in 1859 (*C. R.* 49, 87; *J.* 1859, 430) prepared tetrethyl-phosphonium iodide by the action of ethyl iodide on crystallised zinc phosphide (obtained by heating the metal in phosphorus vapour at 180°).

In 1882 Letts a. N. Collie (*Tr. E.* 30 pt. i. 181) investigated the action of benzyl chloride on sodium phosphide, and found that tetra-benzyl-phosphonium chloride was produced in abundance.

2. *Action of organo-metallic bodies on trichloride of phosphorus.* The action of zinc alkyls on phosphorus trichloride was first investigated by Hofmann a. Cahours (*A. Ch.* [3] 51), and was further studied by Hofmann (*A. Ch.* [3] 62; 63 · 64). By this method tertiary phosphines are exclusively formed: $3R_2Zn + 2PCl_3 = 2R_3P + 3ZnCl_2$. It is necessary to treat the product of the reaction with caustic potash, in order to decompose the compound of the phosphine with zinc chloride. By this reaction Hofmann a. Cahours obtained PMe_3 and PEt_3, and showed that they resemble the corresponding amines in many respects, especially in the readiness with which they combine with alkyl iodides to give quaternary compounds. On the other hand, they proved that, unlike the amines, tertiary phosphines readily combine with oxygen to give very stable compounds of the general formula R_3PO.

3. *Action of alcohols on phosphonium iodide; and 4. Action of alkyl iodides on phosphonium iodide and oxide of zinc* (Hofmann's methods). In the year 1871 Hofmann again took up the study of the phosphines (*B.* 4, 205), and by the action of alkyl iodides on phosphuretted hydrogen obtained not only tertiary and quaternary compounds, but also primary and secondary bases. Hofmann took advantage of the fact that phosphonium iodide when heated with alcohol yields phosphuretted hydrogen, ethyl iodide, and water. When phosphonium iodide (1 mol.) is heated with alcohol (3 mols.) for 8 hours at 180° the crystalline product is a mixture of PEt_3HI and PEt_4I, and, on addition of caustic soda, triethyl-phosphine separates as a clear liquid, while the solution gives, on evaporating, beautiful crystals of tetrethyl-phosphonium iodide. If the tubes are heated for four hours only, two layers of liquid are visible on cooling, and the tubes show great pressure when opened. It may be taken for granted, then, that the reaction occurs in two phases, in the first of which EtI is liberated, which then acts upon PH_3 in the same way as it acts on ammonia. Hofmann employed this method successfully in the methyl (*B.* 4, 209), ethyl (*B.* 4, 205), propyl (*B.* 6, 292), butyl (*B.* 6, 296), and amyl (*B.* 6, 297) series. Hofmann (*B.* 4, 372) endeavoured to prepare the primary and secondary bases according to the equations:

$$PH_4I + C_2H_6O = C_2H_5PH_2.HI + H_2O$$
$$PH_4I + 2C_2H_6O = (C_2H_5)_2PH.HI + 2H_2O,$$

by altering the proportions of phosphonium iodide and alcohol, but without success, the tertiary base being produced alone or mixed with the quaternary compound, while with the proportions required for the second equation the tubes invariably exploded.

In the meantime Drechsel a. Finkenstein (*B.* 4, 352) believed that they had succeeded in obtaining the primary bases by saturating EtI or MeI with PH_3, and allowing the solutions to remain for some time at the ordinary temperature, or by heating them at 100°, and also by heating an ethereal solution of ZnI_2 saturated with PH_3 together with MeI. Hofmann (*B.* 4, 372) repeated these experiments, and showed that only tertiary and quaternary derivatives were formed. The idea then occurred to him of heating the alkyl iodide with phosphonium iodide in presence of a metallic oxide, with the happiest results; for on heating a mixture of phosphonium iodide (2 mols.) with ethyl iodide (2 mols.) and zinc oxide (1 mol.) in sealed tubes at 150° for from six to eight hours, a complete reaction occurred, the tubes when cold containing a crystalline mass consisting exclusively of the hydriodates of the primary and secondary bases, the former being the chief product, while the latter was only formed in small quantities. The addition of water to the product of the reaction liberated the primary phosphine alone, which was distilled off in a hydrogen atmosphere, while the secondary phosphine was subsequently set at liberty by the action of an alkali. By means of this general method Hofmann prepared methyl (*B.* 4, 430), ethyl (*B.* 4, 605), propyl (*B.* 6, 292), butyl (*B.* 6, 296), amyl (*B.* 6, 297), and benzyl (*B.* 5, 100) phosphines.

4. *Michaelis's methods.* Hofmann's methods, although of excellent service for obtaining the phosphines of those radicles which form alcohols, could not be employed in the preparation of phosphines containing purely aromatic radicles (*B.* 5, 100). Michaelis, on the other hand, not only succeeded in obtaining all the phenyl-phosphines, but also in discovering a fairly general method for the production of primary phosphines. The substance forming the starting-point for the preparation of phosphines by these methods is trichloride of phosphorus. One atom of chlorine is first replaced in that body by one or other of the following processes:—

(A) The mixed vapours of a hydrocarbon and the trichloride are repeatedly passed through a red-hot tube. Thus when benzene is employed 'phosphenyl' chloride is obtained: $PCl_3 + C_6H_6 = (C_6H_5)PCl_2 + HCl$.

(B) A mercury alkyl is heated with the trichloride under pressure: $PCl_3 + (C_2H_5)_2Hg = (C_2H_5)PCl_2 + Hg(C_2H_5)Cl$.

(C) By digesting a hydrocarbon with the trichloride and aluminum chloride, the reaction being the same as (1). Other substances besides hydrocarbons yield substituted phosphorus chlorides when submitted to this reaction. Thus a mixture of acetone, PCl_3, and aluminium chloride react spontaneously, according to the equation:

$$2(CH_3)_2CO + PCl_3 = 2HCl + (CH_3.CO.CH_2)_2PCl.$$

By means of these different reactions Michaelis and his pupils have obtained a considerable number of substituted phosphorus chlorides, among which are: Phenyl phosphorus-chloride by methods 1, 2, and 3 (*B.* 6 [1873], 601; 8 [1875], 922; 12 [1879], 1009). Tolyl phosphorus-chloride by method 3 (*B.* 13, 653). Xylyl phosphorus-chloride by method 3 (*A.* 212, 203, 209). Ethyl phosphorus-chloride by method 2 (*B.* 13, 2174). Propyl phosphorus-chloride by method 2 (*B.* 13, 2174). Naphthyl phosphorus-chloride by method 2 (*B.* 9, 1051). Acetonyl phosphorus-chloride by method 3 (*B.* 17, 1273). The substituted chlorides resemble PCl_3 in properties. As a rule they are fuming liquids, combining readily with chlorine to give solid compounds analogous to pentachloride of phosphorus; treated with water, they yield phosphinous (phosphinic) acids. Thus phenyl phosphorus-chloride gives phenyl phosphinous (benzene phosphinic) acid: $(C_6H_5)PCl_2 + 2H_2O = (C_6H_5)PH_2O_2 + 2HCl$. The products of addition which they form with chlorine react with water to give phosphinic (phosphonic) acids: $(C_6H_5)PCl_4 + 3H_2O = (C_6H_5)PH_2O_3 + 4HCl$. Michaelis was unable to obtain more than mere traces of the primary phosphine by the action of nascent hydrogen on the substituted chlorides. When gaseous HI is passed into the chloride, chlorine is gradually displaced by iodine: $C_6H_5PCl_2 + 3HI = C_6H_5PI_2HI + 2HCl$. From this iodide Michaelis obtained phenyl-phosphine by the action of alcohol: $3C_6H_5PI_2HI + 9C_2H_6O = C_6H_5PH_2 + 2C_6H_5PO_3H_2 + 3H_2O + 9C_2H_5I$. In later experiments he employed a simpler method, namely the destructive distillation of the phosphinous (phosphinic) acid which, as already stated, is produced by the action of water or alcohol on the substituted chloride: $3C_6H_5PO_2H_2 = C_6H_5PH_2 + 2C_6H_5PO_3H_2$. From phenyl phosphorus chloride Michaelis obtained diphenyl-phosphine by the following reactions: (1) The chloride is digested with mercury diphenyl at 200°:

$$(C_6H_5)PCl_2 + Hg(C_6H_5)_2 = (C_6H_5)_2PCl + HgCl(C_6H_5)$$

(*B.* 8, 1304); or it is heated for some time at 280°, when the following reaction occurs:

$$2(C_6H_5)PCl_2 = (C_6H_5)_2PCl + PCl_3.$$

(2) Diphenyl phosphorus chloride when heated with water or dilute soda solution decomposes in the following manner: $2(C_6H_5)_2PCl + 2H_2O = (C_6H_5)_2PH + (C_6H_5)_2HPO_2 + 2HCl$ (Michaelis a. Gleichmann, *B.* 15, 801). He also obtained the tertiary base; at first by acting upon a mixture of phenyl-phosphorus chloride and bromo-benzene with sodium: $(C_6H_5)PCl_2 + 2C_6H_5Br + 3Na = 2NaCl + NaBr + (C_6H_5)_3P$, but later this method was modified in a remarkable way, by substituting for phenyl phosphorus chloride, phosphorus chloride alone, the reaction occurring quite easily and very energetically at ordinary temperatures according to the equation:

$$PCl_3 + 3(C_6H_5)Br + 6Na = 3NaCl + 3NaBr + (C_6H_5)_3P.$$

5. *Action of alcohols on a mixture of phosphorus and phosphorus iodide.* Letts a. Blake (*Tr. E.* pt. 2) have shown that very remarkable reactions occur when benzyl alcohol acts upon a mixture of phosphorus and phosphorus iodide (in the proportions employed for obtaining phosphonium iodide by the action of water), whereby a number of the phosphorus derivatives of benzyl are obtained. The action occurs spontaneously at ordinary temperatures, and, although its mechanism was found difficult to investigate, the following equations account for the formation of the different products:—

(1) $PI_2 + C_7H_7OH + H_2O = (C_7H_7)H_2PO_2 + HI + I$
(2) $PI_2 + C_7H_7OH + 2H_2O + I = (C_7H_7)H_2PO_3 + 3HI$
(3) $PI_2 + 2C_7H_7OH = (C_7H_7)_2HPO_2 + HI + I$
(4) $PI_2 + 3C_7H_7OH + HI = (C_7H_7)_3PO + 2H_2O + 3I$
(5) $PI_2 + 4C_7H_7OH + 4HI = (C_7H_7)_4PI + 4H_2O + 5I$
(6) $PI_2 + 2H_2O = H_3PO_2 + HI + I$
(7) $PI_2 + 4H_2O + 3I = H_3PO_4 + 5HI$
(8) $2HI + C_7H_7OH = C_7H_8 + H_2O + I_2$
(9) $P + I_2 = PI_2$

All the products indicated by the above equations were obtained in quantity, especially benzyl phosphinic acid, di-benzyl phosphinic acid, and tri-benzyl phosphine oxide, and the method is undoubtedly the easiest and best for the preparation of those substances. Whether other alcohols behave in a similar manner to benzyl alcohol with a mixture of phosphorus and its iodide has not yet been ascertained.

General properties of the primary phosphines. The following primary bases have been obtained:

Name	Condition	Boiling-point
Methyl-phosphine [1]	Gas	-14°
Ethyl " [2]	Liquid	25°
Iso-propyl " [3]	"	41°
Iso-butyl " [4]	"	62°
Iso-amyl " [5]	"	106°
n-Octyl " [6]	"	184°–187°
Phenyl " [7]	"	160°–161°
Benzyl " [8]	"	180°–183°
p-Tolyl " [9]	Solid at +4°	178°

[1] Hofmann, *B.* 4, 209.
[2] Hofmann, *B.* 4, 432.
[3] Hofmann, *B.* 6, 292.
[4] Hofmann, *B.* 6, 296.
[5] Hofmann, *B.* 6, 297.
[6] Moslinger, *B.* 9, 1005.
[7] Michaelis, *B.* 7, 6, 1688.
[8] Hofmann, *B.* 5, 100; Letts a. Blake, *Tr. E.* 35 pt. 2.
[9] Michaelis a. Panek, *A.* 212, 233.

Most of the primary bases are liquids, insoluble in water, but soluble in ether. They fume in the air, and grow very hot, their vapour igniting spontaneously at times. The products of this oxidation appear to have been investigated only in a few cases, and chiefly in the aromatic series. Phenyl phosphine (Michaelis, *B.* 10, 807) and tolyl phosphine (Michaelis a. Panek, *A.* 212, 234) both absorb a molecule of oxygen, and are converted into phosphinous (phosphinic) acids, which are monobasic, and therefore probably have the constitution RPH(OH):O. These acids are readily decomposed by heat, giving the primary phosphine, and the corresponding phosphinic (phosphonic) acid $3RPH_2O_2 = RPH_2 + 2RPH_2O_3$, a reaction analogous to that which gives rise to phosphoretted hydrogen and phosphoric acid when hypophosphorous and phosphorous acids are heated. Letts and Blake (*Tr. E.* 35, pt. 2) find that benzyl phosphine yields a mixture of benzyl phosphinous (phosphinic) and benzyl phosphinic (phosphonic) acids with some phosphoric acid. Submitted to the action of strong nitric acid, many of the primary phosphines (and probably all) absorb three atoms of oxygen, and are converted into phosphinic (phosphonic) acids. This has been shown by Hofmann (*B.* 5, 110) to be the case in the methyl, ethyl, isopropyl, isobutyl, and isoamyl series.

The phosphinic acids are solid substances, which, with the lower members of the fatty series, can be distilled unchanged (Hofmann, *B.* 6, 303). But in some other instances a different reaction occurs: thus phenyl phosphinic (benzene phosphonic) acid when heated slowly to 200° gives a pyro-acid, while when rapidly heated to 250° it decomposes into benzene and metaphosphoric acid: $C_6H_5PH_2O_3 = C_6H_6 + HPO_3$. The phosphinic (phosphonic) acids are all dibasic, and no doubt have the structure $RPO(OH)_2$. All the primary phosphines have distinct alkaline properties. They combine readily with hydracids forming crystalline compounds, which can, as a rule, be volatilised (with dissociation more or less complete), and which resemble the compounds of phosphoretted hydrogen in being instantly decomposed by water with liberation of the phosphine. The hydrochlorides combine with chloride of platinum to give chloroplatinates. The salts of the primary bases with oxyacids have been scarcely at all investigated. The action of halogens on primary phosphines has not been sufficiently investigated. Methyl and ethyl phosphine take fire when they come in contact with chlorine or bromine (Hofmann, *B.* 4, 433, 609). Benzyl-phosphine yields with bromine a mixture of its own hydrobromide and substitution-products (Letts a. Blake, *Tr. E.* 35, pt. 2).

Sulphur acts on the primary bases. With the methyl and ethyl derivatives, compounds have been obtained but not investigated (Hofmann, *B.* 4, 433, 610). With phenyl phosphine sulphur acts slowly in the cold, rapidly at a high temperature (Michaelis, *B.* 10, 810). Two substances are produced, one, a thick liquid, soluble in ether, having the composition $(C_6H_5)PH_2S$, the other a crystalline product to which Michaelis assigns the formula $(C_6H_5P)_3S$. The first of these bodies decomposes when heated in the following manner:

$$2C_6H_5PH_2S = C_6H_5PS + C_6H_5PH_2 + H_2S.$$

When benzyl phosphine is warmed with sulphur the following reaction occurs (Letts a. Blake, *l.c.*):

$$2C_7H_7PH_2 + 6S = (C_7H_7)_2P_2S_3H_2 + H_2S$$

and the resulting pyro-benzyl-thiophosphinic acid when boiled with water is decomposed, yielding mono-thio-benzyl phosphinic acid:

$$(C_7H_7)_2P_2S_3H_2 + 4H_2O = 2C_7H_7PS(OH)_2 + 3H_2S.$$

In view of the analogies existing between nitrogen and phosphorus, considerable interest is attached to the action of carbonyl chloride and bisulphide of carbon on the primary phosphines. Bisulphide of carbon acts upon both methyl and ethyl phosphine (Hofmann, *B.* 4, 433, 610), but the products have not been investigated. Michaelis a. Dittler (*B.* 12, 338) have studied the action of both reagents on phenyl phosphine. When carbonyl chloride is passed slowly into that substance, an energetic reaction occurs in the following manner:

$$2COCl_2 + C_6H_5PH_2 = C_6H_5PCl_2 + 2CO + 2HCl.$$

Phenyl phosphine and bisulphide of carbon act upon each other when heated in a sealed tube at 150°, and sulphuretted hydrogen is liberated. The product of the reaction is a resinous body $(C_6H_5PHCS)_2S$, and the reaction itself proceeds according to the equation

$$2C_6H_5PH_2 + 2CS_2 = (C_6H_5PHCS)_2S + H_2S.$$

Michaelis a. Dittler were not successful in their attempts to prepare a phosphorised mustard oil from this compound.

They were equally unsuccessful in obtaining a phosphorised carbylamine by the action of chloroform and caustic potash on phenyl phosphine. It is true that a reaction occurs, but its course is completely different from that which takes place with an amine, viz.:

$$C_6H_5PH_2 + 4KHO + CHCl_3 = C_6H_5PHKO_2 + 3KCl + CH_3OH + H_2O.$$

It thus appears that, in their behaviour with carbonyl chloride and a mixture of caustic potash and chloroform, primary phosphines behave in an entirely different manner from the corresponding amines, though there is a certain degree of analogy as regards the action of both on bisulphide of carbon. This difference is no doubt due to the strong affinity of phosphorus for electronegative elements, such as the halogens, oxygen, and sulphur. Chloracetic and bromacetic acid react with benzyl phosphine, and chloroformic ether appears to form a product of addition (Letts a. Blake, *l.c.*). Probably other phosphines act in a similar manner with these reagents.

Primary phosphines readily combine with alkyl iodides to give hydriodides of secondary phosphines.

General properties of the secondary phosphines. The following secondary phosphines have been obtained:

Name	Condition	Boiling-point
Dimethyl phosphine [1]	Liquid	25°
Di-ethyl " [2]	"	85°
Di-isopropyl " [3]	"	118°
Di-isobutyl " [4]	"	153°
Di-isoamyl " [5]	"	210°–215°
Di-phenyl " [6]	"	280° (about)
Methyl-isopropyl " [7]	"	78°–80°
Iso-propyl, isobutyl " [8]	"	139°–140°
Di-benzyl " [9]	?	Decomposes when boiled

[1] Hofmann, *B.* 4, 610.
[2] Hofmann, *B.* 4, 433.
[3] *Ibid. B.* 6, 294.
[4] *Ibid. B.* 6, 296.
[5] *Ibid. B.* 6, 298.
[6] Michaelis, *B.* 15, 801 a.
[7] *Ibid. B.* 6, 295.
[8] Hofmann, *B.* 6, 300.
[9] Letts a. Blake, *l.c.*

All the secondary phosphines obtained as yet are liquids, having a powerful odour. They are insoluble in water, but soluble in ether &c.

They have as a rule a strong attraction for oxygen, fuming and growing hot on exposure to the air, and often inflaming spontaneously. In some cases they appear to have even a greater affinity for oxygen than the primary bases. This is so according to Hofmann with all the secondary phosphines of the fatty series which he obtained. But apparently it is not the case with diphenyl phosphine. The products of this spontaneous oxidation do not appear to have been examined except in the case of dibenzyl phosphine, which yields dibenzyl phosphinic (phosphonic) acid and possibly the oxide also $(C_7H_7)_2PO$ (Letts a. Blake, *l.c.*). But the products of their oxidation by nitric acid have been investigated, chiefly by Hofmann (*B.* 5, 104; 6, 303). These are in all cases phosphinic acids, R_2PHO_2, which are monobasic, and no doubt have the constitution $R_2P(OH)O$.

These acids are probably also produced when the chlorides R_2PCl are oxidised by nitric acid. Such is at least the case with $(C_6H_5)_2PCl$. Some of them can be distilled unchanged, *e.g.* dimethyl phosphinic acid; others, *e.g.* diphenyl and dibenzyl phosphinic acid, lose water, and give pyro-acids.

Secondary phosphines combine with acids, the resulting salts being far more stable than those of the primary bases. Thus in most cases they are not decomposed by water, though some are (*e.g.* salts of diphenyl phosphine). Comparatively little is known regarding secondary phosphines, and very few of their compounds have been investigated.

Sulphur acts upon them, and in the case of diethyl phosphine, according to A. W. v. Hofmann a. Mahla (*B.* 25, 2436), triethyl phosphine sulphide and diethyl dithiophosphinic acid. PEt_2SSH are formed, together with a third substance which probably has the composition $PSEt_2.S.S.S.PSEt_2$. Bisulphide of carbon also acts upon them, but the products do not appear to have been investigated. They readily combine with alkyl iodides, giving hydriodides of tertiary phosphines.

General properties of tertiary phosphines. The following tertiary bases have been obtained:

Name	Condition	Boiling-point
Trimethyl phosphine [1]	Liquid	40°–42°
Tri-ethyl " [2]	"	127°
Tri-isopropyl " [3]	"	?
Tri-isobutyl " [4]	"	215°
Tri-isoamyl " [5]	"	about 300°
Tri-phenyl " [6]	Solid	above 360°
Tri-benzyl " [6a]	"	"
Ethyl-isopropyl-isobutyl " [7]	Liquid	about 190°
Methyl-diphenyl " [8]	"	284°
Ethyl-diphenyl " [9]	"	293°
Di-ethyl-phenyl " [10]	"	220°
Di-methyl-ethyl " [11]	"	83°–85°
Di-ethyl-methyl " [12]	"	110°–112°
Di-ethyl-propyl " [13]	"	146°–149°
Di-ethyl-isoamyl " [14]	"	185°–187°
Di-ethyl-benzyl " [15]	"	252°–255°
Ethyl-dibenzyl " [16]	"	320°–330°
Dimethyl *p*-tolyl " [17]	"	210°
Di-ethyl *p*-tolyl " [18]	"	240°
Dimethyl xylyl " [19]	"	230°
Diethyl xylyl " [20]	"	260°

[1] [2] Hofmann a. Cahours, *A. Ch.* [3] 51, 35.
[3] [4] [5] Hofmann, *B.* 6, 292, 304.
[6] Michaelis, *B.* 15, 801.
[6a] Letts a. Blake, *l.c.*
[7] Hofmann, *B.* 6, 304.
[8] Michaelis, *A.* 181, 345.
[9] [10] Michaelis a. Link, *A.* 107, 210.
[11] [12] [13] [14] [15] [16] Collie, *C. J.* 1888, 714.
[17] [18] [19] [20] Czimatis, *B.* 15, 2014.

The tertiary phosphines hitherto obtained are, with the exception of triphenyl and tribenzyl phosphine, liquids at ordinary temperatures, having a powerful odour. They are insoluble in water, but soluble in ether &c. As a rule, they oxidise rapidly in contact with the air, fuming and growing hot, and in some cases igniting spontaneously. The product of this oxidation is a tertiary phosphine oxide of the formula R_3PO, and, no doubt, of the constitution $R_3P:O$.

The final products of the oxidation of phosphuretted hydrogen, and of primary, secondary, and tertiary phosphines, are therefore respectively: H_3PO_4, RH_2PO_3, R_2HPO_2, R_3PO, the amount of oxygen absorbed by the phosphine decreasing in a regular manner as the series is ascended.

The oxides of tertiary phosphines are solid substances of remarkable stability. They can in the majority of cases be distilled, and even boiled with nitric acid, without change. By no means as yet discovered can they be reduced. Hydracids combine with them, and they give crystalline compounds with a number of metallic salts, such as the chlorides of platinum, zinc, mercury, iron, cobalt, &c., also in some cases with chloride of acetyl, bromine, and sulphur.

Tertiary phosphines also combine with the elements of the sulphur group, forming compounds analogous to the oxides.

The salts of tertiary phosphines are readily obtained by dissolving the bases in acids. They are stable, and are not, as a rule, decomposed by water. Their compounds with hydracids have been chiefly studied; those containing oxy-acids have not been investigated (with very few exceptions). The haloid salts dissociate to a greater or less extent on heating. Their hydrochlorides combine with chloride of platinum to give chloroplatinates of normal composition.

Some of the tertiary phosphines combine with chloracetic acid to give hydrochlorides of phosphorised betaines. At present only two or three of these substances have been obtained – tri-methyl phosphorus betaine by Meyer (*B.* 4, 734), the corresponding ethyl derivative by Hofmann (*Pr.* 11, 530), and in addition to these two the closely allied compound, tri-methyl phosphorus benzo-betaine hydrochloride, by Michaelis a. Czimatis (*B.* 15, 2018), $(CH_3)_3PCl.C_6H_4.COOH$.

The compounds of these phosphorised betaines are stable and well-defined substances. Letts (*Tr. E.* 30, pt. 1, 285) has investigated the reactions and decompositions of the ethylated body, which are of some interest.

The hydrate and the salts of this betaine lose carbonic anhydride when heated, and give rise to the hydrate or salt of methyl-tri-ethyl-phosphonium

$$(C_2H_5)_3PX.CH_2.COOH = CO_2 + (C_2H_5)_3PX.CH_3,$$

a reaction which is entirely analogous to that occurring when the corresponding sulphur compounds (*thetines*) are heated: $(CH_3)_2SX.CH_2.COOH = CO_2 + (CH_3)_2SX.CH_3$. While it is perfectly different from that which the true (nitrogen) betaines experience, as they either dissociate into the original trialkyl-amine and the group $X.CH_2.COOH$ (or the products of its decomposition), or distil unchanged (Brühl, *A.* 177, 214).

Treated with caustic potash, all the salts of tri-ethyl phosphorus betaine yield tri-ethyl phosphine oxide: $(C_2H_5)_3PX.CH_2.COOH + 2KHO = (C_2H_5)_3PO + KX + CH_3.COOK + H_2O$.

Several of the tertiary phosphines combine directly and energetically with a molecule of bisulphide of carbon to give highly characteristic compounds, usually of a red colour, and possibly having the constitution, $R_3P{<}\begin{array}{l}S\\C{:}S\end{array}$. So characteristic and so readily formed is this compound in the case of tri-ethyl phosphine, that its production may be employed as a test either for bisulphide of carbon or for the phosphine itself. As yet these (bisulphide) compounds have been obtained only with methyl, ethyl, and iso-propyl phosphine, and with those of the aromatic phosphines containing ethyl or methyl groups.

According to Czimatis (*B.* 15, 2016) these mixed phosphines combine very easily with bisulphide of carbon if they contain methyl, the readiness with which combination occurs diminishing, however, in proportion to the molecular weight of the aromatic radicle, while, if they contain ethyl, combination occurs only slowly and with difficulty. Hofmann (*Tr.* 1860, 431) has somewhat exhaustively studied the compound of tri-ethyl phosphine and the bisulphide, which forms with explosive violence. Among its properties are the following: It is insoluble in water, difficultly soluble in ether, but easily dissolves in hot alcohol, from which it separates on cooling in red needles like chromic anhydride. From an ethereal solution it is deposited by spontaneous evaporation in large deep-red monoclinic crystals exhibiting dichroism, which melt at 95° and volatilise at 100°. It is soluble in strong hydrochloric acid, and if the solution is mixed with platinic chloride, a yellow amorphous compound is produced, $2(C_2H_5)_3PCS_2,PtCl_4$. When heated with silver oxide or nitrate, it is decomposed as follows: $(C_2H_5)_3PCS_2 + 2Ag_2O = Ag_2S + Ag_2 + CO_2 + (C_2H_5)_3PS$, and moist air produces a similar change. But if is heated with water to 100°C., the following reaction occurs:—

$$4(C_2H_5)_3PCS_2 + 2H_2O$$
$$= 2(C_2H_5)_3PS + (C_2H_5)_3PO + (C_2H_5)_2(CH_3)POH + 3CS_2.$$

Heated with sulphuretted hydrogen, it suffers the following change: $3(C_2H_5)_3PCS_2 + H_2S$
$= 2(C_2H_5)_3PS + (CH_2S)(C_2H_5)_3PCS_2 + CS_2$.

The action of halogens upon tertiary phosphines has not been very fully studied. Probably direct addition would occur in all cases. This has been proved to take place with tri-ethyl phosphine if the halogen is allowed to act very gradually upon it. The chloride $(C_2H_5)_3PCl_2$ thus obtained is crystalline, melting at 100° and volatilising readily, though its boiling-point is high. Similar compounds of bromine and iodine have been obtained.

Compounds of tri-methyl and tri-ethyl phosphine with mustard oils are formed easily, and give crystalline hydrochlorides. They, no doubt, have the constitution, $S{:}C{:}NR{:}PR_3$.

[*Note.*—Some of the aromatic tertiary phosphines, especially tri-phenyl phosphine, have properties which differ materially from those of other tertiary phosphines. Thus tri-phenyl phosphine is a crystalline solid having scarcely any odour, and it does not oxidise spontaneously. It is remarkably stable, and is not attacked by chlorine even when heated. The hydriodide and hydrochloride are formed when it is dissolved in the warm concentrated hydracids, and are crystalline, but on adding water they dissociate. By treating the phosphine with bromine and an alkali, or by oxidising it with hydrochloric acid and chlorate of potash, the hydrate $(C_6H_5)_3P(OH)_2$ is obtained as a crystalline solid. This when heated to 100° readily loses water, and is converted into the oxide, a substance which is not acted upon by bromine, oxygen, sulphur, &c. By dissolving the phosphine in fuming nitric acid a nitrate of the formula $(C_6H_5)_3P(NO_3)_2$ is obtained.]

Tertiary phosphines, apparently without exception, unite with alkyl iodides to form phosphonium salts.

General Properties of Quaternary Compounds (*Phosphonium Salts*). So many of these bodies have been obtained that a list appears inadvisable. It would include derivatives of the series C_nH_{2n+1} to the 5th term, one or two of the series C_nH_{2n-7}, and a large number of mixed phosphoniums containing various radicles, among which are vinyl, allyl, and ethylene.

The phosphonium salts are the most stable of all organic phosphorus compounds. None are decomposed by water, and most of them can be obtained readily in the crystalline state by evaporating their solutions.

As a rule, they are soluble in water and in alcohol. They are readily prepared from their iodides, either by double decomposition with a silver salt, or by first obtaining their hydrates (by the action of moist oxide of silver), and subsequently neutralising the solution with the acid.

The hydrates R_4POH are solid substances, having a powerful alkaline reaction and many properties similar to those of an alkali. Indeed, in the case of tetrethyl phosphonium hydrate, the only remarkable point of difference between it and caustic potash (so far as its reactions with metallic salts &c. are concerned) is that, when added to a zinc or aluminium salt, the zinc or aluminium hydrate, which is at first precipitated, is insoluble in an excess. Phosphonium hydrates are decomposed when heated, and in some cases, when their solutions are boiled or at the moment of production, into a tertiary phosphine oxide and a hydro-carbon,

$$R_4POH = R_3PO + R - H.$$

The action of heat upon the salts of the phosphoniums has been investigated in a number of cases, partly by Letts and N. Collie (*Tr. E.* 30, part 1, 213; *P. M.* August 1886), and partly by the latter chemist alone.

As regards the haloid salts, the chlorides decompose almost quantitatively into a hydrocarbon and a tertiary phosphine hydrochloride (Collie), furnishing an excellent method for 'retrograding' from quaternary to tertiary bodies.

'When the phosphonium chloride contains several ethyl groups, then if more than one of the latter is present, ethylene is always formed, *e.g.*

$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)P.HCl + C_2H_4.$$

But when only one ethyl group is present, then, although ethylene is still formed, two decompositions occur, *e.g.* (1)

$$2(C_2H_5)(CH_3)_3PCl = 2(C_2H_5)(CH_3)_2P.HCl + C_2H_4$$

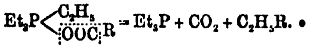
(2) $(C_2H_5)(CH_3)_3PCl = (CH_3)_3P.HCl + C_2H_4$.

If we compare the decomposition by heat of phosphonium chlorides with the decomposition of any of the compound ammonium salts, it must be with the hydroxides and not with the corresponding chlorides' (Collie, *C. J.* 1888, 636, 714), *e.g.*

$$\begin{aligned}(C_2H_5)_4PCl &= (C_2H_5)_3P.HCl + C_2H_4\\(C_2H_5)_4NOH &= (C_2H_5)_3N + C_2H_4 + H_2O\\(C_2H_5)_3(C_7H_7)P(OH) &= (C_2H_5)_3PO + C_7H_8\\(C_2H_5)_3(CH_3)NCl &= (C_2H_5)_3N + CH_3Cl.\end{aligned}$$

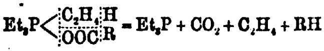
The effect of heat on phosphonium salts derived from oxyacids is completely different. In the case of the ethyl series at all events, they suffer, as a rule, at least two, and occasionally three, different and distinct decompositions. In one of these the molecule splits up into three new groups, consisting respectively of carbonic anhydride, a (paraffin) hydrocarbon, and the tertiary phosphine. In the other, two hydrocarbons are formed—namely, an olefine and a paraffin—in addition to carbonic anhydride and the tertiary phosphine. Whilst in the third, a totally different change occurs, in which only two products are formed—namely, the oxide of the tertiary phosphine and a ketone,

(1)



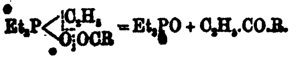
$$Et_3P<\begin{smallmatrix}C_2H_5\\OOC\,R\end{smallmatrix} = Et_3P + CO_2 + C_2H_5R.$$

(2)



$$Et_3P<\begin{smallmatrix}C_2H_4\,H\\OOC\,R\end{smallmatrix} = Et_3P + CO_2 + C_2H_4 + RH$$

(3)



$$Et_3P<\begin{smallmatrix}C_2H_5\\O\,OCR\end{smallmatrix} = Et_3PO + C_2H_5.CO.R.$$

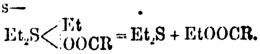
It is possible, if not indeed probable, that the third reaction occurs subsequently to the first, and that it really depends upon the reducing action of the triethylphosphine upon the carbonic anhydride, at the high temperature at which the decomposition usually occurs, whereby carbonic oxide is liberated, which combines with the hydrocarbon radicle *in statu nascendi*, forming a ketone:

$$Et_3P + CO_2 + (Et) + (R) = Et_3PO + EtCOR$$

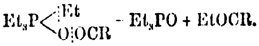
$$(\text{or } Et_3P + (OCO - R) + (Et) = Et_3PO + EtCOR).$$

If we merely consider the third kind of decomposition alone, it appears to be, to a certain extent, analogous to the decomposition which a sulphine compound suffers when heated, the difference depending on the greater attraction which phosphorus has for oxygen, compared with that of sulphur for the same element. In both cases a hydrocarbon group is detached from the molecule, and also the residue of the acid, but while with the sulphur compounds these two simply combine (forming a compound ether), and leave a hydrocarbon sulphide, in the case of the phosphonium salt the acid residue is reduced by the tertiary phosphine, and the group thus left combines with the hydrocarbon radicle, forming a ketone.

Thus—



$$Et_2S<\begin{smallmatrix}Et\\OOCR\end{smallmatrix} = Et_2S + EtOOCR.$$



$$Et_3P<\begin{smallmatrix}Et\\O\,OCR\end{smallmatrix} = Et_3PO + EtOCR.$$

A result of this kind is in perfect harmony with the views expressed by Crum Brown and Letts (*Tr. E.* 28, 371; Letts, *Tr. E.* 30, 285) regarding the analogies and differences existing between phosphorus and sulphur and their compounds.

When the phosphonium salts contain ethylene they suffer a different decomposition under the influence of heat; at least this has been ascertained to be the case with the bromide of bromo-ethylene-triethylphosphonium, and the bromide of hydroxy-ethylene-triethyl phosphonium, which decompose as follows (Hofmann):—

$$C_2H_4Br.P(C_2H_5)_3Br = HBr + (C_2H_3)(C_2H_5)_3PBr$$

$$C_2H_4(OH).P(C_2H_5)_3Br = H_2O + (C_2H_3)(C_2H_5)_3PBr$$

and also in that of the hydrate of ethylene-hexethyl diphosphonium, which decomposes according to the equation: $C_2H_4(P(C_2H_5)_3OH)_2 = C_2H_4 + (C_2H_5)_3P + (C_2H_5)_3PO + H_2O$.

Masson and Kirkland (*C. J.* 1889, 126) have studied the action of bromine and chlorine on the salts of tetrethyl phosphonium, the results showing a very close similarity between the polyhaloid derivatives of tetrethyl phosphonium and those of trimethyl sulphine and of tetramethyl ammonium previously described by Dobbin and Masson (*C. J.* 1885, 56; 1886, 846). The tendency to form solid poly-haloid compounds is, however, more marked. For the table, containing a list of the new substances, the methods of forming them, and their chief properties, the original memoir should be consulted.

Organic Phosphorus Compounds which cannot be placed in any of the above Groups.—A phosphorised cacodyl $(CH_3)_4P_2$ (the methyl analogue of liquid phosphoretted hydrogen) was obtained by Thénard (*C. R.* 21, 144, 25, 829) by the action of chloride of methyl on phosphide of calcium, and is interesting not alone as being the sole representative (as yet prepared) of its class, but also as having been probably the first phosphine obtained. Thénard describes it as a colourless, highly refractive liquid, of an odour recalling that of cacodyl itself, insoluble in water, and boiling at about 250°. It inflames spontaneously in contact with air, but if oxidised slowly gives a crystalline acid $(CH_3)_4P_2H_2O_4 = (CH_3)_2PHO_2$ (dimethyl phosphinic acid?), analogous to cacodylic acid. Treated with an excess of hydrochloric acid, it is converted into trimethyl phosphine, and a solid yellow substance $(CH_3)_2P_4$ (which is also formed in the original reaction), and which Thénard regarded as the methyl analogue of solid phosphide of hydrogen.

Michaelis (*B.* 10, 807) obtained a substance, which he named *diphosphenyl* or *phosphobenzene* $C_6H_5.P{:}P.C_6H_5$ (corresponding to azobenzene), by the action of phenyl phosphorous chloride on monophenyl phosphine $C_6H_5PCl_2 + C_6H_5PH_2 = (C_6H_5)_2P_2 + 2HCl$. It is a pale-yellow powder, insoluble in water, alcohol, and ether, but readily soluble in hot benzene, and is slowly oxidised by the air to $(C_6H_5)_2P_2O$. Treated with chlorine, phenyl phosphorous chloride is regenerated. With nitric acid it is oxidised to phenyl phosphinous (benzene phosphinic) acid $C_6H_5PH_2O_2$ if the acid is dilute, but to phenyl phosphinic (benzene phosphonic) acid $C_6H_5PH_2O_3$ if the acid is strong. Treated with hydrochloric acid, it reacts so as to regenerate the substances from which it is formed.

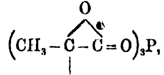
Michaelis (*B.* 7, 499) also obtained a substance, which he called *di-phospho-benzene hydrate* $C_6H_5.P{:}P.OH$, by the action of spontaneously inflammable phosphoretted hydrogen on phenyl phosphorous chloride. It is a yellow powder, soluble with ease in bisulphide of carbon, taking fire on exposure to air, and oxidised by nitric acid to phenyl phosphinic (benzene phosphonic) and phosphoric acids. In addition to the above, Michaelis (*B.* 11, 885) obtained a phenylated solid phosphide of hydrogen $(C_6H_5)HP_4$ by treating phenyl phosphorous chloride with a quantity of water insufficient for complete decomposition (for instance, by keeping it in a badly-stoppered bottle). It is a dark-yellow amorphous body, having a faint odour of phenyl phosphine, soluble in hot bisulphide of carbon, but insoluble in water, alcohol, and ether. Treated with chlorine it reacts as follows: $(C_6H_5)HP_4 + 6Cl_2 = 8PCl_3 + (C_6H_5)PCl_2 + HCl$. Nitric acid oxidises it to a mixture of phenyl phosphinic (benzene phosphonic) and phosphoric acids.

The action of phosphonium iodide on aldehydes has been studied by Girard (*A. Ch.* [7] 2, 50), while that of phosphoretted hydrogen and hydrochloric acid on the same bodies and on ketonic acids has been investigated by Messinger and Engels (*B.* 21, 328, 2919). Girard obtained products of addition containing four molecules of the aldehyde (valeric, propionic, salicylic, and benzoic) to one of phosphonium iodide.

Messinger and Engels obtained similar bodies by acting on the aldehydes with hydrochloric acid and phosphoretted hydrogen. The compounds thus formed are for the greater part solid, crystalline, and fairly stable. By treatment with water they are decomposed, and the aqueous solution gives the reactions of hydrochloric acid and phosphoretted hydrogen. Their constitution is probably represented by the formula $(R.CHOH)_4PCl$. Chloride of tetra-hydroxy-ethylidene phosphine $(C_2H_5O)_4PCl$ is decomposed by caustic potash into the free phosphine $(C_2H_5O)_3PC_2H_4O$ and the hydrate $(C_2H_5O)_4P(OH)$. Benzaldehyde and its mono-nitro- derivative give compounds which differ from those obtained in the fatty series in that they contain no hydracid.

Messinger and Engels have summarised the results of their researches as follows: (1) Phosphoretted hydrogen does not act on an aldehyde alone, but is absorbed if at the same time a hydracid is present. The absorption occurs more completely if the aldehyde is largely diluted with ether. (2) The aldehydes of the fatty series combine with a molecule of phosphoretted hydrogen and a molecule of hydracid, while those of the aromatic series combine with phosphoretted hydrogen only, though in order that the compound shall be formed the presence of the hydracid is necessary. (With benzoic aldehyde the compound has the formula $(C_6H_5COH)_1PH_3$.) (3) The phosphorised derivatives of the fatty series have an unpleasant smell, and are decomposed by water, while those of the aromatic series have no odour, and are nearly insoluble in water. All are soluble with difficulty in ether, and in some cases are insoluble.

By the substitution of a ketonic acid for an aldehyde in the above reaction, compounds are produced in certain cases. Thus lævulic acid gives an oil, and pyruvic acid a solid compound,

either $(CH_3.CO.CO)_3P$ or 

$$\left(CH_3-\overset{\overset{O}{\frown}}{C}-C{=}O\right)_3P,$$

which is a well-defined crystalline body, having neither basic nor acid properties, soluble in alkalis with decomposition, and also decomposed when heated with acids. It dissolves, however, without change in glacial acetic acid, and crystallises out on cooling. Boiled with water, it is decomposed into the substances from which it was originally produced. It forms crystalline compounds with aniline, phenyl hydrazine, and toluene diamine. E. A. L.

PHOSPHINIC ACIDS. The name oxy-ethyl-phosphinic acid has been given to the acid $CHMe(OH).PO(OH)_2$, which is got from aldehyde by successive treatment with PCl_3 and water. A more appropriate name for this acid is, however, oxy-ethane-phosphonic acid, the term phosphinic acid being reserved for acids $R'P(OH)_2$ containing trivalent phosphorus.

PHOSPHINO-BENZENE $C_6H_5PO_2$. *Phosphenylic anhydride.* [100°]. Formed from phosphenylic acid and $POCl_3$ (Michaelis a. Rothe, *B.* 25, 1747). White crystalline powder, v. sol. water, being reconverted into phosphenylic acid.

PHOSPHINO-ψ-CUMENE $C_6H_2Me_3PO_2$. [216°]. Formed from $C_6H_2Me_3.PO(OH)_2$ and $C_6H_2Me_3POCl_2$ (Michaelis a. Rothe, *B.* 25, 1749). Plates (from benzene), v. e. sol. chloroform. Converted by hot water into ψ-cumene phosphonic acid.

PHOSPHINO-TOLUENE $C_6H_4Me.PO_2$. *Toluene phosphonic anhydride.* [101°]. Formed from $C_7H_7.PO(OH)_2$ and $C_7H_7.POCl_2$ (Michaelis a. Rothe, *B.* 25, 1748). Converted by water into toluene phosphonic acid.

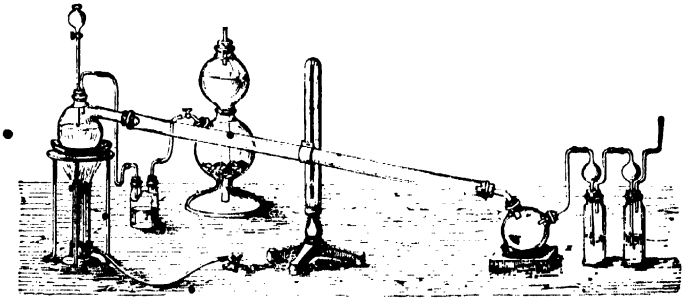
PHOSPHITES. Salts of the acid H_3PO_3; *v.* PHOSPHORUS, OXYACIDS OF, p. 151.

PHOSPHO-. *Use of this prefix applied to inorganic compounds;* for *phospho- acids, phospho- salts,* &c., *v.* the acids, salts, &c., to which *phospho-* is prefixed. Thus, phosphomolybdic acid and phosphomolybdates are described under MOLYBDENUM, ACIDS OF, AND THEIR SALTS.

PHOSPHO-AMIDO-BENZENE SULPHONIC ACID $PO_3H_2.NH.C_6H_4.SO_3H$. The *chloride* $C_6H_5NSPO_3Cl_2$ [158°] is formed from *p*-amido-benzene sulphonic acid and PCl_5 (Laar, *J. pr.* [2] 20, 250). It is converted by MeOH and alcohol into Me_3A''' [114°] and Et_3A''' [102°] respectively.

PHOSPHOBENZENE $C_6H_5P{:}PC_6H_5$. [150°]. Formed by slowly adding $C_6H_5PH_2$ to $C_6H_5PCl_2$ in a current of H (Köhler a. Michaelis, *B.* 10, 812). Yellowish powder, insol. water, alcohol, and ether, sol. benzene. On exposure to air it is oxidised to $(C_6H_5P)_2O$. Dilute HNO_3 oxidises it to phosphenylic acid. Chlorine, diluted with CO_2, forms $C_6H_5PCl_4$. Conc. HClAq forms phenyl-phosphine and $C_6H_5PO_2H_2$.

PHOSPHONIUM COMPOUNDS. PH_3 combines with the halogen acids HX to form compounds PH_3HX. The reactions of these compounds are most simply expressed by regarding them as salts of the radicle PH_4; following the analogy of the ammonium compounds, the bodies PH_4X are called *phosphonium* compounds. The mol. weights of these compounds have not been determined.



PHOSPHONIUM BROMIDE PH_4Br. H.F. $[PH^3,HBr] = 23{,}000$; $[P,H^4,Br] = 44{,}100$ (solid PH_4Br from H, solid P, and liquid Br) (Ogier, *C. R.* 89, 705). Colourless cubes; melts at 30°. V.D. 27·7 corresponding with that required by $PH_3 + HBr$ (Bineau, *A. Ch.* [2] 68, 431). Deliquesces in air; decomposed violently by water to PH_3 and HBrAq. Prepared by bringing together PH_3 and HBr (Serullas, *S.* 64, 238); by leading PH_3 into cold conc. HBrAq (Ogier, *C. R.* 89, 705); by heating conc. HBrAq with P to 100°-120° (Damoiseau, *C. R.* 91, 883).

PHOSPHONIUM CHLORIDE PH_4Cl. Formed in colourless crystals, melting at c. 25°, by subjecting a mixture of equal volumes HCl and PH_3 to 20 atmos. pressure at 14°, or by cooling to −25° under ordinary pressure (Ogier, *C. R.* 89, 705). Skinner (*Pr.* 1887. 283) found the critical temp. to be 48° under 95 atmos.; and the maximum vapour-pressure line to be below those of HCl and PH_3 at all temperatures; from −30° to 10° the line was normal, above 10° combination began; at temperatures near the critical the volume of liquid PH_4Cl formed was nearly half that of the liquid constituents.

PHOSPHONIUM HYDROXIDE. (?)PH_4OH. When PH_3 is strongly compressed in presence of water the PH_3 liquefies and floats on the water. If the pressure is now suddenly decreased, white crystals are formed; these crystals are probably PH_4OH (no analyses have been made). The production and dissociation of the crystals occur at definite pressures and temperatures. No formation occurs above 28° at any pressure. The crystals can be distilled from one part of the tube to another by gently warming (Cailletet a. Bordet, *C. R.* 95, 58). When equal volumes PH_3 and CO_2 are compressed in presence of water, below 22°, the gases disappear and white crystals are formed, which C. a. B. (*l.c.*) take to be a mixture of PH_4OH and the hydrate $CO_2.8H_2O$ discovered by Wroblewski (*C. R.* 94, 954).

PHOSPHONIUM IODIDE PH_4I. H.F. $[P,H^4,I] = 29{,}500$ (solid PH_4I from H, solid P, and solid I); $[PH^3,HI] = 24{,}100$ (solid PH_4I from gaseous PH_3 and HI) (Ogier, *C. R.* 89, 705). This compound was discovered by Labillardière and Gay-Lussac (*A. Ch.* [2] 6, 304), and more fully examined by Serullas (*S.* 64, 238) and H. Rose (*P.* 24, 151; 46, 636).

Formation.—1. By bringing together PH_3 and HI as gases or in conc. aqueous solutions.—2. By the action of gaseous PH_3 on I (Hofmann, *A.* 103, 355).—3. By the action of red P on conc. HIAq at 160° (Oppenheim, *Bl.* [2] 1, 163).—4. Along with P_2I_4, by the action of HI gas on P at ordinary temperatures (Damoiseau, *C. R.* 91, 883).—5. By the action of a little water on PI_3 (*v. Preparation*).—6. By the reaction of HI on H_3PO_2 and warming the product in CO_2 (Lissenko, *B.* 9, 1313).

Preparation.—P and I are combined in CS_2 solution, and the product is decomposed by a little water (Baeyer, *A.* 155, 269; Hofmann, *B.* 6, 286). Hofmann (*l.c.*) gives the following directions: 400 g. P are dissolved in the same weight of dry CS_2 in a retort of 1 litre capacity, and to this solution, *kept cool,* 680 g.

I are added by small portions. The *whole* of the CS_2 is then distilled off on a water-bath, an operation which takes 9 or 10 hours. The retort is then connected with a long wide condensing tube, and a two-necked globular receiver, from which a connecting tube passes to two condensing bottles, the first containing dilute HIAq, the second water (see fig.). Heat is then applied to the retort, gently at first, and 240 g. water are *slowly* added through the drop-funnel. PH_4I and HI are formed; the HI collects in the condensing bottles, and the PH_4I forms a crust, chiefly in the tube, and in smaller quantity in the globular receiver, which, to prevent stoppage, should be connected with the long tube by a wide tube. To prevent the liquid in the condensing-bottles from being forced back in consequence of the rapid absorption, a slow stream of CO_2 is passed through the apparatus during the whole operation. A well-conducted sublimation may be completed in 8 or 9 hours. When it is finished one end of the long condensing tube is closed with a cork, and the PH_4I is detached by means of a stout wire bent and sharpened at the end. Hofmann expresses the reaction thus: $13P + 9I + 21H_2O = 7PH_4I + 3H_4P_2O_7 + 2HI$. The PH_4I may be sublimed in dry HI.

Properties.—Large, clear, lustrous, pyramidal crystals; boils at c. 80°; may be sublimed in HI.

Reactions.—1. With *carbon compounds* reacts as a very energetic reducing agent, and is much used in preparing phosphines &c. (*v.* PHOSPHINES).—2. Decomposed rapidly by *water* or *alkali solution*, evolving non-inflammable PH_3 (*v.* PHOSPHORUS TRIHYDRIDE, *Preparation* 2, p. 136). 3. With *alcohol* forms EtI and PH_3; if the reaction is conducted in a sealed tube PEt_3 and PEt_4I are produced.—4. With *phosphorus trichloride* forms P_2I_4, HCl, PH_3, and solid P_2H (de Wilde, *B.* 16, 217).—5. PH_4I is inflamed by contact with many conc. *acids*, *e.g.* HNO_3, HCl, HBr, HI.

PHOSPHONIUM SULPHATE. When PH_3 is passed into H_2SO_4 at ordinary temperatures much heat is produced, S separates, and SO_2 is formed. The reaction is much slower if the acid is cooled by ice and salt; if the H_2SO_4 is cooled to −20° or −25° (by rapid evaporation of CH_3Cl) a syrupy liquid is formed, from which a white, crystalline, very deliquescent solid separates; this solid seems to be phosphonium sulphate [?$(PH_4)_2SO_4$] (Besson, *C. R.* 109, 644). Exposed to air, H_3PO_4, H_3PO_3, and H_3PO_2 are formed with SO_2, S, and a little H_2S; dissolves in water with hissing noise and evolution of PH_3, but no reduction of the H_2SO_4. M. M. P. M.

PHOSPHORIC ACIDS. In this article are described the three acids, H_3PO_4, HPO_3, and $H_4P_2O_7$; the salts of these acids are described under PHOSPHATES (p. 106); for the other oxyacids of P and their salts *v.* PHOSPHORUS, OXYACIDS OF, AND THEIR SALTS (p. 149). The oxide P_2O_5 is the anhydride of three acids: cold water added to P_2O_5 forms HPO_3, the long-continued action of moist air on HPO_3 produces $H_4P_2O_7$, and H_3PO_4 is formed by boiling for some time an aqueous solution of HPO_3 or $H_4P_2O_7$. The three acids may be formulated as $P_2O_5.H_2O$, $P_2O_5.2H_2O$, and $P_2O_5.3H_2O$ (*cf.* PHOSPHATES, p. 106).

ORTHOPHOSPHORIC ACID H_3PO_4. (*Phosphoric acid. Tribasic phosphoric acid.*) S.G. 1·88 (Schiff, *A.* 113, 183). Melts at 41·75°; liquid solidifies at 38°, temperature rising to 40·5° (Berthelot, *Bl.* [2] 29, 3). H.F. $[P,O^4,H^3]$ = 302,600 (formation of solid acid); 300,080 (formation of molten acid); $[P,O^4,H^3,Aq]$ = 305,290 (*Th.* 2, 225). Heat of fusion = −2520 (*Th.*, *l.c.*). One mol. w. of the molten acid in grams occupies 52·02 c.c. (*Th.*, *l.c.*). μ_A 1·3584, μ_D 1·363, μ_H 1·3746, for H_3PO_4Aq, S.G. 1·11 (=29 p.c.) (Gladstone, *C. J.* [2] 8, 101, 147). Affinity in aqueous solution = c. 25 (HNO_3 = 100) (Ostwald).

Formation.—1. By oxidising P, by long exposure to moist air (Leeds, *A.* 200, 286; Wenzell, *Ph.* [3] 14, 24), or by HNO_3, $HClO_3$, $HClO_4$, SO_3, NO_2, &c.; phosphates are formed by treating P with many metallic oxides, and with alkali carbonates.—2. By oxidising H_3PO_3Aq or H_3PO_2Aq by ClAq, BrAq, or IAq, HClOAq, HNO_3, or by Ag_2O or HgO; H_3PO_3Aq is oxidised to H_3PO_4Aq by standing in air.—3. By reaction of boiling water with P_2O_5, HPO_3, or $H_4P_2O_7$.—4. By burning PH_3 in moist air or O.—5. By reaction of water with $POCl_3$, or much water with PCl_5.—6. By oxidising, by HNO_3Aq, the mixture of H_3PO_3Aq and H_3PO_4Aq obtained in making HI by the action of P, I, and H_2O (Pettenkofer, *A.* 138, 57).—7. By decomposing many phosphates, *e.g.* $Ca_3P_2O_8$, by H_2SO_4; $Pb_3P_2O_8$ decomposed by H_2S in presence of water gives H_3PO_4Aq. For production from bones *v.* DICTIONARY OF APPLIED CHEMISTRY.—8. By decomposing $(NH_4)H_2PO_4$ by warm conc. HClAq, separating NH_4Cl after cooling, and evaporating with HNO_3 till all NH_4 salts and HCl are expelled (Joly, *C. R.* 102, 316).

Preparation.—One part P is mixed with 10–12 parts HNO_3Aq (free from H_2SO_4) S.G. 1·2 (the acid must not be more conc. than this) (Kranthausen, *Ar. Ph.* [3] 10, 410) in a large retort, the beak of which passes loosely into a receiver placed in cold water; about ·3 to ·6 g. I is added for 100 g. P; the retort is gently warmed until the P has completely dissolved. Should any liquid distil over, it is returned to the retort. Oxidation proceeds more regularly, and at a lower temperature, when a little I is present than when HNO_3Aq alone is used (Horn, *Ph.* [3] 10, 468; Ziegler, *D. P. J.* 258, 239). If I is not added, and the acid is more conc. than S.G. 1·2, violent explosions may occur. Von Schrötter recommends the employment of amorphous P and acid more conc. than S.G. 1·2. When the P is all dissolved, the contents of the retort are boiled, and 5–7 parts of the liquid are distilled off (the distillate is HNO_3Aq, S.G. 1·1 to 1·14). During this part of the process copious evolution of NO_2 often occurs, due to the oxidising action of HNO_3 on H_3PO_3. According to Reinsch (*J. pr.* 28, 385) little NO, but much N, is formed during the oxidation of P by HNO_3 at boiling temperature in absence of air, but much NO is produced in an open vessel at low temperatures. The liquid in the retort is evaporated in a basin until the fumes cease to turn blue litmus red. During this operation NO_2 is often freely given off (especially if little or none of this gas has been produced in the retort), as the oxidation of H_3PO_3 is not always completed until the liquid has been evaporated; should no gas be evolved it is advisable to add a little conc. HNO_3Aq to the liquid in the basin after concentration, and again evaporate till acid fumes cease to come off. The liquid in the basin is diluted with water, saturated with H_2S, kept in a warm place for 24 hours, and filtered from As_2S_3 (and Sb_2S_3); which may separate (ordinary P generally contains As). The filtrate is then evaporated, at a temperature not above 150°, until it becomes a thick syrup on cooling, and the cold liquid is placed over H_2SO_4, when it slowly solidifies. By evaporating the syrup *in vacuo* over H_2SO_4, crystalline tablets of H_3PO_4 are obtained; a fragment of these placed in acid S.G. 1·8 (or more conc.) immediately causes crystallisation (Huskisson, *B.* 17, 161).

Properties.—A thick semi-solid mass, S.G. 1·88 (Schiff, *A.* 113, 183); also obtained in crystalline tablets by evaporation of the syrup S.G. 1·88 *in vacuo* over H_2SO_4. According to Berthelot (*Bl.* [2] 29, 3) crystals of H_3PO_4 melt at 41·75°; the liquid solidifies at 38°, with a rise of temperature to 40·5°. H_3PO_4 is tribasic, forming salts $M^IH_2PO_4$, $M^I_2HPO_4$, and $M^I_3PO_4$ (*v.* PHOSPHATES, p. 107). The affinity of H_3PO_4 in aqueous solution is about 25 ($HNO_3 = 100$) (Ostwald). Both crystalline and syrup-like H_3PO_4 deliquesce in air. The acid dissolves readily in water; Hager (in his commentary to the *Pharmacopœia Germanica*) gives the adjoining table.

Sp. gr.	Per cent. P_2O_5	Per cent. H_3PO_4	Sp. gr.	Per cent. P_2O_5	Per cent. H_3PO_4
1·809	68	93·67	1·325	35	48·21
1·800	67·5	92·99	1·319	34·5	47·52
1·792	67	92·30	1·314	34	46·84
1·783	66·5	91·61	1·308	33·5	46·15
1·775	66	90·92	1·303	33	45·46
1·766	65·5	90·23	1·298	32·5	44·77
1·758	65	89·54	1·292	32	44·08
1·750	64·5	88·85	1·287	31·5	43·39
1·741	64	88·16	1·281	31	42·70
1·733	63·5	87·48	1·276	30·5	42·01
1·725	63	86·79	1·271	30	41·33
1·717	62·5	86·10	1·265	29·5	40·64
1·709	62	85·41	1·260	29	39·95
1·701	61·5	84·72	1·255	28·5	39·26
1·693	61	84·03	1·249	28	38·57
1·685	60·5	83·34	1·244	27·5	37·88
1·677	60	82·65	1·239	27	37·19
1·669	59·5	81·97	1·233	26·5	36·50
1·661	59	81·28	1·228	26	35·82
1·653	58·5	80·59	1·223	25·5	35·13
1·645	58	79·90	1·218	25	34·44
1·637	57·5	79·21	1·213	24·5	33·75
1·629	57	78·52	1·208	24	33·06
1·621	56·5	77·83	1·203	23·5	32·37
1·613	56	77·14	1·198	23	31·68
1·605	55·5	76·45	1·193	22·5	30·99
1·597	55	75·77	1·188	22	30·31
1·589	54·5	75·08	1·183	21·5	29·62
1·581	54	74·39	1·178	21	28·93
1·574	53·5	73·70	1·174	20·5	28·24
1·566	53	73·01	1·169	20	27·55
1·559	52·5	72·32	1·164	19·5	26·86
1·551	52	71·63	1·159	19	26·17
1·543	51·5	70·94	1·155	18·5	25·48
1·536	51	70·26	1·150	18	24·80
1·528	50·5	69·57	1·145	17·5	24·11
1·521	50	68·88	1·140	17	23·42
1·513	49·5	68·19	1·135	16·5	22·73
1·505	49	67·50	1·130	16	22·04
1·498	48·5	66·81	1·126	15·5	21·35
1·491	48	66·12	1·122	15	20·66
1·484	47·5	65·43	1·118	14·5	19·97
1·476	47	64·75	1·113	14	19·28
1·469	46·5	64·06	1·109	13·5	18·60
1·462	46	63·37	1·104	13	17·91
1·455	45·5	62·68	1·100	12·5	17·22
1·448	45	61·99	1·096	12	16·53
1·441	44·5	61·30	1·091	11·5	15·84
1·435	44	60·61	1·087	11	15·15
1·428	43·5	59·92	1·083	10·5	14·46
1·422	43	59·23	1·079	10	13·77
1·415	42·5	58·55	1·074	9·5	13·09
1·409	42	57·86	1·070	9	12·40
1·402	41·5	57·17	1·066	8·5	11·71
1·396	41	56·48	1·062	8	11·02
1·389	40·5	55·79	1·058	7·5	10·33
1·383	40	55·10	1·053	7	9·64
1·377	39·5	54·41	1·049	6·5	8·95
1·371	39	53·72	1·045	6	8·26
1·365	38·5	53·04	1·041	5·5	7·57
1·359	38	52·35	1·037	5	6·89
1·354	37·5	51·66	1·033	4·5	6·20
1·348	37	50·97	1·029	4	5·51
1·342	36·5	50·28	1·025	3·5	4·82
1·336	36	49·59	1·021	3	4·13
1·330	35·5	48·90	1·017	2·5	3·44

According to Sieber (*Ph.* [3] 9, 598), H_3PO_4Aq containing ·5 p.c. acid (or even less) stops putrefaction.

Reactions.—1. *Heated* to c. 213°, $H_4P_2O_7$ is formed; at a higher temperature HPO_3 begins to be formed, and at full red heat only HPO_3 is produced.—2. Is not decomposed by electric current, according to Luckow (*Fr.* 1880. 1); by electrolysis of H_3PO_4Aq, using C poles, Bartoli a. Papasogli (*G.* 11, 239, 468; 12, 113, 117, 125) obtained a substance containing C and P, which they called *phosphomellogen.* Molten H_3PO_4, on electrolysis, gives off H and O, and forms $H_4P_2O_7$, then HPO_3, and then H_3PO_3, and inflammable P hydride (Janecek, *C. C.* 1888. 273).—3. It is not certain whether *water* forms hydrates with H_3PO_4, when the acid is dissolved in water (*v.* Crompton, *C. J.* 53, 116).—4. By adding *alkali* solutions to H_3PO_4Aq till neutral, salts M_2HPO_4 are formed; addition of considerable excess of alkali produces M_3PO_4. For connection between quantity of alkali added and electrical conductivity of the solution, *v.* D. Berthelot (*C. R.* 113, 851).—5. Reacts with *phosphorus pentachloride* at ordinary temperatures to form $POCl_3$ and HCl; with *phosphorus oxychloride* when hot to form HPO_3 and HCl, or $H_4P_2O_7$ and HCl, according to the relative quantities of H_3PO_4 and $POCl_3$; with *phosphorus trichloride* to form HPO_3, H_3PO_3, and HCl; and with *metaphosphoric acid* to form $H_4P_2O_7$ (Geuther, *J. pr.* [2] 8, 359). For reactions of salts of H_3PO_4 *v.* PHOSPHATES, p. 107. For *nitriles* of H_3PO_4 *v.* PHOSPHAM (p. 104), and PHOSPHORUS OXYNITRIDE (p. 144); for *amide* and *imido amide* *v.* PHOSPHAMIDES (p. 105) and PHOSPHAMIDO-IMIDE (p. 105). For *thio-amide* *v.* PHOSPHORUS SULPHOCHLORIDE, *Reaction* 7 (p. 148).

PYROPHOSPHORIC ACID, $H_4P_2O_7$.

Preparation.—1. An impure acid, containing some H_3PO_4 and HPO_3, is obtained by heating H_3PO_4 to 213° until a little dissolved in cold

water gives a white pp., without a trace of yellow Ag_3PO_4, with $AgNO_3Aq$, after neutralisation by NH_3Aq.—2. Péligot (*A. Ch.* [2] 73, 286) obtained crystals of $H_4P_2O_7$ by allowing glacial HPO_3 to stand in moist air in a bottle for some years. Crystals of H_3PO_4 formed at the top of the bottle, a liquid S.G. 1·7 in the middle, and crystals of $H_4P_2O_7$ at the bottom.—3. An aqueous solution of $H_4P_2O_7$ is obtained by decomposing $Pb_2P_2O_7$ suspended in water by H_2S, filtering from PbS, and allowing the H_2S to evaporate at the ordinary temperature (Geuther, *J. pr.* [2] 8, 359).—4. By heating together H_3PO_4 and HPO_3 in the ratio HPO_3:H_3PO_4.—5. By the reaction of H_3PO_4 and $POCl_3$ in the ratio $5H_3PO_4$:$POCl_3$ (G., *l.c.*).

Properties and Reactions. — A glass-like solid; Péligot (*A. Ch.* [2] 73, 286) obtained the acid in non-transparent crystals resembling loaf-sugar. Dissolves readily in water; dilute solutions remain unchanged at ordinary temperatures (Graham), when heated H_3PO_4Aq is formed. The solution, neutralised by NH_3Aq, gives a white pp. of $Ag_4P_2O_7$ with $AgNO_3Aq$. $H_4P_2O_7$ is tetrabasic; for description of salts *v.* PHOSPHATES, p. 107. When heated with PCl_5 reacts according to relative masses used: (1) $H_4P_2O_7 + 5PCl_5 = 7POCl_3 + 4HCl$; (2) $H_4P_2O_7 + PCl_5 = 2HPO_3 + POCl_3 + 2HCl$ (Geuther, *J. pr.* [2] 8, 359). PCl_3 heated with $H_4P_2O_7$ forms HPO_3, H_3PO_3, and HCl; $POCl_3$ produces HPO_3 and HCl (G., *l.c.*). For the *amic acids* of $H_4P_2O_7$, and other amic acids derived from hypothetical condensed pyrophosphoric acids, *v.* PHOSPHAMIC ACIDS (p. 105).

METAPHOSPHORIC ACID HPO_3 (Graham, *T.* 1833. 253).

Preparation.—1. H_3PO_4Aq or $H_4P_2O_7Aq$ is evaporated to dryness and the residue heated to full redness until H_2O ceases to be evolved.—2. PbP_2O_6 is suspended in water and decomposed by H_2S, the filtrate from PbS is evaporated to dryness and heated to full red heat.—3. By heating together H_3PO_4 and $POCl_3$ in the ratio $2H_3PO_4$:$POCl_3$, or $H_4P_2O_7$ and $POCl_3$ in the ratio $2H_4P_2O_7$:$POCl_3$, or $H_4P_2O_7$ and PCl_3 in the ratio $3H_4P_2O_7$:PCl_3 (Geuther, *J. pr.* [2] 8, 359).—4. By reacting on H_3PO_3Aq with Cl or Br.—5. A solution of P_2O_5 in a little cold water contains HPO_3.

Properties and Reactions.—According to Tammann (*J. pr.* [2] 45, 417), two varieties of HPO_3 exist; one is a soft, silky mass, formed by heating H_3PO_4 until one molecule of H_2O is removed; the other is obtained by heating H_3PO_4 until it sets to a glassy mass on cooling. A transparent, colourless, glass-like solid. Ordinary *glacial phosphoric acid* is impure HPO_3, generally containing considerable quantities of Na salts, and some H_3PO_4 or $H_4P_2O_7$. Very hygroscopic, soon deliquesces in air. Volatilised completely at bright-red heat (H. Rose, *A.* 76, 2, 13; 77, 319). Not dehydrated by heat nor by the action of dehydrating agents. Heated with PCl_5 forms $POCl_3$ and HCl, HPO_3Aq is changed to H_3PO_4Aq, slowly at ordinary temperatures, more rapidly by boiling or by adding HClAq or HNO_3Aq. (For rate of change *v.* Sabatier, *C. R.* 106, 63; 108, 738, 804.) HPO_3 is monobasic; several series of metaphosphates, some polymeric and some isomeric, exist (*v.* PHOSPHATES, p. 106).

M. M. P. M.

PHOSPHORIC ETHER *v.* TRI-ETHYL-PHOSPHATE.

PHOSPHOROUS ACID H_3PO_3 *v.* PHOSPHORUS, OXYACIDS OF, p. 149.

PHOSPHOROUS ETHER *v.* ETHYL PHOSPHITES.

PHOSPHORSELLIC ACID *v.* vol. iii. p. 782.

PHOSPHORUS. P. At. w. 30·96. Mol. w. 123·84 and 61·92 (*v. infra*). *The following data apply to ordinary crystalline* P. Melts at 44·3° (Schrötter, *P.* 81, 299); at 44·2° (Desains, *C. R.* 23, 149). Boils at 290° (Pelletier, *A. Ch.* 4, 3); at 250° (Heinrich, *Gm.-K.* [6th ed.] 2, 102); at 287·3° at 762 mm., 165° at 120 mm. (Schrötter *J.* 1847-48). S.G. 1·8367 at 0°, 1·8232 at 20°. 1·8068 at 40° (Pisati a. de Franchis, *B.* 8, 70). S.G. at b.p. 1·485 (Ramsay a. Masson, *C. J.* 39, 50). V.D. 62·7 to 65·1 at 500°-1000° (Dumas, *A. Ch.* [2] 49, 210; Mitscherlich, *A.* 12, 137; Deville a. Troost, *C. R.* 49, 241). V.D. at 1700° c. 45 (Biltz a. V. Meyer, *B.* 22, 725). S.H. solid, −78° to 10° = ·1699, 7° to 13° = ·1884 (Regnault, *A. Ch.* [3] 26, 286); 13° to 36° = ·202 (Kopp, *T.* 155, 71); *liquid* = ·2045 (Person, *A. Ch.* [3] 21, 295). S.V.S. c. 17; at b.p. c. 21 (Ramsay a. Young, *C. J.* 39, 50). S.V. of P in PCl_3 and PBr_3 = 25·3. C.E. ·0003674 + ·00000211*t* from 50° to 280°; C.E. liquid P from 50° onwards = ·0005167 + ·00000037 (*t* = 50) (*Graham-Otto*, 1881. II. 2, 283; *v.* also Kopp, *A.* 93, 129; Pisati a. de Franchis, *B.* 8, 70; Leduc, *C. R.* 113, 259).

Refraction-equivalent $\left(\frac{\mu-1}{d} . \text{ At. w.}\right)$ 14·93; spec. refractive power for H line α = ·4816 (Haagen, *P.* 131, 117). H.C. $[P^2, O^5]$ = 369,900, $[P^2, O^5, Aq]$ = 405,500, $[P^2, O^3, Aq]$ = 250,060 (*Th.* 2, 408). Crystallises in dodecahedra and octahedra (Trantwein a. Buchner; Whewell, *C. N.* 39, 144; Story-Maskelyne; Mitscherlich, *B. B.* 1855. 409; Hermann, *B.* 6, 1415). For spectrum, *v. B. A.* 1884. 434.

The following data apply to red amorphous P. S.G. 2·106 at 17 (Schrötter, *J.* 3, 262), 2·19° (Hittorf); in powder S.G. = 1·964 at 10° (S.), 2·6 (H.). S.H. 15° to 98° = ·1698 (Regnault, *P.* 89, 496). S.V.S. c. 15. E.C. (Ag at 0° = 100) ·0000123 at 20° (Matthiessen, *P.* 103, 428). H.C. $[P^2, O^5]$ = 362,820 (Troost a. Hautefeuille, *C. R.* 78, 748).

The following data apply to crystalline metallic P. S.G. 2·34 at 155°. S.V.S. c. 13·2 (Hittorf, *P.* 126, 193).

Historical.—In the early part of the seventeenth century a substance was prepared by heating heavy spar with combustible organic matter, *e.g.* egg-white and charcoal, and this substance glowed in the dark (Kopp, *Geschichte der Chemie*, iv. 42). From this time the name phosphorus was given to any substance which emitted light in the dark without being ignited (φωσφόρος = light-bearer). The substance now known as phosphorus was prepared for the first time about 1670; Brand seems to have been the discoverer, but the discovery is sometimes attributed to Kunkel or to Boyle (for details *v.* Kopp's *Geschichte der Chemie*, iii. 327).

For a long time P was prepared in very small quantities; it was obtained by evaporating urine, mixing the residue with sand, and heating in a very hot fire. In 1737 charcoal was mixed with the sand and urine-residue. The discovery of

**phosphates in bones by Scheele in 1771, and in minerals by Gahn in 1780, led to the preparation of P on a comparatively large scale. The discovery of P played an important part in the development of the phlogistic theory. Phosphorus was supposed to be a compound of phlogiston with the acid which was formed when P was burnt; this acid was composed of phlogiston and muriatic acid according to Stahl, and of vitriol and muriatic acid according to Hofmann. Marggraf in 1743 determined that P increased in weight when burnt, and that P was obtained by heating phosphoric acid with combustible matter. In 1777 and 1780 Lavoisier showed that P was a constituent of phosphoric acid (*cf.* Kopp, *l.c.*).

Occurrence.—P is not found uncombined. Phosphates of Al and Ca occur in large quantities in many rocks; phosphates of Fe, Pb, Mg, and NH_4 &c. are also widely distributed minerals. Coprolites (the fossilised excrements of former land-animals) and guano (the excrement of certain birds) consist very largely of Ca phosphate. Phosphates also occur in some kinds of coal (Carnot, *C. R.* 99, 154). Phosphates of Ca and Mg are found in the ashes of plants and the bones of animals; P occurs in combination with C, H, and N in the yolk of eggs, in blood, in semen, and in nerve and brain matter.

Formation.—Ordinary phosphorus is formed: 1.—By heating $CaPO_3$ with powdered charcoal, $3Ca(PO_3)_2 + 10C$
$= 4P + 10CO + Ca_3(PO_4)_2$; or with SiO_2 and charcoal, $2Ca(PO_3)_2 + 10C + 2SiO_2$
$= 4P + 10CO + 2CaSiO_3$.—2. By reducing $Pb_3(PO_4)_2$ with charcoal (Donovan, *P. M.* [4] 2, 202; Fourcroy a. Vauquelin, *Gmelin's Handb.* [6th edit.] i. 2, 95).—3. By decomposing a strongly-heated mixture of $Ca_3(PO_4)_2$ and C by HCl (Cari-Montrand, *C. R.* 38, 864).

Red phosphorus is formed: 1. By the action of light, heat, or electricity on ordinary P, whether the P be solid or in solution, dry or moist, at ordinary temperature or at −14° (Schrötter, *W. A. B.* 1, 130; 8, 241; 9, 414; Corenwinder, *A. Ch.* [3] 30, 242; Lallemand, *C. R.* 70, 182; Hittorf, *P.* 126, 193; V. Meyer, *B.* 15, 297; Grove, *C. J.* 16, 269).—2. By heating common P with a little I. One part of I suffices to transform c. 100 parts of P into the red variety, by melting the P, mixing in the I, and heating again; the mass becomes red at 100°, at 120°-130° a red powder separates, at 200° a more or less explosive action occurs and the change is complete (Brodie, *J. pr.* 58, 171).—3. By adding a little I to a solution of common P in CS_2, evaporating to dryness, adding water, and washing with CS_2 (Corenwinder, *A. Ch.* [3] 30, 242; Lallemand, *C. R.* 70, 182; Brodie, *J. pr.* 58, 171). Rüdorff (*P.* 128, 463) supposed the red substance thus formed to be a hydride of P.

1. **Crystalline ordinary phosphorus** is formed: 1. By heating red P in a vacuous sealed tube to 447° (Hittorf, *P.* 126, 193).—2. By dissolving ordinary P in molten lead and crystallising therefrom (H., *l.c.*).

Preparation.—1. The details of the preparation of **ordinary phosphorus** from bone-ash are described in DICTIONARY OF APPLIED CHEMISTRY, vol. iii. Ordinary P frequently contains notable quantities of As, derived from the H_2SO_4 used; this can be removed only by repeated treatment with dilute HNO_3Aq, S.G. 1·1, a process which involves the loss of about $\frac{5}{8}$ of the P (Herz a. Bärwald, *B. B.* 32, 2, 133; *cf.* Dulk, *ibid.* 34, 1, 247; also Wackenroder, *J. pr.* 2, 340; and Liebig, *A.* 11, 260). Traces of red P may be removed by shaking in a closed vessel with conc. $K_2Cr_2O_7$Aq and H_2SO_4 (Wöhler, *A.* 45, 249). Lockyer (*C. N.* 40, 101) found that a specimen of dry P gave off considerable quantities of H when heated *in vacuo*.

2. **Red or amorphous phosphorus.**—A small flask of hard glass is fitted with a good cork carrying a short tube and an exit-tube which dips just beneath the surface of a little Hg; the entrance tube is fitted with a stopcock. Dry CO_2 is passed through the apparatus for some time; a dry stick of common P is then placed in the flask, and the stream of CO_2 is continued for a little, after which the stopcock is closed, and the flask is heated on a sand-tray or in an oil-bath, to 240°-280°, for 50-60 hours. After cooling, a layer of red P is found at the bottom of the flask, generally covered by a mixture of the two kinds of P. The ordinary P is melted by running in a little water at 50°-60°; the water and melted P are poured off; the residual red P is washed repeatedly with CS_2 (addition of $CaCl_2$Aq, 38°-39° *Beaumé*, causes the CS_2 solution to rise to the surface; Nicklès, *C. R.* 42, 646), or with boiling KOHAq S.G. 1·3, and then with water containing a little HNO_3; the red P is finally washed with water, and dried at c. 100° (Schrötter, *W. A. B.* 1, 130; 8, 241; 9, 414).

The change of common into red P occurs in ten minutes by heating the former to 300° in sealed tubes of thick glass, from which the air has been pumped out (Hittorf, *P.* 126, 193; V. Meyer, *B.* 15, 297).

3. **Crystalline metallic phosphorus.** Hittorf (*P.* 126, 193) claimed to have formed a distinct variety of P by heating red P in sealed tubes of hard glass to c. 447° (in vapour of S); and also by dissolving common P in molten lead and crystallising. A wide tube of hard glass is closed at one end, filled to $\frac{1}{4}$ with common P, and then filled with pieces of lead; the open end is narrowed, and the air is pumped out of the tube, which is then sealed. The tube is embedded in calcined MgO, placed in an iron tube, and heated above the melting-point of Pb for 8-10 hours. After cooling, the Pb is dissolved in HNO_3Aq, S.G. 1·1, and violet-black crystals of P remain; these crystals have not, however, been obtained quite free from lead.

Properties.—P exists in three, and perhaps in more than three, modifications.

1. ***Ordinary, octahedral, or stick phosphorus*** is a semi-transparent, colourless, crystalline solid, with a very distinct smell. The smell is very probably due to a mixture of ozone and P_2O_3, formed by the oxidation of the P (Schönbein, *P.* 65, 377; Thorpe a. Tutton, *C. J.* 57, 573). When melted and cooled quickly P is opaque; when cooled slowly it is nearly as clear as water. P must be kept under water; if the water is free from air the P remains transparent (Baudrimont, *C. R.* 61, 857). In ordinary water**

P becomes covered with a whitish film, but this again becomes transparent at c. 50° (H. Rose, *P.* 27, 563; Baudrimont, *l.c.*). According to Marchand (*J. pr.* 20, 506) the white film contains from ·4 to ·7 p.c. water; Pelouze (*A. Ch.* [2] 50, 83) regarded this substance as a hydrate of P, and Mulder (*J. Ph.* 23, 20) as a compound of oxide with hydride of P. When melted in large quantity and allowed to cool slowly, fairly large dodecahedral and octahedral crystals separate (Hautwein a. Buchner, *Kastn. Arch.* 10, 127, 504; Whewell, *C. N.* 39, 144; Hermann, *B.* 6, 1415). At ordinary temperatures P is as soft as wax; when cooled it becomes brittle. Exposed to light, P soon becomes yellow and then red on the surface. In a vacuum tube, or in a tube filled with an indifferent gas, P easily sublimes in colourless, transparent, very lustrous crystals (Hermann, *B.* 6, 1415; Mitscherlich, *B. B.* 1855. 409; Blondlot, *C. R.* 63, 397; Desains, *C. R.* 23, 149). Melted P often remains liquid many degrees below its m.p.; this is shown especially when P is melted by warming with alcoholic KOH solution, or when a solution of P in CS_2 is gradually evaporated under water (H. Rose, *P.* 32, 469; Kallhofert, *J. pr.* 50, 1). In some cases P remains liquid at c. −15°. P may be obtained in finely-divided particles by melting it under water, and shaking carefully in a flask until the P solidifies; if pure P is melted under a solution of sugar, gum, dextrin, NH_4Cl, $(NH_4)_2CO_3$, &c., and shaken until it solidifies, the P is obtained in a state of extremely fine division (Casaseca, *J. Ph.* 16, 202; Blondlot, *J.* 1865. 126; Schiff, *A.* 118, 88; also *A. Suppl.* 4, 37). P is slightly sol. water, alcohol, ether, ethereal and fatty oils, and hot conc. acetic acid (Vulpius, *Ar. Ph.* [3] 13, 38). Water shaken with P loses the smell and taste of P, and ceases to glow in the dark when it has been exposed to air for a time (Müller, *B.* 3, 84). P is very soluble in CS_2, S_2Cl_2, and liquid P_2S.

P volatilises in water-vapour, even at the ordinary temperature; when P is distilled in steam and the distillate is cooled rapidly, the P is obtained as a white snow-like mass (Remsen a. Kaiser, *Am.* 4, 459); it is also often obtained in this form by distilling crude HIAq containing P (Hell, *J.* 1883. 312).

P oxidises very easily; slowly when exposed to low temperatures, and more rapidly as the ignition-temperature, 60°, is approached. When P is burnt in air or O it emits very bright yellow-white light, and much heat is produced. But if H is passed over slightly warmed P, or if a stream of the warm gas is charged with a very little P, the issuing gas glows with a very feeble greyish-white light, scarcely visible in daylight; the temperature of this flame is very low: if the H is ignited an emerald-green cone appears in the interior of the H flame (for spectrum of this green cone *v.* Christofle a. Beilstein, *C. R.* 56, 399; Salet, *A. Ch.* [4] 28, 56). The glowing of P in the dark was formerly supposed to be due to the evaporation of the P (Corne, *J. Ph.* [5] 6, 17; Marchand, *J. pr.* 50, 1). It was shown that P glows in an indifferent gas only when small quantities of O are present; also that P neither oxidises nor glows in pure O at the ordinary pressure, but only when the O is diluted with an indifferent gas or the pressure is diminished; and also that the glowing is stopped by the presence of H_2S, PH_3, SO_2, CS_2, Br, Cl, N_2O, NO_2, &c. (Fischer, *J. pr.* 35, 342; 39, 48; Schrötter, *J. pr.* 58, 158; Müller, *B.* 3, 84; Joubert, *C. R.* 78, 1853; Deschamps, *C. R.* 52, 355; Müller-Erzbach, *B.* 12, 2130; Chappuis; *Bl.* [2] 35, 419; *cf.* Thorpe, 'On the Glow of Phosphorus,' *N.* 41, 523). Much work has been done to determine whether ozone or H_2O_2, or both, is formed when P oxidises in moist air; the question is not yet finally settled (McLeod, *C. J.* 37, 118; Kingzett, *C. J.* 37, 792); Leeds (*N. Y. Acad. of Sciences*, 1, 363, and 3, 150) has given a full index to the memoirs on the subject. Schmid (*J. pr.* 98, 414) determined that ozone is not formed when P oxidises in dry O. P is extremely poisonous; the lethal dose for adults is from ·2 to ·5 g. Burns with P are very dangerous; the parts should be rapidly and thoroughly washed with dilute bleaching powder solution.

The atomic weight of P has been determined, (1) by ppg. Ag and Au solutions by P and determining the ratio of Ag : P and Au : P (Berzelius, *G. A.* 53, 433; *P.* 8, 17); (2) by finding the Ag needed to ppt. Cl from PCl_3 (Pelouze, *C. R.* 20, 1047; Dumas, *A. Ch.* [3] 55, 174); (3) by oxidising red P in O to P_2O_5 (Schrötter, *J. pr.* 53, 435); (4) by analysing and determining V.D. of PCl_3, PF_5, &c.; (5) by measuring S.H. of P.

Determinations of the S.G. of P vapour made by Dumas, Mitscherlich, and Deville a. Troost at temperatures from 500° to 1000° gave numbers agreeing with the molecular wt. $P_4 = 124$. Biltz a. V. Meyer (*B.* 22, 725) obtained the values 52·5 at 1480°, 46·7 at 1680°, and 45·5 at 1700° for V.D. of P, showing that at a white heat the mol. formula is probably P_2 (V.D. = 31).

The mol. wt. of ordinary P in solution in C_6H_6 was determined by Paterno a. Nasini (*B.* 21, 2153) by the cryoscopic method; values were obtained between P_2 and P_4. Hertz, using the same method and the same solvent, obtained the value $124 = P_4$ (*Z. P. C.* 6, 358). Beckmann also found $124 = P_4$ for P in solution in CS_2 by the method of raising of boiling-point of the solvent (*Z. P. C.* 5, 76).

The action of light, heat, or electricity on P changes it into allotropic red P. Light affects the change whether the P be in air or another gas, or *in vacuo*, whether water be present or not (Schrötter, *W. A. B.* 1, 130, 8, 241; 9, 414), at temperatures as low as −14°, and whether the P be solid or dissolved in CS_2 (Corenwinder, *A. Ch.* [3] 30, 242; Lallemand, *C. R.* 70, 182). For an account of the action of tropical sunlight on P in CS_2 *v.* Pedler, *C. J.* 57, 599. The action of heat begins at c. 215° at the ordinary pressure; diminution of pressure causes a slackening of the rate of change, and the action stops at 393 mm. pressure, temp. being 215°. The change is complete by heating to 260° for c. 8 days; at 300°, in a sealed tube, it is finished in a few minutes (Schrötter, *l.c.*; Hittorf, *P.* 126, 193; V. Meyer, *B.* 15, 297; *cf.* DISSOCIATION, vol. ii. p. 391). The change is accomplished by electricity by passing the current through a little P in a closed tube with Pt wires fused into the ends (Grove, *C. J.* 16, 269; Geissler, *P.* 152, 171). Hittorf (*P.* 126, 193) regards the action as due to the heating of the P vapour by the current. Certain reagents also effect the change: *e.g.* heating with a very little I (Brodie, *J. pr.* 58, 171); or heating a solution of P in CS_2 with I (Corenwinder, *A. Ch.* [3]. 30, 242; Lallemand, *C. R.* 70, 182), but Rüdorff (*P.* 128, 463) says the product is a hydride of P. In the change of 62 g. ordinary P into red P c. 7,100 g.-units of heat are produced; and there is a contraction of volume (*v.* Petersen, *Z. P. C.* 8, 601).

2. *Amorphous or red phosphorus* is a dull, dark carmine, odourless, tasteless powder, which becomes darker on heating, and black when boiled with KOHAq. It is brittle, and shows no trace of crystalline form. Amorphous P is heavier, and conducts electricity much better, than crystalline P, although its conductive power is very small compared with the metals (*v.* data at beginning of this article). Amorphous P does not melt when heated to redness in a sealed tube (Hittorf, *l.c.*); vapour is formed in the tube, and on cooling this solidifies as crystalline P, but the unvapourised portion remains amorphous. When distilled, amorphous P becomes crystalline; the action begins at c. 260° (Schrötter, *l.c.*). The process, like the reverse change of crystalline into amorphous P, is essentially one of dissociation (*v.* DISSOCIATION, vol. ii. pp. 391-3). Amorphous P takes fire at c. 250°-260° (Hittorf, Schrötter, *l.c.*), but active combustion begins at c. 300°; it does not oxidise in dry air, but in presence of moisture oxidation proceeds slowly, with the smell of ozone and the formation of an acid liquid (Personne, *C. R.* 45, 113; Wilson, *Ph.* 17, 410; Pedler, *C. J.* 57, 599). Red P does not glow in the air; it is not poisonous (De Vrij, *J.* 1851. 313). This variety of P is insoluble in the menstrua which dissolve ordinary P; boiling turpentine, and a few liquids of high boiling-points, dissolve a little and change it into ordinary P.

3. *Crystalline metallic phosphorus* is described by Hittorf (*P.* 126, 193) as forming long, black, thin, rhombohedral crystals which appear red in transmitted light; S.G. 2·34 at 15·5°; less volatile than amorphous P; heated in a sealed tube drops of ordinary P appear at c. 358°. It is doubtful whether this is a distinct variety of P; it does not seem to have been obtained free from Pb (for preparation, *v. ante*). According to Troost and Hautefeuille (*C. R.* 78, 748), the S.G. and heat of combustion of red P change continuously with temperature; at 580° ruby-red crystals appear, which have the S.G. of Hittorf's metallic P.

Thénard observed that P became black when heated and suddenly cooled (*Gm.-K.* [6th ed.] i. 2, 102); some experimenters claim this to be a special variety of P (*v.* Reichardt, *Ar. Ph.* [3] 9, 442; P. Thénard, *C. R.* 95, 409); according to others it contains foreign substances. Blondlot obtained it only when a trace of Hg was present (*C. R.* 70, 856; 78, 1130); Ritter found the presence of As necessary (*C. R.* 78, 192).

Napoli (*C. R.* 25, 369) thought that a special yellow modification of P was produced by keeping freshly-melted ordinary P under water.

The atom of P is trivalent in most gaseous molecules, *e.g.* PCl_3, PH_3, PF_3, &c.; it is pentavalent in the gaseous molecule PF_5. P acts as a non-metallic element; its oxides are acidic, although some of them combine with less acidic oxides to form salt-like compounds. P is closely related to As, Sb, and Bi, and also to N, V, Nb, Di, Er, and Ta; these elements form Group V. For a detailed consideration of the chemical relations of P *v.* NITROGEN GROUP OF ELEMENTS, vol. iii. p. 571. The specific volume of P at its b.p. is 20-21 (Pisati a. de Franchis, *B.* 8, 70; Ramsay a. Young, *C. J.* 39, 50); the specific volume of P in combination is c. 25·3 (Thorpe, *C. J.* 37, 333).

Reactions and Combinations.—1. P combines with *oxygen* to form P_4O, P_2O_3, and P_2O_5; the reaction begins at ordinary temperature with crystalline P, and at c. 250°-260° with amorphous P. (For more details *v.* PHOSPHORUS, OXIDES OF, p. 138.) P does not combine with pure O at the ordinary pressure, but only when an indifferent gas is present, or the pressure is diminished (for references *v. Properties of P*, p. 128). The combination of P in O is arrested in proportion to the dryness of the O (Baker, *C. J.* 47, 349; *Pr.* 46, 1). Amorphous P does not oxidise in dry *air*, but the oxidation proceeds slowly in moist air. Ordinary P oxidises readily in moist air; it is not yet finally settled whether or not ozone is produced (*v.* McLeod, *C. J.* 37, 118). In moist air H_3PO_3 is formed; this may be a direct product of oxidation, or it may result from the reduction of H_3PO_4 formed by the direct oxidation of the P (*v.* Schönbein a. Bohlig, *J.* 1863. 167; Blondlot, *C. R.* 66, 351; Stiassny, *D. P. J.* 199, 414).—2. P is easily changed to P_2O_5 by *oxidising agents*, *e.g.* HNO_3, CrO_3, KNO_3, &c. A mixture of P and $KClO_3$ explodes violently when struck or rubbed; the explosion is less violent with amorphous P. Amorphous P is inflamed when rubbed with CrO_3, PbO_2, Pb_3O_4, HgO, $K_2Cr_2O_7$, or Ag_2O, and when heated with MnO_2, CuO, or KNO_3.—3. P combines with *sulphur*, the *halogens*, and many *non-metals* when heated with these. The reactions occur at lower temperatures, and more rapidly, with ordinary than with amorphous P, yet amorphous P combines with Br and Cl at the ordinary temperature.—4. P decomposes solutions of *salts of copper*, *silver*, and some *other metals*, with separation of the metal, which often combines with the P.—5. Boiling *water* is slightly decomposed by P *in presence of air*, with formation of PH_3, H_3PO_2Aq, and H_3PO_4Aq (Cross a. Higgin, *C. J.* 35, 254); at 250° the reaction is more rapid (Schrötter); with amorphous P the action is slow (C. a. H.).—6. *Concentrated hydrochloric acid* is decomposed by P at 140°, with formation of PH_3 and H_3PO_3Aq (Oppenheim, *Bl.* [2] 1, 163).—7. *Hydriodic acid* reacts with P to form PH_4I and PI_2; *hydrobromic acid* reacts at 100°-120° to produce PH_4Br (Damoiseau, *C. R.* 91, 883).—8. *Chlorosulphonic acid* [$SO_2.OH.Cl$] reacts explosively with ordinary P at 25°-30°, and more slowly and at a higher temperature with amorphous P, to form SO_2, HCl, and H_3PO_4 (Heumann a. Köcklin, *B.* 15, 416).—9. *Sulphuryl chloride* [SO_2Cl_2] produces PCl_3 and SO_2; the reaction is violent, even with amorphous P (H. a. K., *B.* 15, 1736).—10. Adie (*C. J.* 59, 230) describes the action of *sulphur trioxide* on P as producing $3P_2O_4.2SO_3$.—11. With *boiling solutions of alkalis* P forms PH_3 and alkali salts of H_3PO_2. P left for a long time in contact with *ammonia solution* probably forms P hydride and NH_4 phosphite (*v.* Blondlot, *C. R.* 57, 1250; Commaille, *C. R.* 68, 263; Flückiger, *J.* 1868, 171). Red P is not acted on by NH_3Aq (F., *l. c.*).—12. Heated with the *alkaline earths* P forms phosphides and phosphates.—13. When P is strongly heated with *anhydrous alkali carbonates* C is separated. For an account of the technical applications of P *v.* Dictionary of Applied Chemistry; for description of the methods of testing for P and estimating it a *manual of analysis* must be consulted.

Phosphorus, acids of. The *phosphoric acids* are described under that heading (p. 124), the other acids under the heading Phosphorus, oxy-acids of, and their salts (p. 149). For *phosphamic acids v.* p. 105, and for *thiophosphamic acids v.* Thiophosphoryl chloride, *Reaction* No. 7, p. 148.

Phosphorus, bromides of. P and Br combine violently; two products of the reaction have been isolated, PBr_3 and PBr_5. These formulæ are probably molecular.

Phosphorus tribromide, PBr_3 (*Phosphorous bromide*). B.P. = 172·9° at 760·2 mm. (Thorpe, *C. J.* 37, 335). S.G. $\frac{0°}{4°}$ 2·92311 (T., *l.c.*). Does not solidify at −13·6°. A colourless liquid, with very penetrating odour; fumes in the air. PBr_3 is formed by the direct union of P and Br. If P is added to Br, the Br must be kept in a freezing mixture, and the P must be added in extremely small pieces until a colourless liquid is obtained; the process is dangerous. Lieben (*A.* 146, 314) recommends to pass CO_2 through slightly warmed Br, to lead the gas over small pieces of dry P, and to distil the liquid thus produced after it has stood for some days. Schorlemmer uses amorphous P. The P is placed in a flask connected with an inverted condenser, and having a dropping funnel passing through the cork. Br is added drop by drop from the funnel: the first few drops combine, with a production of flame, but after a little the Br may be added more freely; the PBr_3 is distilled from the excess of P (*v.* also Pierre, *A. Ch.* [3] 20, 5; Kekulé, *A.* 130, 16; Löwig, *Gm.-K.* i. 2, 334).

PBr_3 is not acted on by O; reacts with S to form $PSBr_3$ (Gladstone, *P. M.* [3] 35, 345); Cl forms PCl_5 and Br; $HgCl_2$ forms PCl_3 and $HgBr_2$; H_2S produces P_2S_3 and HBr. PBr_3 is decomposed slowly by cold water, rapidly at 25°, to HBrAq and H_3PO_3Aq (Löwig, *l.c.*). P and I dissolve in PBr_3.

Phosphorus pentabromide, PBr_5 (*Phosphoric bromide. Perbromide of phosphorus*). Produced by adding excess of Br to PBr_3, stirring well with a glass rod, and after a time removing the excess of Br by warming very gently in a stream of dry CO_2. Also formed by action of Br on PCl_3 in presence of a little I (Gladstone, *P. M.* [3] 53, 345). PBr_5 forms a citron-yellow solid; fumes in the air; melts to a red liquid when gently warmed, which solidifies again to rhomboidal crystals, which are yellow if cooling has been rapid, and red if cooling has been slow. The red crystals become yellow when rubbed (Baudrimont, *Bl.* 1861. 118); at a higher temperature (below 100°) gives red vapours that condense to yellow needles. PBr_5 is separated at c. 100° into PBr_3 and Br, which re-combine on cooling. (Ogier, *C. R.* 92, 83) gives the following heats of formation: $[P,Br^5] = 63,000$ from liquid Br; $= 83,000$ from gaseous Br; $= 62,300$ from solid Br; in each case solid PBr_5 is formed.

Reactions.—1. Heated to 200° in *oxygen*, PBr_5 inflames with formation of P_2O_5 (Baumstark, *A.* 140, 75).—2. Neither *hydrogen* nor *sulphur* reacts in the cold with PBr_5.—3. *Chlorine* forms PCl_5 and Br; *iodine* produces PBr_3 and IBr_3.—4. In *moist air*, $POBr_3$ is formed (*q. v.*).—5. A *little water* produces HBr and $POBr_3$; with *much water* HBr and H_3PO_4 are formed.—6. PBr_5 reacts with *hydroxides* to substitute OH by Br; the reaction is similar to, but not so energetic as, that of PCl_5.—7. *Hydrogen sulphide* forms $PSBr_3$ and HBr.—8. *Phosphorus hydride* forms at first PBr_3, and then also P and HBr.—9. *Hydriodic acid* has no action; dry *boric acid* forms some BBr_3 (Gustavson, *B.* 3, 426); dry *oxalic acid* produces $POBr_3$, HBr, CO, and CO_2. 10. *Antimony sulphide* produces $SbBr_3$ and $PSBr_3$ (Baudrimont, *Bl.* 1861. 118).—11. With many *metals* at high temperatures, PBr_5 produces phosphides and bromides.

Combination.—With *ammonia* to form $PBr_5.9NH_3$. Prepared by passing dry NH_3 into a solution of PBr_5 in CCl_4 (Besson, *C. R.* 111, 972).

Phosphorus, bromochlorides of. Several compounds of P, Br, and Cl are formed by the reaction of PCl_3 with Br. PBr_2Cl_3, PBr_4Cl_3, or PBr_8Cl_3 is produced according to the relative quantities of PCl_3 and Br used; and from one or other of these the compounds PBr_7Cl_2 and $PBrCl_4$ are obtained. According to Stern (*C. J.* 49, 815) PBr_2Cl_3 is formed, and on addition of more Br the compound PBr_3Cl_2 is produced, and unites with Br to form PBr_5Cl_2; the whole of the Cl in PCl_3 cannot be thus replaced by Br (Michaelis, *B.* 5, 9, 411; Wichelhaus, *A. Suppl.* 6, 277; Stern, *C. J.* 49, 815; Geuther, *J. Z.* 10, 128; Michaelis a. Geuther, *J. Z.* 6, 242; Prinvault, *C. R.* 74, 868). Michaelis regarded PBr_4Cl_3 and PBr_8Cl_3 as compounds of PBr_2Cl_3 with Br_2 and $3Br_2$ respectively; Prinvault looked on PBr_4Cl_3 as $PBr_3Cl_2.BrCl$, and PBr_8Cl_3 and PBr_7Cl_3 as $PBr_5.3BrCl$ and $PBr_5.2BrCl$, respectively. Against Prinvault's view it was urged by Michaelis that if the compounds contain PBr_5 they must give $POBr_3$ and BrCl by reacting with SO_2, whereas the products are $POCl_3$, SBr_4, and Br; but Geuther showed that $POBr_3$ reacts with BrCl to give $POCl_3$ and Br. Geuther regarded the compounds as containing trivalent Br atoms.

Phosphorus dibromotrichloride, PBr_2Cl_3. Yellow-red crystals, melting at 35°; obtained by gradually adding 160 pts. Br to 137·5 pts. PCl_3, and keeping in a closed tube in a freezing mixture for some time (M.). Addition of 18 pts. water reacts thus (G. a. M.): $3PBr_2Cl_3 + 3H_2O = 2POCl_3 + POBr_3 + 3HCl + 3HBr$. If SO_2 is passed into the contents of the tube, SBr_4 and $POCl_3$ are formed (M.)

Phosphorus tetrabromotrichloride PBr_4Cl_3. Large dark-red crystals with a blue sheen; formed by adding Br slowly to PCl_3 till two layers are produced, the lower of which is dark and oily, and then adding PBr_2Cl_3 until the lower layer solidifies (G.). Also produced by warming PBr_5 with PCl_5 to 40°:

$4PBr_5 + 6PCl_5 = 5PCl_3 + 5PBr_4Cl_3$ (G.), when heated PBr_4Cl_3 melts and separates into two layers, which unite again on cooling. A little H_2O produces $POCl_3$, $POBr_3$, HCl, HBr, and Br: much H_2O forms H_3PO_4, HCl, HBr, and Br; SO_2 produces $POCl_3$, SBr_4, and Br.

PHOSPHORUS OCTOBROMOTRICHLORIDE PBr_8Cl_3. Brown needles, melting at 25°. Formed by adding 4⅔ pts. Br to 1 pt. PCl_3 (*i.e.* in the ratio $8Br : PCl_3$), heating to 65°, and allowing the oily liquid to cool to c. 4°; much heat is produced in the reaction (P.). Geuther (*l.c.*) says the compound is also produced by adding BrCl to PBr_5 in the ratio $PBr_5 : 3BrCl$.

PHOSPHORUS HEPTABROMODICHLORIDE PBr_7Cl_2. Prismatic crystals. Obtained by rapidly distilling the preceding compound at a little above 90° (P.); also by dropping PCl_3 into Br until two layers are formed, and allowing to stand. Soluble in PCl_3.

PHOSPHORUS MONOBROMOTETRACHLORIDE $PBrCl_4$. According to Prinvault (*l.c.*) this compound is obtained, as yellow crystals, by heating to boiling a solution of the preceding compound in PCl_3, also by the reaction of PCl_3 with BrCl. P. says that PBr_8Cl_3 and PCl_3 react in accordance with the equation $PBr_8Cl_3 + PCl_3 = PBr_7Cl_2 + PBrCl_4$.

Phosphorus, bromofluoride of, PBr_2F_3. A liquid, which fumes in the air, and is violently decomposed by water; also decomposed easily by heat to PBr_3 and PF_5; formed by passing PF_3 into Br (Moissan, *C. R.* 100, 1348).

Phosphorus, bromonitride of, PBr_2N. This compound is said to be formed by heating the product of the action of NH_3 on PBr_5, in a sealed tube, to 250°–275°, with twice its weight of PBr_5 for twelve hours, and then heating the resulting substances under reduced pressure, when PBr_5 sublimes, and then at 200° a white crystalline sublimate of PBr_2N is formed; the compound is purified by resubliming *in vacuo*. The crystals melt at 188°–190°; sublime at 150° *in vacuo*; sol. ether, less sol. CS_2 or $CHCl_3$, insol. water (Besson, *C. R.* 114, 1479).

Phosphorus chlorides of. P and Cl combine directly and easily, with the production of light and much heat. Two compounds are thus produced, PCl_3 and PCl_5; these formulæ are molecular. According to Donny a. Mareska (*C. R.* 20, 717), and Dumas (*A. Ch.* [3] 55, 172), liquid Cl surrounded by solid CO_2 combines with P.

PHOSPHORUS TRICHLORIDE PCl_3 (*Phosphorous chloride*). Mol. w. 137·07. Boils at 75·95° at 760 mm. (Thorpe, *C. J.* 37, 333; *v.* also Pierre, *A. Ch.* [3] 20, 5; Haagen, *P.* 131, 122). S.G. $\frac{0°}{4°}$ 1·61275 (Thorpe, *l.c.*); V.D. 70·6 (Dumas, *A. Ch.* [3] 55, 172). S.H. of vapour ·1347, equal weight of air = 1; ·64, equal vol. of air = 1 (Regnault, *J.* 1863. 85). μ for H line $a = ·3222$; $\frac{\mu - 1}{d}$. Mol. w. = 44·3 (Haagen, *P.* 131, 122). H.F. [P,Cl^3] = 75,300 (*Th.* 2, 408; formation of liquid PCl_3). Regnault (*J.* 1863. 65) gave the vapour pressures of PCl_3 in mm. of Hg as follows:—87·98 at 0°, 62·68 at 10°, 100·55 at 20°, 155·65 at 30°, 233·78 at 40°, 341·39 at 50°, 485·63 at 60°, 674·23 at 70°.

Formation.—1. By direct union of P and Cl.—2 By reaction of P with $HgCl_2$, $FeCl_3$, $CuCl_2$, ICl_3, S_2Cl_2, or $SeCl_2$ (*Gm.-K.* **1**. **2**, 390).—3. By reaction of Cl or $HgCl_2$ with PBr_3 or PI_3 (*l.c.*).—4. By decomposing PCl_5 by heat aided by H, P, PH_3, I, HI, S, or one of several metals.—5. By heating HPO_3 with NaCl (*Gm.-K.*, *l.c.*).—6. By heating Na_2HPO_4 with NH_4Cl (H. Rose).—7. By heating P with conc. HClAq (Oppenheim, *Bl.* [2] 1, 163).—8. By passing $POCl_3$ through a tube filled with glowing charcoal (Riban, *C. R.* 95, 1160).

Preparation.—About 500–600 g. P, in pieces about 1 inch long, are dried quickly, twice, between filter-paper, and placed in a dry retort of c. 1 litre capacity, through the neck of which a stream of dry CO_2 is kept passing. The beak of the retort is now passed into a well-cooled receiver, and the tubulus is connected with an apparatus which is evolving dry Cl. The tube through which the Cl passes into the retort is fixed somewhat loosely in the cork, so that it may be moved up or down easily. The retort is placed in warm water until the P is melted; after the action has fairly begun, the heat produced suffices to keep the P molten. A large basin with cold water is kept beneath the retort in case the latter should break. The reaction is regulated by moving the tube from the Cl apparatus near to, or away from, the surface of the P; if this tube is too near the P, the heat of the reaction vaporises much of the P, which then condenses in a reddish layer in the upper part of the retort; if the delivery-tube is too far from the P, solid PCl_5 forms and deposits on the upper part of the retort in yellow crystals. As the reaction proceeds, pieces of red P appear here and there in the retort. Towards the end much red P is formed; this must be heated carefully with a lamp, a process in which the retort is apt to be cracked. The distillate is digested with a little P for a few days, to decompose any PCl_5, and then redistilled from a retort heated on a water-bath (Donny a. Mareska, *C. R.* 20, 717; Dumas, *A. Ch.* [3] 55, 172). Thorpe (*C. J.* 37, 333) recommends to heat red P in dry Cl; he says that the reaction is very regular, and that large quantities of PCl_3 may be prepared thus with great ease and rapidity; the red P should be washed with water, then with alcohol, then with ether, and dried at a gentle heat.

Properties.—A clear, colourless, highly refractive, liquid, which can be vaporised without decomposition in absence of moisture; fumes in air with decomposition; does not redden dry blue litmus paper; vapour has an acrid smell and excites tears. Does not solidify at −115° (Natterer, *P.* 62, 133). Does not conduct electricity. Dissolves P; also I (Gladstone, *P. M.* [3] 35, 345). Mixes with C_6H_6, Et_2O, $CHCl_3$, and CS_2. In a gas-flame or alcohol-flame, PCl_3 burns brightly. Sinks in water and then begins to decompose to H_3PO_3Aq and HClAq; if a little warm water is used, amorphous P separates. Slowly decomposes in the dark to PCl_5 and P (Casselmann, *A.* 83, 247). Combines with Cl to form PCl_5. Not acted on by O at ordinary temperatures; $POCl_3$ is slowly formed at b.p. of PCl_3. $POCl_3$ is formed by action of ozone and various O compounds which readily part with O (*v. Reactions*).

Testing PCl_3 *for* $POCl_3$.—PCl_3 has little action on zinc-dust at ordinary temperatures; POCl$_3$ produces P$_2$O$_5$ and Zn phosphide, which is decomposed by H$_2$O, giving inflammable P hydride. To apply this reaction, a few drops of the liquid are added to a little zinc-dust in a test tube, and then a few drops of water; if POCl$_3$ is present, small bubbles of gas are given off, and take fire in the air (Denigès, *Bl.* [3] 2, 787).

Reactions.—1. *Water* produces H$_3$PO$_3$ and HCl; the reaction proceeds somewhat slowly. If a little warm water is added to PCl$_3$, amorphous P separates as the product of a secondary reaction —3 H$_3$PO$_3$Aq + 2PCl$_3$ = 3HPO$_3$Aq + 6HClAq + 2P (Michaelis, *B.* 8, 504; but *cf.* Geuther, *J. Z.* [2] 3, 2*nd Suppl.* 116).—2. *Oxygen* does not react at ordinary temperatures, but POCl$_3$ is slowly formed at b.p. of PCl$_3$ (Michaelis, *J. Z.* 6, 93; Remsen, *Am. S.* [3] 11, 365).—3. *Ozone* rapidly forms POCl$_3$ (Remsen, *l.c.*).—4. *Potassium chlorate* produces POCl$_3$.—5. *Sulphur trioxide* reacts violently, forming POCl$_3$ and SO$_2$ (Michaelis, *J. Z.* 6, 239; 7, 110; Armstrong, *J. pr.* [2] 1, 255; *cf.* Rose, *P.* 44, 304).—6. *Selenion dioxide* produces POCl$_3$ and Se at 110°; if the SeO$_2$ is in excess, SeCl$_2$ and P$_2$O$_5$ are also formed; SO$_2$ has no action at 140° (M., *l.c.*).—7. Heated in a closed tube at 130° with *arsenious oxide*, forms As, AsCl$_3$, and P$_2$O$_5$ (Michaelis, *l.c.*).—8. *Thionyl chloride* forms PCl$_5$, POCl$_3$, and PSCl$_3$. *Chromyl dichloride* produces POCl$_3$, P$_2$O$_5$, PCl$_5$, and CrCl$_3$. 9. *Nitrogen trioxide* or *pentoxide* reacts with strongly cooled PCl$_3$ to form NOCl, P$_2$O$_5$, POCl$_3$, and P$_2$O$_3$Cl$_4$ (Geuther a. Michaelis, *B.* 4, 766).—10. Many *metallic oxides* withdraw Cl from PCl$_3$ forming metallic chlorides; PbO forms Pb and Pb(PO$_3$)$_2$ besides PbCl$_2$.—11. Many *metallic sulphides* when heated with PCl$_3$ react to form P$_2$S$_3$ and metallic chlorides; *e.g.* K$_2$S, BaS, CaS, Sb$_2$S$_3$, PbS, &c. (*v. Gm.-K.* i. 2, 320).—12. *Sulphur* reacts at c. 130° with production of PSCl$_3$ (Henry, *B.* 2, 638).—13. *Antimony* forms SbCl$_3$ and P (*Gm.-K.*, *l.c.*).—14. Red-hot *iron filings* produce Fe phosphide and FeCl$_2$ (*Gm.-K.*).—15. *Zinc*, at 100°, forms ZnCl$_2$ and P (Most, *B.* 13, 2029).—16. *Platinum* and *silver* are not acted on by PCl$_3$ (*Gm.-K.*).—17. *Sulphuric acid* reacts slowly in the cold, rapidly when hot, to form SO$_2$, HCl, P$_2$O$_5$, and SO$_2$.OH.Cl (Michaelis, *J. Z.* 6, 239).—18. *Phosphorous acid* produces P$_2$O$_5$ (*Nacquet's Chem.* German ed. 1868. p. 218). 19. *Hydriodic acid* reacts at the ordinary temperature, forming PI$_3$ and HCl (Hautefeuille, *Bl.* [2] 7, 198, 200, 203).—20. PSCl$_3$ and PCl$_5$ are formed by heating for some hours at 160° with *sulphur chloride.*—21. *Iodine pentabromide* is said to form ICl$_3$ and PBr$_3$.—22. *Phosphorus hydride* produces HCl and solid P$_2$H (Besson, *C. R.* 111, 972). SbH$_3$ is said to be without action (Mahn, *Z.* [2] 5, 729).—23. Heated with *hydrogen sulphide*, HCl and P$_2$S$_3$ are formed (Baudrimont, *A. Ch.* [4] 2, 5).—24. *Ammonia* seems to form various compounds which have not been fully examined (*v.* Phospham, p. 104).—25. Passed over heated *ammonium chloride*, phospham (*q. v.*) is formed.—26. With many *carbon compounds containing hydroxyl*, PCl$_3$ reacts to substitute Cl for OH.

Combinations.—1. With *chlorine*, to form PCl$_5$ (*q. v.*). — 2. With *bromine* to form several bromochlorides (*q. v.*).—3. With *iodine* to form PI$_2$Cl$_3$ (*v.* **Phosphorus iodochloride**, p. 138).—4. With *titanium chloride* to form PCl$_3$.TiCl$_4$ (Bertrand, *M. S.* [3] 10, 1331); also with a few other metallic chlorides, *e.g.* AuCl.—5. With dry *ammonia* to form PCl$_3$.5NH$_3$ (Rose; Besson, *C. R.* 111, 972).

Phosphorus pentachloride PCl$_5$ (*Phosphoric chloride. Phosphorus perchloride*). Mol. w. 207·81. Melts at 148° under pressure; boils at 160°–165°, with partial decomposition to PCl$_3$ and Cl. V.D. varies with temperature; c. 103 in an atmosphere of PCl$_3$ (*v. Properties*). H.F. [P,Cl^5] = 104,996 (*Th.* 2, 408).

Formation.—1. By combining PCl$_3$ with Cl, or by the action of excess of Cl on P.—2. By reacting with PCl$_3$ on PH$_3$, S$_2$Cl$_2$, or SOCl$_2$.—3. By the action of SbCl$_5$ on PH$_3$ (Mahn, *Z.* [2] 5, 729).

Preparation.—PCl$_5$ may be prepared by the action of Cl on P, but the PCl$_5$ is apt to retain pieces of unchanged P, the presence of which may lead to violent explosions; it is, therefore, better to prepare PCl$_5$ from PCl$_3$. PCl$_3$ is placed in a strong flask with a wide neck; the flask is surrounded by a freezing mixture, and dry Cl is passed in by a *wide* tube which reaches almost to, but does not touch, the surface of the liquid. As the contents of the flask get semi-solid they must be thoroughly broken up by a glass rod. The whole of the PCl$_3$ is not changed to PCl$_5$ until Cl has passed for a considerable time; the change is not complete until, after closing the flask, shaking thoroughly, and allowing to stand for some time, the presence of greenish-yellow gas in the flask is quite apparent. Excess of Cl is finally removed by the long-continued passage of a slow stream of dry CO$_2$ (Müller, *Z.* 1882. 295; Gräbe, *Ar. Sc.* [3] 5, 477).

Properties.—A white, or slightly yellow, crystalline solid with a strong odour; crystallises in rhombic plates; fumes in moist air, with decomposition; sublimes without melting under 100°, but melts at c. 148° under considerable pressure; boils at c. 160°–165°, with partial dissociation to PCl$_3$ and Cl, which re-combine on cooling. PCl$_5$ does not conduct electricity (*Gm.-K.* i. 2, 390). Decomposed by O at c. 300°. Burns in a candle-flame.

Vapour density.—The S.G. of the vapour obtained by heating PCl$_5$ is less than that calculated for PCl$_5$, and it decreases as temperature increases until it is equal to half the calculated value. Wanklyn a. Robinson (*C. R.* 56, 547) showed that the vapour contained free Cl, by diffusing into CO$_2$, and that PCl$_3$ was present in the residue. Deville noticed that the vapour showed the colour of Cl, and that the intensity of colour increased as temperature rose (*A.* 141, 147). The V.D. was determined by Cahours at different temperatures, with the following results (*A.* 141, 42; *v.* also Gibbs, *Am. S.* [3] 18, 277, 371):—

Temp.	S.G. (air = 1)	P.c. Dissociation
182°	5·08	41·7
190	4·99	44·3
200	4·85	48·5
230	4·80	67·4
250	4·00	80·0
274	3·84	87·5
288	3·67	96·2
289	3·69	95·7
300	3·65	97·3

The temperature whereat 50 p.c. is dissociated is c. 202°. Wurtz (*B.* 3, 572) showed that, making certain assumptions, the S.G. of PCl_5 vapour formed in an atmosphere of PCl_3 is c. 7·4-6·8, which agrees with that calculated for PCl_5, viz. 7·2.

Reactions.—1. *Heat* dissociates PCl_5 into PCl_3 and Cl, which recombine on cooling (*v. ante*).—2. PCl_5 is decomposed by *water* to HClAq and $POCl_3$, and finally to H_3PO_4Aq with some HPO_3Aq (*Gm.-K.* i. 2, 390). Thomsen gives $[PCl^5,Aq] = 123,440$ (*Th.* 2, 322).—3. *Boric acid* and *antimonic hydrate* react similarly to water (Gerhardt, *A.* 87, 66, 290; Schiff, *A.* 102, 111; 106, 116). *Boric oxide* when heated with PCl_5 forms $B_2O_3.P_2O_5$ and BCl_3 (Gustavson, *B.* 3, 426).—4. *Hydroxides* generally, including *carbon compounds which contain the group OH*, exchange OH for Cl, with production of $POCl_3$ and chloride of the radicle before in combination with OH.—5. *Compounds containing the group SH* generally react similarly to OH compounds; *e.g.* SH.H gives ClH and $PSCl_3$.—6. *Oxides* generally exchange O for Cl_2; *carbon compounds containing the group CO* generally also react in this way.—7. *Oxygen* reacts with vapour of PCl_5 at c. 300°, producing $POCl_3$, P_2O_5, and Cl (*Gm.-K.* i. 2, 390; Wanklyn a. Robinson, *C. R.* 56, 547).—8. PCl_5 vapour mixed with *hydrogen* and passed through a red-hot tube produces HCl, PCl_3, and P (Baudrimont, *Gm.-K.* i. 2, 394).—9. Heated with *phosphorus* PCl_3 is produced.—10. The compound PS_2Cl_5 is formed by distilling PCl_5 with 8 parts of *sulphur* (Gladstone, *C. J.* 3, 5).—11. *Selenion* produces Se_2Cl_2 and PCl_3.—12. *Iodine* forms PCl_3, and ICl which combines with part of the PCl_5 to produce $PCl_5.ICl$ (*Gm.-K.*, *l.c.*).—13. PCl_5 reacts with many *metals* to form metallic chlorides and PCl_3; sometimes P and metallic phosphides are formed (Baudrimont, *J. pr.* 87, 300; 88, 78; Casselmann, *A.* 98, 213). Among the metals which react with PCl_5 are Al, As, Cd, Au, Fe, Pt, K, Na, Sn, and Zn. The metallic chloride formed often combines with the undecomposed PCl_5; this occurs, *e.g.*, with $AlCl_3$, $FeCl_3$, $HgCl_2$, $PtCl_4$, and $SnCl_4$ (Wöhler, *B.* 13, 875; *cf.* Goldschmidt, *C. C.* 1881. 489).—14. *Phosphorus hydride* produces PCl_3 and HCl; with excess of PH_3, HCl, and P are formed.—15. *Antimony hydride* forms PCl_3, $SbCl_3$, and HCl; *silicon hydride* acts similarly but more slowly (Mahn, *Z.* [2] 5, 729; *ammonia* forms phospham (*q.v.*, p. 104) and nitrogen phosphochloride (vol. iii. p. 570); also phosphamidoimide (*q. v.*, p. 105; *cf.* also Besson, *C. R.* 114, 1264).—16. *Sulphur dioxide* produces $SOCl_2$ and $POCl_3$ (Schiff, *A.* 102, 111; 106, 116; Persoz a. Bloch, *C. R.* 28, 86; Kremers, *A.* 70, 297).—17. *Sulphur trioxide* forms $S_2Cl_2O_5$ and $POCl_3$ (Schiff, *l.c.*; Michaelis, *J. Z.* 6, 235, 240, 292; Williamson, *Pr.* 7, 11).—18. *Selenion dioxide* when distilled with PCl_5 forms $POCl_3$, $SeCl_2$, and P_2O_5, $SeOCl_2$ being formed as an intermediate product (Michaelis, *Z.* [2] 6, 465).—19. *Phosphoric oxide* produces $POCl_3$.—20. *Boric oxide* reacts slowly when heated to c. 140° with PCl_5; $BOCl_3$ is probably formed, and on heating more strongly BCl_3 and $B_2O_3.P_2O_5$ remain (Gustavson, *B.* 3, 426).—21. *Nitrogen dioxide* produces NOCl and $POCl_3$ (*Gm.-K.* i. 2, 390).—22. *Silicon dioxide* forms $POCl_3$, and $SiCl_4$ which combines with the excess of PCl_5 (Weber, *P.* 107, 375).—23. Vapour of PCl_5 reacts with many *metallic oxides*, when these are strongly heated, to form $POCl_3$, and metallic chlorides which frequently combine with undecomposed PCl_5. The following react in this way—Al_2O_3, As_2O_3, and As_2O_5 (Hurtzig a. Geuther, *A.* 111, 159; Michaelis, *J. Z.* 6, 239), [no reaction with Sb_2O_5; Schiff, *A.* 102, 111], CdO, Cr_2O_3, Fe_2O_3, MnO_2, MoO_3 (Schiff, *l.c.*), SnO, TiO_2 (Weber, *P.* 107, 375; Tüttscheff, *A.* 141, 111), WO_3 (Gerhardt a. Chiozza, *C. R.* 36, 1050; Schiff, *l.c.*).—24. *Phosphorus sulphide* forms $PSCl_3$ (Weber, *P.* 107, 375; *Gm.-K.* i. 2, 390).—25. *Carbon disulphide* does not react at 100° (Hofmann, *A.* 115, 264); at 200° $PSCl_3$ is produced (Carius a. Fries, *A.* 112, 193), and CCl_4 (Rathke, *Z.* [2] 6, 57).—26. Many *metallic sulphides* when heated are decomposed by vapour of PCl_5 with formation of $PSCl_3$, S_2Cl_2, and metallic chloride; the following react in this way—sulphide of As, Ba, Bi, Cd, Cu, Pb, Na, Sn, Zn (Weber, *l.c.*; Baudrimont, *l.c.*).—27. *Antimony selenide* and *lead selenide* form $SeCl_4$, which forms a double compound with the excess of PCl_5.—28. *Hydriodic acid* produces PCl_3, HCl, and I (Wurtz, *Gm.-K.*, *l.c.*); *hydrobromic acid* is without action (Gladstone, *C. J.* 3, 5); syrupy *phosphoric acid* solution reacts slowly, the vapours of this acid do not act (Gerhardt, *A.* 87, 66, 290; Schiff, *A.* 102, 111; 106, 116; Persoz a. Bloch, *C. R.* 28, 86).—29. Conc. *nitric acid* reacts energetically, forming $POCl_3$ and HCl.—30. *Sulphuric acid* forms $SO_2.OH.Cl$, HCl, and HPO_3, and $S_2Cl_2O_5$ as the result of a secondary reaction (Michaelis, *J. Z.* 6, 235, 240, 292; Williamson, *Pr.* 7, 11; Baumstark, *A.* 140, 75).—31. Many *metallic salts* react with PCl_5; KNO_3 gives NOCl and $POCl_3$ (Nacquet, *Bl.* 1860); sulphites form $SOCl_2$ (Buchanan, *B.* 3, 485); AgF produces AgCl and probably a fluoride of P (Pfaundler, *W. A. B.* 46, 258); $KClO_4$ gives $POCl_3$; KSCy forms $PSCl_3$, S_2Cl_2, and PCl_3; Na_2HPO_4 gives H_3PO_4 and HCl; haloid salts of the alkalis, and also KCy and K_4FeCy_6, are not acted on by PCl_5.

Combinations.—1. With *iodine chloride* to form $PCl_5.ICl$ (*Gm.-K.* i. 2, 390).—2. With *selenion tetrachloride* to form $SeCl_4.2PCl_5$.—3. With many *metallic chlorides* (*cf. Reactions*, Nos. 13 and 23). These compounds are solids, which sublime with partial decomposition when heated, and are decomposed by water (Baudrimont, *J. pr.* 87, 300; 88, 78; Weber, *ibid.* 77, 65; Casselmann, *A.* 83, 258).—4. With *ammonia* to form $PCl_5.8NH_3$; produced by slowly passing dry NH_3 into a solution of PCl_5 in CCl_4 (Besson, *C. R.* 111, 972; 114, 1264).

Phosphorus, chlorobromides of, *v.* PHOSPHORUS BROMOCHLORIDES, p. 130.

Phosphorus, chlorofluoride of, PCl_3F_2. Mol. w. 175·07. V.D. 78. Poulenc (*C. R.* 113, 75).

Preparation.—Two stoppered flasks of c. 500 c.c. capacity are connected by a bent tube, which passes through the stoppers; one flask is filled with dry Cl, and the other with dry PF_3; that containing PF_3 is connected with a bulb full of Hg, which can be caused to flow into the flask and so force the PF_3 into the flask full of Cl. The PF_3 is slowly driven into the other flask, and the PCl_3F_2 thus formed is kept in contact with Hg for some days (without being shaken with the Hg, else some PF_3 may be decomposed) to remove traces of Cl.

Properties — A colourless gas, with very irritating odour; incombustible; liquefied at -8° at ordinary pressure; absorbed and decomposed by water; heated to c. 250° gives PF_5 and PCl_5, also decomposed in the same way by electric sparks.

Reactions.—1. *Heat* produces PF_5 and PCl_5; the action proceeds at c. 250°.—2. *Electric sparks* also produce PF_5 and PCl_5.—3. Heated with *sulphur* to c. 115°, PSF_3 and S_2Cl_2 are formed.—4. Heated with *phosphorus* to c. 120° PF_3 and PCl_3 are formed.—5. Several *metals* when heated to c. 180° produce metallic chloride and PF_3, *e.g.* Al, Fe, Pb, Mg, Ni, and Sn; Hg exerts a slight action at ordinary temperatures, and acts rapidly at 180°; Na seems to absorb PCl_3F_2 entirely.—6. *Water* reacts rapidly; if a little water-vapour is mixed with PCl_3F_2 the products are POF_3 and HCl; if the gas is passed into water, H_3PO_4Aq, HClAq, and HFAq are formed.—7. Absorbed by *alcohol*, with formation of a compound not yet examined.—8. *Ammonia* is absorbed at ordinary temperature, forming a white solid, which is probably $PF_3(NH_2)_2$.

Phosphorus, chloro-iodide of, *v.* PHOSPHORUS IODOCHLORIDE, p. 138.

Phosphorus, chloronitride of, *v.* NITROGEN PHOSPHOCHLORIDE, vol. iii. p. 570. Besson (*C. R.* 114, 1479) recommends to prepare PCl_2N by forming a layer of PCl_5 on the sides of a large flask, by acting on PCl_3 with Cl, then to heat the PCl_5 with NH_3 till it is superficially saturated, and then to heat under reduced pressure.

Phosphorus, compounds of, with hydrogen and oxygen. Those compounds of P, H, and O, which are acids, are described in the articles PHOSPHORIC ACIDS (p. 124), and PHOSPHORUS, OXYACIDS OF, AND THEIR SALTS (p. 149); but two compounds which have been described by Gautier will find a place here. Gautier (*C. R.* 76, 49) says that the compound P_4HO is formed by heating crystallised H_3PO_3 with 5 or 6 times its weight of PCl_3 to 79°, washing with water, and drying at -10°; at between 80° and 100° the products of the reaction are H_3PO_4, HCl, and amorphous P. This compound is described as an amorphous yellow powder; unchanged in air when dry, but oxidised slowly when moist; insoluble in most menstrua; burns when heated in air to c. 260°; burns explosively when heated with CuO; unchanged at 240°-250° in CO_2, but evolves PH_3 at 265°, and at 350°-360° ordinary P distils off; not acted on by dilute acids; oxidised by ordinary HNO_3Aq; conc. H_2SO_4 evolves SO_2 at c. 200°; decomposed by H_2O at c. 170° to H_3PO_2Aq, H_3PO_3Aq, and PH_3; reacts with dilute alkali solutions; NH_3 combines to form a very unstable brown substance. Gautier (*C. R.* 76, 173) described another compound P_5H_3O; obtained by adding PI_2, little by little, to H_2O at 80°-90°, allowing the yellow solution to deposit a flocculent pp., washing this with warm water, and drying *in vacuo*. If water is added slowly to PI_2 the products are HIAq, H_3PO_3Aq, and H_3PO_2Aq. P_5H_3O is described as a pure yellow solid; amorphous, or perhaps showing traces of crystalline form; tasteless and odourless; insoluble in all menstrua; oxidises in air when moist, when dry oxidises slowly at 100°; oxidised violently by HNO_3Aq; evolves SO_2 from H_2SO_4; gives off PH_3 when heated to 135° in CO_2, and ordinary P at 350°; decomposed by dilute alkali solutions to PH_3, H, H_2KPO_2, and HK_2PO_4; combines with NH_3 to form a brown very unstable substance.

Phosphorus, cyanide of, *v.* CYANOGEN PHOSPHIDE, vol. ii. p. 358.

Phosphorus, fluorides of. Two fluorides of P are known, PF_3 and PF_5; these formulæ are molecular. The compounds are gases at ordinary temperatures.

PHOSPHORUS TRIFLUORIDE PF_3. (*Phosphorous fluoride.*) Mol. w. 87·96. V.D. 43·7 (Moissan, *A. Ch.* [6] 6, 433).

Formation.—1. By the reaction of PbF_2 with Cu phosphide (M., *l.c.*).—2. By adding AsF_3 to PF_3 (M., *l.c.*).—3. By the reaction of PbF_2 with PCl_3 or $POCl_3$ (Güntz, *C. R.* 103, 58).—4. By adding PBr_3 to gently heated ZnF_2 (M., *A. Ch.* [6] 19, 286).

Preparation.—1. AsF_3 is dropped into perfectly dry PCl_3; the gas is shaken with a little water, and dried over H_2SO_4 (M., *C. R.* 100, 272). 2. A mixture of well-dried Cu_3P_2 and PbF_2 free from SiO_2 is heated in a brass tube to dull redness, the gas is passed by a leaden tube through two very small bottles (2 or 3 c.c. capacity) containing H_2SO_4, then through pumice soaked in H_2SO_4, and is then collected over Hg.—3. PBr_3 is gradually added to warm ZnF_2, the gas is washed by passing through water, then dried by passing over pumice soaked in H_2SO_4, and collected over Hg (M., *A. Ch.* [6] 19, 286).

Properties.—A colourless gas, condensed to a colourless liquid at -10° and 40 atmos. pressure. The gas is not liquefied at 24° under a pressure of 180 atmos., but liquefaction occurs when the pressure is suddenly reduced to 50 atmos. (Moissan, *l.c.*). PF_3 does not fume in the air; it is very slowly decomposed by water, with formation of H_3PO_3Aq and HFAq; burns when mixed with O; decomposed by heat; also by electric sparks.

Reactions and Combinations.—1. Decomposed by *heat*; in a glass apparatus P and SiF_4 are formed; in contact with Pt black a gas is formed, probably containing F (Moissan, *C. R.* 102, 763).—2. *Electric sparks* slowly decompose PF_3, forming PF_5 and P (Moissan, *C. R.* 102, 763).—3. Burns when mixed with pure *oxygen* and ignited; a mixture of 1 vol. PF_3 and ½ vol. O explodes violently when sparked, with formation of POF_3 (M., *C. R.* 102, 1245).—4. Very slowly decomposed by *water*, with formation of H_3PO_3Aq and HFAq; more rapidly decomposed by steam at 100°.—5. According to Berthelot (*A. Ch.* [6] 6, 358) *potash solution* produces a fluophosphorous acid probably analogous to fluoboric or fluosilicic acid; Moissan (*C. R.* 99, 655) says that a fluoride and a phosphite are formed.—6. Absorbed rapidly by *bromine* with formation of PBr_2F_3 (*v.* PHOSPHORUS BROMOFLUORIDE, p. 131), also by *chlorine*, with formation of PCl_2F_3 (*v.* PHOSPHORUS CHLOROFLUORIDE, p. 133).—7. Decomposed rapidly by solutions of *chromic acid* or *potassium permanganate*.—8. Decomposed by hot *sodium*, *copper*, *boron*, and *silicon* (M., *C. R.* 99, 655).—9. Combines with *ammonia* to form white, flocculent compound, which is decomposed by water (M., *l.c.*).—10. Combines with *fluorine* to form PF_5 (Moissan, *Bl.* [3] 5, 454).

Determination of composition.—The compound was analysed by Moissan (*C. R.* 100, 272) by heating a known volume in a glass vessel, measuring the volume of SiF_4 formed, dissolving the P deposited in HNO_3Aq, and estimating as $Mg{-}NH_4$ phosphate.

Phosphorus pentafluoride PF_5 (*Phosphoric fluoride*). Mol. w. 125·96. V.D. 63·2 to 65·1 (Thorpe, *A.* 182, 201; Moissan, *C. R.* 102, 763; 103, 1257).

Formation.—1. By passing PF_3 into Br at −15°, PBr_2F_3 is formed, and when heated this gives PF_5 and PBr_5 (Moissan, *C. R.* 101, 1490). 2. By the reaction of AsF_3 with PCl_5.—3. By direct combination of PF_3 with F (M., *Bl.* [3] 5, 454).

Preparation.—AsF_3 is added gradually to PCl_5 surrounded by a freezing mixture; the gas which comes off is passed through PCl_5 contained in a tube which is kept cold, and is collected over Hg (Thorpe, *A.* 182, 201).

Properties and Reactions.—A colourless, strongly-smelling gas, which fumes in air and rapidly attacks the membranes of the mouth and the bronchial tubes. Condensed at 15° and 46 atmos. to colourless liquid which does not act on glass (Moissan, *C. R.* 101, 1490); on partially releasing pressure the liquid solidifies, but soon again becomes liquid (M., *l.c.*). Decomposed by powerful *electric sparks* (150–200 mm. long) to PF_3 and F (M., *C. R.* 103, 1257), but not by ordinary sparking (Thorpe, *l.c.*). Incombustible and does not support combustion. Not acted on by heating with *phosphorus* to dull redness, nor with *sulphur* vapour at 440°, nor *iodine* at 500° (M., *l.c.*). In presence of trace of *water* acts on glass, forming SiF_4 and POF_3. Passed over gently-heated *spongy platinum* is partially decomposed to PF_3 and F; when the Pt is heated to dull redness a compound of Pt with P and F, probably $PF_3.PtF_2$, is formed (M., *Bl.* [3] 5, 454).

Phosphorus, fluobromide of; *v.* Phosphorus bromofluoride, p. 131.

Phosphorus, fluochloride of; *v.* Phosphorus chlorofluoride, p. 133.

Phosphorus, haloid compounds of. P combines readily with the halogens, with production of much heat, to form compounds PX_3 and PX_5; besides these, the compound PI_2 is also known. Several compounds of the type PX_3, and at least one of the type PX_5 (viz. PF_5), have been gasified, so that the formulæ are molecular. The haloid compounds of P are decomposed by water, the fluorides only very slowly, with formation of oxyacids of P and halogen acids; these compounds also combine with many other haloid compounds, both of metals and non-metals, to form double salts.

Phosphorus, hydrides of. P and H do not combine directly; but hydrides of P are produced by evolving H in contact with phosphites or hypophosphites. Three hydrides of P have been isolated; PH_3, PH_2 (or P_2H_4), and P_2H (or P_4H_2). Janssen (*Repert. Chim. app.* 3, 393) obtained a crystalline, explosive substance by the reaction of milk of lime with P, to which he gave the formula P_2H_6. At the ordinary temperature and pressure the first hydride is gaseous, the second liquid, and the third solid. The formula PH_3 is molecular; Croullebois (*C. R.* 78, 496) said that the V.D. of the liquid compound shows the mol. w. to be P_2H_4, but no details are given; the mol. w. of the solid compound is unknown. The liquid hydride takes fire in contact with air; the gas inflames in air at c. 150°, and the solid at c. 200°; the processes for preparing gaseous PH_3 generally also produce more or less liquid P_2H_4, the resultant gas is therefore spontaneously inflammable. PH_3 resembles NH_3 in its reactions, but it is much less decidedly alkaline; phosphonium compounds, *e.g.* PH_4I, similar to ammonium compounds, are known.

Phosphorus trihydride PH_3 (*Phosphoretted hydrogen. Phosphine*). Mol. w. 33·96. Liquefies −90°; solidifies −133·5°; melts at −132·5°; boils c. −85° (Olszewski, *M.* 7, 371). S.G. (air = 1) 1·185. V.D. 17·2. H.F. $[P,H^3]$ = 36,600 (Ogier, *C. R.* 87, 210). S. ·112 (Dybrowski, *J.* 1866. 735).

Formation.—The gas obtained by the following methods is never pure PH_3; it contains more or less P_2H_4, and generally also H; it is usually spontaneously inflammable. 1. By evolving H in contact with phosphites or hypophosphites in solution; phosphates are not reduced (*Gm.-K.* i. 2, 138; Fresenius, *Fr.* 6, 203; Herapath, *Ph.* 7, 57). P and H do not combine directly (Fourcroy a. Vauquelin, *A. Ch.* 21, 202; Dusart, *C. R.* 43, 1126).—2. By heating solutions of phosphites or hypophosphites (*Gm.-K.*, *l.c.*).—3. By the action of boiling alkali solutions on P (H. Rose, *P.* 6, 199; 8, 191; 14, 183; 24, 109, 295; 32, 467; 46, 633).—4. By heating P with syrupy H_3PO_4Aq, or with HClAq, HBrAq, or HIAq (Oppenheim, *Bl.* [2] 1, 163).—5. By heating P with water to 200° (Oppenheim, *l.c.*).—6. By long-continued heating P with blood to 35°–41° (Dybrowski, *J.* 1866. 735).—7. By the action of the electric current on moist molten P (Groves, *C. J.* 16, 268).—8. By heating P with H_2O to c. 200°.—9. By decomposing Zn phosphide by dilute acids, or boiling alkali solution (Schwarz, *D. P. J.* 191, 396). According to Lüpke (*C. C.* 1890. ii. 642), the gas obtained by acting on phosphide of Mg, Sn, or Zn with dilute acid is not spontaneously inflammable.—10. By treating Cu phosphide with KCN and a little 80 p.c. alcohol (*Gm.-K.* i. 2, 138).—11. By decomposing phosphides of the alkali or alkaline earth metals by water or dilute acids.

Preparation.—1. A small flask carrying an exit tube is nearly filled with a conc. solution of KOH in 80 p.c. alcohol; small pieces of P are dropped in, and the flask is heated; the gas is passed through a $CaCl_2$ tube to absorb alcohol vapour, and collected over water. The gas thus prepared does not contain more than c. 45 p.c. PH_3 (Hofmann, *B.* 4, 200); it is generally free from the spontaneously inflammable hydride. The gas prepared by the action of KOHAq on P contains some P_2H_4 and much H; it is spontaneously inflammable in air. The simplest way of preparing this gas is to place a few small pieces of P in a little flask which carries a cork with two tubes, one fitted with a stopcock and passing just through the cork, and the other bent like an ordinary gas-delivery tube and dipping under water in a basin; the flask is nearly filled with conc. KOHAq; the tube with the stopcock is attached to the gas-supply, the cork is fitted loosely into the flask, and a stream of coal gas is passed through the apparatus for a few minutes, after which the cork is fitted tightly into the flask, the stopcock is closed, and the flask is heated. During this process the end of the delivery-tube is kept under the surface of the water in the basin. After a few minutes gas is evolved, and each bubble takes fire as it comes into contact with the air after passing upwards through the water in the basin. If the whole of the air is not driven out of the apparatus before the flask is heated, serious explosions may occur.—2. The best way of preparing pure PH_3 is to decompose PH_4I by KOHAq. A small flask is fitted with a caoutchouc cork, which carries a tube furnished with a bulb and stopcock and an exit-tube; pieces of PH_4I about the size of peas are placed in the flask along with several small pieces of glass-rod, KOHAq (c. 1 pt. KOH in 2 pts. H_2O) is allowed to drop from the bulb-tube *very slowly* on to the PH_4I in the flask. Pure PH_3 is evolved without heating; if the KOHAq is added too rapidly the gas may contain a little P_2H_4 and be spontaneously inflammable (Hofmann, *B.* 4, 200; Rammelsberg, *B.* 6, 88). About 1 litre PH_3 is obtained from 7–7½ g. PH_4I (for preparation of PH_4I *v.* PHOSPHONIUM COMPOUNDS, p. 123).

Properties.—PH_3 is a colourless gas, with a very disagreeable smell like that of onions mixed with decaying fish; very poisonous; slightly soluble in water (*v.* beginning of this article). The solution glows in the dark, and deposits amorphous P when exposed to light and air; on boiling, PH_3 is given off. PH_3 is slightly soluble in alcohol, ether, ethereal oils, and blood; it is completely absorbed by solution of bleaching powder, also by Cu_2Cl_2 in HClAq (*v. Combinations*, No. 4). PH_3 combines with the halogen acids to form salts similar to those of NH_4 (*v.* PHOSPHONIUM COMPOUNDS, p. 123); the H of PH_3 is replaceable by organic radicles (*v.* PHOSPHINES, p. 116). PH_3 reduces solutions of salts of heavy metals. PH_3 free from P_2H_4 takes fire in air at c. 150°. The gas prepared as mentioned under *Formation* takes fire immediately on contact with air; it loses this spontaneous inflammability by exposure to sunlight, by passage through a U-tube cooled to −10°, by mixing with small quantities of Al_2O_3, wood charcoal, various gases, &c. (*v.* Graham, *P. M.* 5, 401). These processes remove P_2H_4, to the presence of which the ready inflammability of the gas is due. Addition to PH_3 of $\frac{1}{500}$ of its weight of P_2H_4 causes the gas to become inflammable in air; the presence of $\frac{1}{1000}$ to $\frac{1}{10000}$ of NO_2 produces the same effect (Graham, *l.c.*; *cf.* Landolt, *A.* 116, 193). The gas prepared by the action of KOHAq on PH_4I (*v. Preparation*, No. 2) is described by Hofmann as taking fire when gently warmed, and being sometimes inflamed by the friction of the stopper of the bottle in which the gas may be kept. According to Rammelsberg (*B.* 6, 88), the gas prepared in this way is sometimes spontaneously inflammable. The gas prepared in this way takes fire when passed into conc. $AgNO_3Aq$ (Poleck a. Thümmel, *B.* 16, 2442).

Reactions.—1. PH_3 is decomposed by *heat*; when passed through a red-hot tube, lustrous, amorphous P is deposited (Merz a. Weith, *B.* 13, 718).—2. Decomposed by *electric sparks* to P and H; the process takes place with regularity, 20 c.c. are decomposed in 5–6 mins. with production of P and 30 c.c. H (for description of an apparatus for lecture purposes *v.* Hofmann, *B.* 4, 204).—3. PH_3 burns in *air* at c. 150° with production of P_2O_5 and H_2O; if a cold substance is brought into the flame, yellow-red specks of amorphous P are deposited.—4. No reaction occurs when pure PH_3, free from P_2H_4, is mixed with *oxygen*, but the mixture explodes if the pressure is suddenly lowered; explosion is said to occur after some hours at the ordinary pressure (Labillardière; *v. Gm.-K.* i. 2, 144).—5. Bubbles of PH_3 burn explosively to PCl_3 and HCl if passed into a vessel filled with *chlorine*; if the Cl is diluted with CO_2, the action is slower, and some P separates.—6. *Bromine* and *iodine* react similarly to Cl; if PH_3 is *heated gently with iodine*, some PH_4I is formed.—7. Heated with *sulphur*, H_2S and P sulphide are formed (Jones, *C. J.* [2] 14, 648).—8. *Salts of the alkali metals and of the alkaline earth metals* decompose PH_3, producing phosphites and hypophosphites (Winkler, *P.* 111, 443).—9. Solutions of *salts of heavy metals* generally decompose PH_3, with production of metallic phosphides, which sometimes combine with the excess of the metallic salts (*v.* Kulisch, *A.* 231, 327). $AgNO_3Aq$ forms a yellow compound (? $Ag_3P.3AgNO_3$), and then black Ag_3P which is quickly reduced to Ag (Poleck a. Thümmel, *B.* 16, 2442); $HgCl_2Aq$, according to Ashan (*Chem. Zeitung*, 10, 82, 102), forms a yellow compound $3Hg_3P_2.7HgCl_2$, a red compound $4Hg_3P_2.5HgCl_2$, and a brown compound $Hg_3P_2.HgCl_2$; $PtCl_4$ is said to form $Pt.PH_2$ (Gavazzi, *B.* 16, 2279); chlorides of Cr, Co, Cu, Au, Fe, and Ni are reduced, with formation of phosphides of the metals, or of metal and P.—10. *Potassium permanganate* solution is reduced by PH_3 to Mn_2O_3, K_2HPO_4 being also formed (Gavazzi, *B.* 16, 2279).—11. PH_3 is decomposed by many *oxides, acids*, and *salts, e.g.* by H_2S, SO_2, NO, N_2O, PCl_3, HNO_3 (no reaction at −25°; Besson, *C. R.* 109, 644), H_2SO_4 (*v.* Besson, *l.c.*), $SbCl_3$, &c., also by certain *metals, e.g.* Sb, Cu, Fe, K, and Zn (*v. Gm.-K.* i. 2, 138).—12. With *haloid compounds of arsenic* PH_3 reacts to form haloid acid and phosphide of As (Besson, *C. R.* 110, 1258).—13. With an ethereal solution of *bismuth bromide* forms a black lustrous body, probably $PBrH(BiBr_2)_2$ (Cavazzi a. Tivoli, *G.* 21, ii. 306).

Combinations.—1. With the *halogen acids* to form compounds of the type PH_4X (X = Cl, Br, or I); combination with HI and HBr occurs at the ordinary temperature and pressure, with HCl combination occurs at −30° to −35° under the ordinary pressure, or at 14° under a pressure of 20 atmos. (Ogier, *Bl.* [2] 32, 483; *v.* also Skinner, *Pr.* 42, 283). At very low temperatures PH_3 seems to combine with H_2SO_4 (*v.* PHOSPHONIUM SULPHATE, p. 124). The compounds PH_4X are described under PHOSPHONIUM COMPOUNDS, p. 123.—2. When PH_3 is strongly compressed in presence of *water*, the gas liquefies and floats on the water. If the pressure is now suddenly released, a white crystalline solid is formed, but this decomposes again when the pressure is reduced below a certain amount (Cailletet a. Bordet, *C. R.* 95, 58; *v.* PHOSPHONIUM COMPOUNDS, p. 123).—3. White compounds, easily decomposed on removing pressure, are said to be formed by compressing PH_3 with *carbon dioxide*, and with *carbon disulphide*, in presence of water (C. a. B., *l.c.*).—4. A solution of *cuprous chloride* in HClAq absorbs PH_3 rapidly; a white crystalline mass of $Cu_2Cl_2.2PH_3$ is formed, but this liquefies as more PH_3 is passed in (? with formation of $Cu_2Cl_2.4PH_3$); the crystals $Cu_2Cl_2.2PH_3$ are decomposed by warming, or by addition of water, to PH_3, HCl, and Cu_3P; the liquid compound loses PH_3 in a stream of an indifferent gas, with production of the crystalline compound (*v.* Riban, *Bl.* [2] 34, 385). This behaviour of PH_3 towards Cu_2Cl_2 gives a method for preparing pure PH_3, and also for estimating PH_3 in a mixture of gases.

Phosphorus dihydride PH_2 or P_2H_4 (*Liquid phosphoretted hydrogen*). Mol. w. said to be 65·92, corresponding with V.D. c. 33, but no details given (Croullebois, *C. R.* 78, 496). Gattermann a. Hausknecht (*B.* 23, 1174) failed to determine V.D. as the compound always decomposed. A spontaneously inflammable gas containing P and H was obtained by Gengembre in 1783 (*Crell's Ann.* 1789. 450). The fact that this gas lost its inflammability by standing over air containing water was explained by Dumas (*A. Ch.* [2] 31, 113) by supposing that the gas was a mixture of two hydrides of P, one only of which was spontaneously inflammable; to one of these Dumas gave the formula PH_2 and to the other the formula PH_3. In 1832 H. Rose (*P.* 6, 199; 8, 191) thought that the two gases had the same composition, but were isomeric one with the other. After Graham (*P. M.* 5, 401) had examined the conditions under which spontaneous inflammability was removed from or bestowed on the gas, Le Verrier (*A. Ch.* [2] 60, 174) came to the conclusion that the gas consisted chiefly of PH_3, but that it contained also a very inflammable compound PH_2, which was decomposed by light into PH_3 and a solid hydride PH. In 1845 P. Thénard made a fuller study of the subject (*A. Ch.* [3] 14, 5); he showed that spontaneously inflammable phosphoretted hydrogen, when passed through a tube cooled to under 10°, deposited a liquid having the composition PH_2, which liquid was extremely inflammable, and that this liquid decomposed in light into gaseous PH_3 and a solid to which he gave the formula P_2H. In 1874 Croullebois said that the V.D. of the liquid hydride corresponds with the formula P_2H_4, but no details were given (*C. R.* 78, 496); in 1890 Gattermann a. Hausknecht attempted to determine V.D., but found that the compound decomposed (*B.* 23, 1174).

Preparation.—Impure Ca phosphide is prepared by heating dry CaO to bright redness in a crucible, and adding dried P little by little, the lid being replaced after each addition of P. The crucible should be arranged so that the P is brought under the strongly-heated CaO; this may be done by placing a few pieces of P in a crucible, filling up with dry CaO, covering tightly (but leaving one small hole), placing the crucible in a furnace arranged so that the lower part of the crucible projects downwards through the bottom of the furnace, heating the upper part of the crucible to bright redness, and then warming the lower part so as to vapourise the P. Small quantities are prepared by placing a dry piece of P in the closed end of a tube of hard glass, partly filling the tube with dry CaO, arranged so that there is a little space between the CaO and the P, placing the tube in a combustion furnace, heating the CaO strongly, and then warming the P. The CaO is transformed into a mixture of Ca phosphide and phosphate; the phosphide is nearly black; the unchanged CaO is picked out when the action is over, and the phosphide is at once placed in a stoppered bottle. (For modification of process *v.* Gattermann a. Hausknecht, *B.* 23, 1174.) A three-necked bottle of about 2 litres capacity is filled three-quarters with water; one of the necks carries the tube from a H apparatus, which tube dips considerably under the water, the middle neck carries a piece of tubing about 15 mm. internal diameter, dipping 2 or 3 cm. under the water, and the third neck carries an exit tube in communication with a condenser; between the condenser and the three-necked bottle is placed a test tube, to collect part of the water vapour coming over. The condenser consists of a tube about 100 mm. long and 30 mm. diameter, narrowed so that the lower end forms a tube about 40 mm. long by 12 mm. wide; this condenser is closed by a cork through which pass the entrance tube from the three-necked bottle and an exit tube, which is bent downwards and dips under the surface of water; these two tubes are cut off obliquely just below the cork. The condenser is placed in a deep vessel full of cold water which contains sufficient ice to keep the temperature at 0°. H is passed through the apparatus until all the air is driven out, the three-necked bottle is placed in a water-bath until the contents are warmed to 60°, and Ca phosphide, in pieces the size of peas, is dropped down the wide tube in portions about 2 g. at a time and at a rate such that 50 g. are added in 15 to 20 minutes. Gaseous P hydride passes off and bubbles up through the water, and the liquid hydride collects in the condenser, about 1-2 c.c. being obtained for 50 g. Ca phosphide used (Hofmann, *B.* 7, 531; Gattermann a. Hausknecht, *B.* 23, 1174; the many precautions to be taken in working with this compound are described by G. a. H.).

Properties and Reactions.—A colourless, highly refractive liquid; insol. in water; burns in air, with bright flame to P_2O_5 and H_2O; does not solidify at −10°; boils 57°-58° at 735 mm. (G. a. H., *l.c.*). S. G. 1·007 to 1·016 (G. a. H.). Decomposed by light into PH_3 and solid P_2H; the liquid may be kept for a short time in sealed tubes, but decomposition soon begins, and the tubes explode violently (G. a. H.). The same decomposition is effected by conc. HClAq, air mixed with CO_2, &c. Passage of the gas prepared as described above through a little conc. HClAq removes every trace of PH_2, and hence causes the gas which issues to be non-inflammable. If CO_2 is passed through the U-tube containing liquid PH_2 a nearly invisible greenish light appears at the end of the tube; this flame is not hot enough to ignite a candle (*v.* Hofmann, *B.* 7, 531; Thénard, *A. Ch.* [8] 14, 5; Bonet a. Bonfil, *J. pr.* 55, 247; Gattermann a. Hausknecht, *B.* 23, 1174). The composition of PH_2 was determined by Thénard by decomposing a known quantity by direct sunlight in a graduated tube filled with Hg: 100 parts liquid phosphide gave 61·8 parts gaseous PH_3 and 38·2 parts solid P_2H; *i.e.* 1 molecule P_2H was produced for 3 mols. PH_3, hence the equation $5PH_2 = P_2H + 3PH_3$. This equation was confirmed by G. a. H., who made also direct estimation of H by burning with $PbCrO_4$ in a current of CO_2 (*B.* 23, 1174).

Diphosphorus hydride P_2H or P_4H_2. Mol. w. unknown. H. F. $[P^2,H] = 17,700$ (Ogier, *C. R.* 89, 707).

Formation.—1. By decomposing phosphide of Ca or K (Magnus, *P.* 17, 527) by HClAq.—2. By the action of light, HClAq, Cl (Le Verrier, *A. Ch.* [2] 60, 174), and various other reagents, on PH_2.—3. By the decomposition of PI_2 by water (Rüdorff, *P.* 128, 473). Hittorf (*P.* 126, 193) obtained only amorphous P by this process.

Preparation. — A two-necked bottle is arranged with an exit tube dipping under water, and a wide entrance tube, down which is passed the delivery tube of a H-apparatus; conc. HClAq is placed in the bottle, H is passed through until all air is driven out, the H apparatus is removed, and small pieces of freshly-prepared Ca phosphide (for preparation *v. Preparation of phosphorus dihydride*, p. 137) are dropped slowly into the bottle. The P_2H which forms in the bottle is rapidly washed with cold water, and dried *in vacuo* (P. Thénard, *A. Ch.* [3] 14, 5).

Properties.—A yellow flocculent powder, which becomes orange-yellow in light; tasteless and odourless. When dry may be heated to c. 200° before taking fire; ignited by a blow of a hammer.

Reactions.—1. Ignited by *heating in air* to c. 200°; also by a blow of a hammer.—2. Slowly decomposed in *moist air*, especially if in sunlight, to P_2O_5 and H.—3. *Distillation in hydrogen* produces PH_3 (Thénard, *l.c.*).—4. *Chlorine* forms PCl_5 and HCl.—5. Dissolves in dilute *nitric acid*; oxidised with ignition by conc. HNO_3Aq.—6. *Alcoholic solution of potash* produces PH_3 and H; addition of water to the reddish solution ppts. yellow flocks of ? amorphous P or a lower oxide of P.—7. Explodes when mixed with *potassium chlorate*, *silver oxide*, *mercuric oxide*, or *cupric oxide*, and struck or warmed. – 8. Ppts. metallic phosphides from solutions of *salts of many heavy metals* (Le Verrier, *l.c.*).

Determination of composition.—The quantity of P in the solid hydride was determined by Thénard by heating with a weighed quantity of PbO, and weighing the mixture of PbO and Pb phosphate thus produced; the H was determined by decomposing by red-hot Cu, and collecting the H set free. Rüdorff decomposed the hydride by heat, and collected and analysed the mixture of PH_3 and H thus formed; he also oxidised the compound by HNO_3Aq, and estimated P as Pb phosphate.

Phosphorus, iodides of. P and I combine directly, even at −24°; two iodides, PI_2 and PI_3, have been isolated, and the existence of a third, PI_5, is probable.

Phosphorus di-iodide PI_2 or P_2I_4. Mol. w. not known. H.F. $[P,I^2] = 9,880$ from solid P and I; 20,680 from solid P and gaseous I (Ogier, *C. R.* 92, 83).

Formation.—1. By adding I to P Combination occurs even at −24°, with production of much heat, and ignition of the excess of P if air is admitted; amorphous P is produced besides PI_3 (*v.* Wurtz, *A. Ch.* [3] 42, 129).—2. By the reaction of I with PH_3; also of I in acetic acid on PCl_3 (Hofmann, *A.* 103, 305; Ritter, *A.* 95, 210).

Preparation.—One part by weight of P is dissolved in CS_2, and $8\frac{1}{5}$ parts of I are added little by little. When the colour of the dark brownish-red liquid thus produced has changed to orange it is cooled to 0° for some hours, when the vessel becomes filled with crystals; the crystals are freed from CS_2 by heating in a water-bath, while a stream of dry air is passed over them (Corenwinder, *A. Ch.* [3] 30, 242). The crystals may also be obtained by evaporating the solution in CS_2 in a stream of CO_2 (Berthelot a. Luca, *C. R.* 39, 748). Corenwinder says that from 2 to 3 g. P, and 60 to 75 c.c. CS_2, are convenient quantities to use.

Properties and Reactions.—Large orange-coloured prisms, melting at 110° (Corenwinder, *l.c.*). Heated in O gives P_2O_5 and I (Berthelot, *C. R.* 86, 628, 787, 859, 920; 87, 575, 667). Decomposed by H_2O to H_3PO_3Aq, PH_3, HIAq, and a yellow flocculent solid supposed to be amorphous P (Hittorf, *P.* 126, 193), regarded by Rüdorff as solid P_4H_2 (*P.* 128, 473), and said by Gautier (*C. R.* 76, 49, 173) to be P_5H_3O.

Phosphorus tri-iodide PI_3 (*Phosphorous iodide*). Mol. w. 410·55. H.F. $[P,I^3] = 10,900$ (Ogier, *C. R.* 92, 83). This compound is obtained in large red prisms by dissolving one part of P in CS_2, adding a solution of $12\frac{1}{4}$ parts of I in CS_2, concentrating much out of contact with air, and then placing in a freezing mixture. As the crystals are very sol. CS_2, they should be at once freed from mother-liquor, and dried in a stream of dry air at c. 50°. The crystals melt at 55°, and boil at a higher temperature, with evolution of I. PI_3 is very deliquescent; moist air decomposes it at once to H_3PO_3Aq and HIAq (Corenwinder, *A. Ch.* [3] 30, 242).

Phosphorus penta-iodide PI_5 (*Phosphoric iodide*). Isolation doubtful. Hampton (*C. N.* 42, 180) obtained a dark-crimson, very deliquescent solid, giving numbers on analysis agreeing with 80 p.c. PI_5 + 20 p.c. PI_3, by dissolving P in a little CS_2 in a stream of pure dry N, adding rather more than enough I to form PI_5, distilling off CS_2 (in a N stream) at 45° under reduced pressure, and then warming to 50°; at 55°, under the reduced pressure, I began to sublime.

Phosphorus, iodo-chloride of, PI_2Cl_3. Produced by adding much I to a little PCl_3, allowing to stand in moist air for some days, drying the crystals in a stream of air, dissolving in CS_2, and crystallising: large, red, six-sided crystals, very hygroscopic; decomposed by water to H_3PO_3Aq, HClAq, and HIAq (Moot, *B.* 13, 2029).

Phosphorus, nitride of. No compound of P and N has been isolated with certainty. A substance supposed to be a nitride by Rose (*P.* 24, 308; 28, 529) and Wöhler a. Liebig (*A.* 11, 139) was found to contain H. Briegleb a. Geuther (*A.* 123, 236) think that a compound P_3N_5 is perhaps produced by the reaction of PCl_5 on hot Mg_3N_2 in an atmosphere of N.

Phosphorus, oxides of. P and O combine very readily, with production of much heat; four compounds are produced according to the conditions: P_4O, P_2O_3, P_2O_4, and P_2O_5; the V.D.

of the second of these shows that its mol. formula as a gas is P_4O_6. The oxides P_2O_3 and P_2O_5 are anhydrides; the former reacts with water to produce the acid H_3PO_3, and the latter to produce three acids, HPO_3, H_3PO_4, and $H_4P_2O_7$; the oxide P_2O_4 is not the anhydride of a corresponding acid—with water it produces the two acids H_3PO_3 and H_3PO_4.

The only oxide formed when P glows in air at ordinary temperature is P_2O_5, but P_2O_3 is formed by drawing air over P without the latter glowing (Thorpe a. Tutton, *C. J.* 57, 573); at 50°-60° small quantities of P_2O_3 are produced, and this oxide is produced in larger quantities when the P is actually ignited; at moderately high temperatures and with a limited supply of air the oxide P_4O is formed in addition to P_2O_5 and P_2O_3. If the products of the slow burning of P in dry air are heated together in CO_2, the oxide P_2O_4 is formed, along with some P_4O. The products of burning P in a limited supply of dry air generally contain small quantities of P; this may be removed by sucking the products through a tube heated by steam (Thorpe a. Tutton, *C. J.* 49, 833).

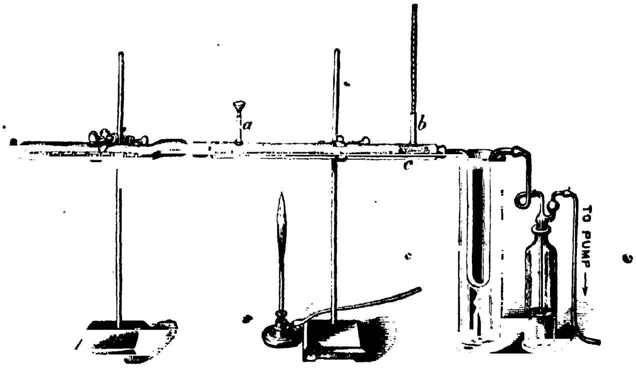
PHOSPHORUS SUBOXIDE P_4O. Mol. w. uncertain. Some doubt still remains concerning the composition of the lowest oxide of P; but the evidence is in favour of the existence of a definite oxide P_4O. Le Verrier (*A.* 27, 167) obtained a yellowish solid by exposing P in PCl_3 or in ether to air, warming the solid thus formed with water, and drying over H_2SO_4. A similar product was obtained by the incomplete combustion of P in air, or by the action on P of such oxidisers as iodic or periodic acid in presence of water (*v. Gm.-K.* i. 2, 107). This substance was generally looked on as an oxide of P; Le Verrier gave it the formula P_4O; Schrötter (*W. A. B.* 8, 246) thought it was only a mixture of ordinary and amorphous P. Reinitzer a. Goldschmidt (*B.* 13, 845) obtained the oxide P_4O by heating $POCl_3$ with P to 200°-250°, also by heating $POCl_3$ with Zn, Mg, or Al at 100°. Thorpe a. Tutton (*C. J.* 49, 833) found that P_4O is one of the products of burning P in a limited supply of air at moderately high temperatures, and that it is formed when the products of the slow burning of P in dry air are heated to c. 300° in CO_2. The experiments of R. a. G. indicate the existence of two varieties of P_4O; one of these reacts with hot alkali solutions, evolving PH_3, and reduces salts of Au and Ag and mercurous salts, and the other is not acted on by alkalis, and does not reduce salts of Au, Ag, or Hg.

Preparation and Properties of P_4O *which reduces salts of* Ag, Au, and Hg.—1. Thin plates of pure Zn are heated with $POCl_3$ in a sealed tube in a water-bath at 100° for some hours, the liquid, with suspended solid matter, is poured off, the solid is allowed to settle and the liquid is decanted off; the solid is heated as before for some time with $POCl_3$ (to remove any Zn present), the liquid is poured off, the solid is washed with $CHCl_3$ to remove $POCl_3$, then with HClAq, and finally with water; the solid is then dried for some days *in vacuo* (Reinitzer a. Goldschmidt, *B.* 13, 849); the other products of the reaction are $ZnCl_2$ and $Zn2PO_3$. As thus prepared P_4O is an orange-red powder. It very obstinately retains water, the sample made by R. a. G. contained c. 8 p.c. water, but the P and O were in the ratio P_4O. This oxide in moist air evolves PH_3; it reacts with boiling alkali solutions forming PH_3 and alkali phosphite and phosphate; solutions of salts of Au and Ag, and mercurous salts, are reduced with ppn. of the metals; heated in H, P is given off, and P_2O_5 remains.—2. PCl_3 is placed in an open flask, of c. 1 litre capacity, containing a layer about 2 cm. thick of P in small pieces; the PCl_3 just covers the P; after c. 2 days the PCl_3 is poured off, the pieces of P and the adhering yellow film are loosened from the flask, and allowed to fall slowly into cold water (if water is added in quantity, heat is produced, and the products of the slow oxidation of P are decomposed). After a little, the water is filtered from suspended P, and the clear yellow filtrate is heated to 80°, when a very finely divided yellow solid settles down; this solid is washed with warm water in a filter, removed from the filter while moist, and placed in a basin, over H_2SO_4 *in vacuo*. Le Verrier's P_4O was tasteless and odourless, did not change in dry air or O, but in moist air it gave off PH_3; it was decomposed somewhat above 360°, giving off P and leaving P_2O_5; oxidised by Cl to PCl_5 and P_2O_5; heated with conc. H_2SO_4, gave SO_2; unacted on by HClAq; oxidised and dissolved by HNO_3Aq; exploded with $KClO_3$; readily combined with H_2O to form $P_4O.H_2O$. The oxide obtained by Thorpe a. Tutton (*C. J.* 49, 833) was formed by slowly burning P in dry air, transferring the products to a tube filled with CO_2, exhausting by a Sprengel pump, and heating to 290°; as the oxide is described as orange-red, it was probably the form of P_4O which reduces salts of Au, Ag, and Hg.

Preparation and Properties of P_4O *which does not reduce salts of* Ag, Au, *and* Hg.—$POCl_3$ is heated with an excess of P in a sealed tube to 200°-250°; the sides of the tube become covered with a scarlet-coloured solid, which is washed with CS_2 (to remove P) and dried *in vacuo* (R. a. G., *l.c.*; the other products are PCl_3, $P_2O_3Cl_4$ and a little P_2O_5). As thus prepared, P_4O is a scarlet-red solid; S.G. 1·88; it is not acted on by water or alkali solutions, and it does not reduce salts of Ag, Au, or Hg. This form of P_4O seems to have been obtained by Pelouze (*A.* 3, 52) by burning P in O; and by Le Verrier (*A.* 27, 175) by burning P in a thin layer on a porcelain plate, washing with water to remove oxyacids, and boiling with PCl_3 to remove P.

PHOSPHOROUS OXIDE P_4O_6. (*Phosphorus trioxide. Phosphorous anhydride.*) Mol. w. 219·6; same in solution in C_6H_6 (Thorpe a. Tutton, *C. J.* 57, 545). Melts at 22·5°; boils at 173·1° (T. a. T.). S.G. $\frac{21°}{4°}$ liquid P_4O_6 1·9431; solid P_4O_6 at $\frac{21°}{4°}$ c. 2·135. S.G. at b.p. = 1·6897 (T. a. T.). V.D. 111·9. S.V. 130·2 (T. a. T.). $\mu_A = 1·5311$; $\frac{\text{Mol. w.}}{\text{S.G.}} \times \mu = 60·5$ (T. a. T.). Mol. w. $\frac{\mu_H - \mu_A}{\text{S.G.}} = 4·17$. M.M. 9·962.

Preparation.—A piece of combustion-tubing about 40 mm. bore is drawn into the shape shown in the figure on following page, and is fitted by a good cork into a brass tube, which is surrounded by a wider tube of brass; water is introduced at *a* between the brass tubes, and a thermometer is placed at *b*. A loose-plug of glass-wool is placed in the inner brass tube at *c*. The U-shaped condenser is of rather narrow bore, the limbs are about 800 mm. long, a small bottle is attached to the vertical piece at the bottom of the condenser, which is itself connected with the inner brass tube by a good cork; the condenser and small bottle are surrounded by ice and salt. The bottle between the condenser and the pump contains oil of vitriol. Two sticks of P are dried between filter-paper, cut into pieces c. 25 mm. long, and placed in the combustion tube, which is then narrowed at the open end and fitted into the brass tube; the pump is set in action, and the P is ignited by holding a small flame beneath the open end of the combustion-tube. Air is sucked over the P as rapidly as possible; if the combustion is too local, much P_2O_5 is formed; considerable quantities of red P_4O are formed near the burning P. When the P has burnt for c. 15 mins. the water in the brass tube is heated to c. 50°, at which temperature it is kept till near the end of the experiment, when it is raised to 60°. P_4O_6 begins to collect in the condenser about 30 mins. after starting the combustion; if the glass-wool is packed properly (it should not be too tight) no P_2O_5 passes into the condenser, and if the temperature of the water does not exceed 60° only very small quantities of P pass over. The process is stopped when c. $\frac{4}{5}$ths of the P is burnt, else the P_4O_6 may be oxidised. The condenser is removed, the P_4O_6 is melted by the heat of the hand, and run down into the little bottle, from which it may be transferred to another bottle which has been filled with dry CO_2; this bottle should have a very tightly-fitting stopper, and should be kept in the dark in an atmosphere of CO_2 (T. a. T., *l.c.*).



Properties.—A white snow-like solid, with an alliaceous odour resembling that of P; when melted and cooled slowly crystallises in long thin prisms, probably monoclinic; melts at 22·5° to a clear, colourless, very mobile liquid, which solidifies again at 21°; the liquid may be cooled in a narrow tube several degrees below m.p. without solidifying; boils at 173·1° in CO_2 or N. Can be gasified in Hofmann's V.D. apparatus at 132°. Mol. w. as gas, and also in solution in C_6H_6 (determined by cryoscopic method), corresponds with P_4O_6. Soluble without change in C_6H_6, CS_2, $CHCl_3$, and ether. Heated to c. 200° in sealed tube begins to decompose to P_2O_4 and P. Decomposed by light, with separation of red P. T. a. T. (*C. J.* 59, 1019) several times obtained clear, transparent, perfectly-formed crystals of P_4O_6 by slow spontaneous sublimation *in vacuo*, which remained unchanged for many days, although exposed to light. Spec. volume at b.p. = 130·2. (For details of thermal expansion and S.G. at b.p. *v.* T. a. T., *C. J.* 57, 545.) Reacts slowly with cold water, forming H_3PO_3Aq; with boiling water reaction is violent, PH_3 is evolved, and red P, or perhaps P_4O, and H_3PO_4Aq are formed. Oxidises to P_2O_5 by exposure to air or O; if temperature is raised the P_4O_6 ignites and may explode. P_4O_6 has a well-marked physiological action; the action of P may be due to P_4O_6, formed by the air oxidising the P (T. a. T., *l.c.* p. 573).

Reactions.—1. *Heat* decomposes P_4O_6, forming P_2O_4 and P (? P_4O); the action begins at c. 210° in a sealed tube, and the whole of the P_4O_6 is decomposed at 440° (T. a. T., p. 552).—2. Rapidly acted on by *light*, becoming yellow and then dark-red (T. a. T., p. 553). The action of light separates red P; the amount obtained after several months' exposure does not exceed 1 p.c. (T. a. T., *C. J.* 59, 1019). By exposing P_4O_6 to light for some months in a sealed tube filled with dry CO_2, then melting, filtering through glass-wool, and repeating this process several times, T. a. T. eventually obtained P_4O_6 which remained perfectly clear and colourless after twelve months' exposure (*l.c.*, p. 1023).—3. Oxidises to P_2O_5 in *air* or *oxygen*; when quite free from P, the oxide is not spontaneously inflammable. Under reduced pressure in O the P_4O_6 glows; on raising temperature to c. 70° at ordinary pressure the glow gives place to flame. Combination occurs between vapour of P_4O_6 and O; ozone is not formed. When P_4O_6 is thrown into O heated to 50°–60° ignition occurs with an intensely brilliant flame (T. a. T., *C. J.* 57, 569).—4. Glows continuously, and oxidises to P_2O_5, when a stream of *ozonised oxygen* is passed over it.—5. Ignites in *chlorine*, burning with a greenish flame; when surrounded by ice and exposed to slow stream of Cl a liquid is formed, which on distillation gives $POCl_3$, while PO_2Cl (?) remains (T. a. T., *C. J.* 57, 572).—6. Reacts violently with liquid *bromine*; using Br vapour at ordinary temperature, T. a. T. (*C. J.* 59, 1020) obtained PBr_3 and P_2O_5, and on then heating $POBr_3$ and PO_2Br (?) were formed.—7. *Iodine* reacts slowly; by heating with I and CS_2 under pressure, P_2O_5 and P_2I_4 are produced (T. a. T., *l.c.*, p. 1021). 8. Heated with *sulphur*, in CO_2 or N, two layers of liquid are formed; at 160° there is violent reaction, and solid $P_4O_6S_4$ is produced (*v.* PHOSPHORUS, SULPHOXIDE OF, p. 149; T. a. T., *l.c.*, p. 1022).—9. Seems to form a Se compound analogous to $P_4O_6S_4$ by heating with *selenium* (T. a. T., *l.c.*, p. 1026).—10. Dissolves very slowly in *water*, forming H_3PO_3Aq (T. a. T., *C. J.* 57, 567); $P_4O_6 + 6H_2O + Aq = 4H_3PO_3Aq$. The action of *hot water* is very energetic; red P, or red P_4O, is ppd., inflammable hydride of P is evolved, and H_3PO_4Aq is formed; if the quantity of P_4O_6 exceeds 2 g. the action of hot water is violently explosive.—11. Dry *hydrogen chloride* is rapidly absorbed; PCl_3 is formed along with H_3PO_3, H_3PO_4, and yellow P (T. a. T., *C. J.* 59, 1022).—12. Conc. *sulphuric acid* reacts violently, forming H_3PO_4 and SO_2; if 1 g. or more P_4O_6 is used, the mass ignites (T. a. T., *l.c.* p. 1026).—13. P_4O_6 is rapidly oxidised to P_2O_5 by *sulphur trioxide*, which is reduced to SO_2; no compound could be obtained (T. a. T., *l.c.* p. 1026). According to Adie (*C. J.* 59, 230), if a little water is present, P_4O_6 and SO_3 form an unstable compound $H_3PO_4.3SO_3$.—14. *Nitrogen tetroxide* seems to react like SO_3, forming P_2O_5 and N_2O_3 or NO (T. a. T., *l.c.* p. 1028).—15. *Phosphorus pentachloride* produces PCl_3 and $POCl_3$; *phosphorus trichloride* reacts at c. 180° in a sealed tube, forming a mixture of P_2O_5, PCl_5, and red P (T. a. T., *l.c.* p. 1028).—16. *Sulphur chloride* reacts violently, producing $POCl_3$, $PSCl_3$, SO_2, and S (T. a. T., *l.c.* p. 1026).—17. *Ammonia* reacts with some violence, probably producing $OH.P.(NH_2)_2$ (*v.* PHOSPHAMIDES, p. 105).—18. *Cold dilute caustic soda*, or *caustic potash solution*, slowly dissolves P_4O_6, forming a solution of Na or K phosphite; *cold conc.* or *hot dilute solution of soda or potash* produces red P (or P_4O ?) and alkali phosphate, and evolves inflammable hydride of P.—19. Ignites in contact with *absolute alcohol*; by allowing the alcohol to drop slowly on to cooled P_4O_6 the acid $P(OEt)_2OH$ is formed (T. a. T., *C. J.* 57, 569). P_4O_6 seems *not* to react with H, PH_3, CO, CO_2, SO_2, N, NO, CN, or C_2H_4 (T. a. T., *C. J.* 59, 1029).

PHOSPHORUS TETROXIDE P_2O_4 (*Phosphoroso-phosphoric oxide. Hypophosphoric oxide*). Mol. w. not determined; corresponding sulphide has mol. w. P_3S_6. Hautefeuille a. Perrey (*C. R.* 99, 33) noticed that a crystalline sublimate is obtained by heating the products of the combustion of P; Thorpe a. Tutton (*C. J.* 49, 833) proved that this sublimate is a definite oxide P_2O_4. Concerning the combustion of P in air *v.* pp. 128 and 139.

Preparation.—P is burnt slowly in a stream of air dried by H_2SO_4 and P_2O_5; the products are collected in a glass tube, surrounded by an outer tube filled with steam, and are then quickly transferred to a tube filled with dry CO_2, the tube is drawn out, exhausted by a Sprengel pump (care being taken to prevent entrance of moisture), and sealed; at c. 290° the white mass becomes orange-coloured, and then red, and a white crystalline sublimate of P_2O_4 is formed, leaving P_2O_3 and P_4O in the lower part of the tube. T. a. T. (p. 838) think that the P_2O_4 is derived from the P_2O_3, thus $7P_2O_3 = 5P_2O_4 + P_4O$; that P_2O_4 is formed by heating P_2O_3 out of contact with O is shown by T. a. T. (*C. J.* 57, 552).

Properties and Reactions.—Colourless crystals, probably orthorhombic; do not melt at 100°. Volatilises at c. 180°. Very deliquescent, forming H_3PO_3Aq and H_3PO_4Aq; from this reaction T. a. T. conclude that P_2O_4 is not the anhydride of $H_4P_2O_6$, as an aqueous solution of this acid does not behave like a mixture of H_3PO_3 and H_3PO_4, and can be boiled without change. Solution of P_2O_4 in water reduces $AgNO_3Aq$ to Ag, and $HgCl_2Aq$ to HgCl; $KMnO_4Aq$ is very slowly decolourised; 'magnesia mixture' gives an immediate pp., and after standing some time the filtrate gives a large pp., with NH_4 molybdate after heating with HNO_3Aq.

PHOSPHORIC OXIDE P_2O_5 (*Phosphoric anhydride. Phosphorus pentoxide*). Formula probably molecular, from analogy of P_2S_5. S.G. 2·387 (Brisson, *Pesanteur spécifique des Corps* [Paris, 1787]). H.F. $[P^2,O^5] = 369,900$; $[P^2O^5,Aq] = 35,600$ (*Th.* 2, 409).

Formation.—1. This oxide is formed by burning P in a large excess of air; concerning the combustion of P in air *v.* pp. 128 and 139.—2. It is also formed by burning P in such gaseous O compounds as NO, NO_2, ClO_2.—3. By distilling $P_2O_3Cl_4$.

Preparation.—A large glass balloon with a wide opening and two side necks is thoroughly dried; through a cork in the wide opening passes a piece of wide tubing, which reaches to about the centre of the balloon, and from the lower end of this tube a small porcelain basin is suspended by Pt wires; one of the side necks is connected with U-tubes containing pumice soaked in H_2SO_4, and the other side neck is connected with a wide-mouthed perfectly dry bottle, which is again in connection with a water-pump, a bottle with H_2SO_4 being placed between the pump and the wide-mouthed bottle. A small piece of well-dried P is placed in the little basin, and is ignited by passing a hot wire down the glass tube, the mouth of which is then closed by a good cork; a rapid stream of air is sucked through the apparatus; the P is burnt to P_2O_5, part of which collects on the bottom of the balloon and part passes into the bottle attached to the side neck. When the P is burnt another small piece is dropped down the glass tube into the little basin, and the process is continued. When sufficient P_2O_5 has collected in the bottle this is closed by a well-fitting stopper (Delalande, *A. Ch.* [2] 76, 117). For other forms of apparatus *v.* Marchand, *J. pr.* 16, 373; Mohr, *Gm.-K.* i. 2, 120. Grabowski (*A.* 136, 119) has described a vessel of tinplate for preparing large quantities of P_2O_5.

Shenstone says that P_2O_5, prepared by the ordinary process, has generally reducing powers, and is not, therefore, trustworthy as a drying agent. S. recommends to heat for some days at c. 300° in a *very slow* stream of dry O; then to

**heat at 300° in a more liberal, but still limited, supply of dry O until the reddish colour produced by the first heating has disappeared; then to heat at 300° in a more rapid stream of dry O so long as sublimation occurs; and finally to sublime, fractionally, in a current of dry O, from retorts of hard glass into receivers of the same material. The first portions of the sublimate should be rejected. The whole of these processes may be done in glass vessels. The retorts used in the final sublimation may be heated in a combustion furnace (*private communication*).

Hautefeuille a. Perrey (*C. R.* 99, 33) say that P_2O_5 can be obtained in three forms: crystalline, amorphous and powdery, and glass-like. They say that when P is burnt in a glass tube in dry air, the crystalline form of P_2O_5 is deposited on the colder part of the tube, the amorphous powdery form on the hotter part, and the vitreous form on that part of the tube which is heated to redness. These authors assert that crystalline P_2O_5 is obtained free from the other forms by distilling the products of the burning of P; that heating the crystals in vapour of S produces the powdery amorphous form; that the vitreous variety is formed by heating either of the others to low redness; and that this vitreous form yields crystalline P_2O_5 when sublimed at a red heat. Considering the facts brought to light by the work of Thorpe a. Tutton on the combustion of P (*C. J.* 49, 833; 57, 545; *v.* beginning of this article, p. 139), the existence of various modifications of P_2O_5 must be looked on as very doubtful. T. a. T. (*C. J* 49, 838) think it very likely that the crystalline form of P_2O_5 obtained by H. a. P. was P_2O_4; and it is probable that the differences in the properties of the powdery and vitreous P_2O_5 were due to admixture with P_2O_3. No analytical data are given by H. a. P. Shenstone (*priv. comm.*) says that P_2O_5 purified by his method is crystalline, but becomes amorphous when suddenly heated.

Properties.—A snow-white, amorphous, inodorous, very deliquescent, solid. Melts and sublimes below red heat (Lautermann, *A.* 113, 240); according to Davy (*A. Ch.* [2] 10, 218) volatile only at white heat. Absorbs water very rapidly; hence is used as a very efficacious drying agent. P_2O_5 is the anhydride of three phosphoric acids: HPO_3, H_3PO_4, and $H_4P_2O_7$. Dry P_2O_5 does not change the colour of dry litmus paper. Commercial P_2O_5 often contains traces of P, which cause it to redden in light, and also traces of As_2O_3 derived from the impure P used; it generally has more or less marked reducing powers.

Reactions. — 1. *Water* produces HPO_3; $H_4P_2O_7$ is formed from HPO_3 by the long-continued action of moist air; and H_3PO_4 is produced by continued heating of HPO_3Aq.—2. P_2O_5 removes H_2O from many *compounds which contain water or the elements of water*; *e.g.* it produces anhydrides when heated with several acids, H_2SO_4 gives SO_3, HNO_3 gives N_2O_5, and hydrocarbons are often formed by heating P_2O_5 with compounds of C, H, and O.—3. Heated with several *metals*, *e.g.* Fe, K, Na, Zn, metallic oxide, phosphide, and phosphate are formed.—4. *Salts of acids the anhydrides of which are volatile* are decomposed by heating with P_2O_5, with formation of phosphates and volatilisation of the anhydrides (Odling, *P. M.* [4] 18, 168).—5. $POCl_3$ is formed by heating P_2O_5 with *sodium chloride*, or with *phosphorus pentachloride*.—6. Heated with *phosphoryl chloride*, $P_2O_3Cl_4$ and $P_7O_{15}Cl_5$ (which may be a mixture) are formed (Huntly, *C. J.* 59, 202).—7. *Ammonia* produces $PONH_2(OH)_2$ and $P_2O_3(NH_2)_2(OH)_2$ (*v.* PHOSPHAMIC ACIDS, p. 105).—8. Heated with *boron chloride* to 200° for 2–3 days, $P_2O_5.B_2O_3$ and $POCl_3.BCl_3$ are formed (Gustavson, *B.* 4, 976). $P_2O_5.B_2O_3$ is also formed by heating P_2O_5 with *boric acid.*

Combinations.—1. With *water* (*v. supra, Reactions*, No. 1).—2. With *sulphur trioxide* to form $P_2O_5.3SO_3$, decomposed at 30° (Weber, *B.* 20, 86).—3. With *silica and water* to form $P_2O_5.SiO_2.4H_2O$; formed by heating conc. H_3PO_4Aq with silica (Hautefeuille a. Margottet, *C. R.* 104, 156). Similar compounds with *oxides of titanium, zirconium*, and *tin* are described by H. a. M. (*C. R.* 102, 1017).

Phosphorus, oxyacids of. The three phosphoric acids are described in the article PHOSPHORIC ACIDS, p. 124, and the salts of those acids in the article PHOSPHATES, p. 106; the other oxyacids of P and their salts are described under PHOSPHORUS, OXYACIDS OF, AND THEIR SALTS, p. 149.

Phosphorus, oxybromide of, $POBr_3$ (*Phosphoryl tribromide*). Mol. w. 286·2. Melts at 55° (Baudrimont, *A. Ch.* [4] 2, 58); at 45°–46° (Ritter, *A.* 95, 210). Boils at 195° (Ritter, *l.c.*); at 193° (Gladstone, *P. M.* [3] 35, 345). V.D. 145·5. S.G. 2·822 (Ritter, *J.* 8, 301). H.F. $[P,O,Br^3] = 108,000$ from liquid Br; 120,000 from gaseous Br (Ogier, *C. R.* 92, 83).

Formation.—1. By the action of moist air or a very little H_2O on PBr_5 (Gladstone, *P. M.* [3] 35, 345).—2. By the action of oxalic or acetic acid on PBr_5 (Baudrimont, *A. Ch.* [4] 2, 58; Ritter, *A.* 95, 210).—3. By passing O into boiling PBr_3; explosions generally occur (Demole, *Bl.* [2] 34, 201).

Preparation.—To 137·5 parts PCl_3 are added 18 parts H_2O, and then 160 parts Br are added drop by drop, HBr and HCl are evolved, and $POCl_3$ and $POBr_3$ remain (part of the PCl_3 is decomposed to H_3PO_3 and HCl, and the H_3PO_3, Br, and remaining PCl_3 react, (?) thus $2PCl_3 + H_3PO_3 + 3Br_2 = 2POCl_3 + POBr_3 + 3HBr$); the liquid is distilled, the portion boiling above 150° being kept separate and surrounded by a freezing mixture till it solidifies (Geuther a. Michaelis, *J. Z.* 6, 242).

Properties and Reactions.—Large colourless plates, which melt and boil in dry air without decomposition; soluble in conc. H_2SO_4, reppd. by H_2O; soluble in $CHCl_3$, CS_2, ether, and turpentine. Decomposed rapidly by *water* to HBrAq and H_3PO_4Aq; *bromine chloride* forms $POBrCl_2$ or $POCl_3$, and Br, according to the quantity used (Geuther, *J. Z.* 10, 130); *hydrogen sulphide* probably forms $PSBr_3$; *chlorine* forms $POCl_3$ and Br; *bromine* seems to form an additive compound which separates into $POBr_3$ and Br on heating (Gladstone, *l.c.*); *tin* and *antimony* remove Br (Baudrimont, *l.c.*).

Phosphorus, oxybromochlorides of. Two of these compounds are known, but it is doubtful whether the second is a definite compound or a mixture of $POCl_3$ and $POBr_3$.

Phosphorus oxybromodichloride $POBrCl_2$. (*Phosphoryl bromodichloride*). Mol. w. 197·4. Melts at 11°; boils at 137·6 (Thorpe, *C. J.* 37, 348). S.G. $\frac{0^\circ}{4^\circ}$ 2·12065 (Thorpe, *l.c.*). A colourless liquid, which solidifies, when cooled below 0°, to large colourless tablets which melt at 11°; when repeatedly distilled, or more quickly when heated in a closed tube to c. 185°, decomposed to $POCl_3$ and $POBr_3$ (Chambon, *J. Z.* 10, 92); decomposed by H_2O to H_3PO_4Aq, HClAq, and HBrAq; with a little alcohol forms $POCl_2(OEt)$ and HBr. Prepared by the reaction of $POBr_3$ with BrCl in the ratio $POBr_3 : BrCl$ (Geuther, *J. Z.* 10, 130); by the action of PBr_5 on $P_2O_3Cl_4$ (G. a. Michaelis, *J. Z.* 7, 103). By reacting on $P.OEt.Cl_2$ with Br (Menschutkin, *A.* 139, 343); 80 g. Br are allowed to drop slowly into 74 g. $P.OEt.Cl_2$ kept well cooled and constantly shaken; the reaction is very violent; the $POBrCl_2$ is separated from the C_2H_5Br formed by fractionation (Thorpe, *C. J.* 37, 343). The $P.OEt.Cl_2$ is prepared by slowly dropping absolute alcohol into well-cooled PCl_3 in the ratio $C_2H_6O : PCl_3$, allowing to stand for some time, and fractionating; the boiling-point is 117°–118°.

Phosphorus oxydibromochloride $POBr_2Cl$ (*Phosphoryl dibromochloride*). By the reaction of $POBr_3$ and BrCl, in the ratio $POBr_3 : 2BrCl$, Geuther (*J. Z.* 10, 130) obtained a liquid boiling between 150° and 160°, and decomposing very easily by heat into $POCl_3$ and $POBr_3$; analyses agreed with the formula $POBr_2Cl$, but the liquid was possibly a mixture of $POCl_3$ and $POBr_3$ ($3POBr_2Cl = POCl_3 + 2POBr_3$).

Phosphorus, oxychlorides of. Two oxychlorides of P have been isolated, $POCl_3$ and $P_2O_3Cl_4$. A third substance obtained by Gustavson (*B.* 4, 853) by heating together P_2O_5 and $POCl_3$, and said by him to be PO_2Cl, is declared by Michaelis (*G. O.* [1881] 2, 396) not to be a definite compound, and this is confirmed by Huntly (*C. J.* 59, 202).

Phosphoryl chloride $POCl_3$. Mol. w. 153·3. Boils at 107·2° (Thorpe, *C. J.* 37, 337). Melts at −1·5° (Geuther a. Michaelis, *B.* 4, 769). S.G. $\frac{0^\circ}{4^\circ}$ 1·71163 (Thorpe, *l.c.*). V.D. at 150° = 77·2 (Cahours, *A. Ch.* [3] 20, 369). For expansion by heat *v.* Thorpe (*l.c.*). S.V. 101·4 (T., *l.c.*). H.F. $[P,O,Cl^3] = 145,960$; $[PCl^3,O] = 70,660$ (*Th.* 2, 325).

Formation.—1. By heating PCl_3 in air or O, or with ozone, SO_3, SO_2Cl_2, and various other oxidisers.—2. By strongly heating PCl_5 in O, or with SO_3, SO_2, B_2O_3, &c., or by decomposing by a little H_2O.—3. By distilling NaCl mixed with P_2O_5 (Kolbe a. Lautemann, *A.* 113, 240).—4. By passing CO and Cl over Ca_32PO_4 mixed with C and heated to redness (Riban, *C. R.* 95, 110; Oglialoro, *G.* 13, 328).—5. By heating PCl_5 with P_2O_5.—6. By the reaction of Cl with P_2O_3 (Thorpe a. Tutton, *C. J.* 57, 572).

Preparation.—An intimate mixture of 1 part P_2O_5 with 2·9 parts PCl_5 is distilled, and the product is again distilled, that boiling at 106°–108° being collected separately; the equation $P_2O_5 + 3PCl_5 = 5POCl_3$ is realised.

Properties.—A colourless, highly refractive, strongly smelling liquid, which fumes in the air; the fumes strongly affect the eyes and respiratory organs; solidifies at −10°, when touched with a glass rod, to long, colourless tablets, which melt again at −1·5° (Geuther a. Michaelis, *B.* 4, 769). $POCl_3$ does not conduct electricity even when heated (Buff, *A.* 110, 257).

Reactions.—1. *Water* reacts rapidly, forming HClAq and H_3PO_4Aq $[POCl^3,Aq] = 72,190$ (*Th.* 2, 325).—2. *Alcohol* produces HCl and $PO.OEt.Cl_2$.—3. *Sulphur trioxide* at 160° forms $P_2O_3Cl_4$ and P_2O_5 (Michaelis, *G. O.* 2, 393).—4. *Sulphuric acid* produces $SO_2.OH.Cl$, HCl, and HPO_3 (Michaelis, *l.c.*).—5. Most *organic acids* react similarly to H_2SO_4, producing acid chlorides; *e.g.* $C_2H_3O.OH$ forms $C_2H_3O.Cl$; *salts of organic acids* react similarly, forming acid chloride and metaphosphate.—6. *Sulphates* form SO_2Cl_2 and orthophosphates.—7. *Sulphites* are partially changed to SO_2, mixed with metallic chloride and phosphate (Divers a. Shimidzu, *C. J.* 47, 208).—8. *Nitrates* produce chlorides and P_2O_5 &c.; *nitrites* give chlorides and phosphates and NO_2 (D. a. S., *l.c.*).—9. $POCl_3$ separates I from *potassium iodide* (Schiff, *A.* 102, 181).—10. *Chromyl chloride* forms Cl, P_2O_5, $CrCl_3$, and Cr_2O_3 (Casselmann, *A.* 91, 241; 98, 213).—11. *Phosphorus pentasulphide* at 150° produces $PSCl_3$ and P_2O_5.—12. *Phosphorus pentoxide* reacts at c. 200°, forming $P_2O_3Cl_4$ and a substance $P_7O_{15}Cl_9$, which may prove to be a mixture (Huntly, *C. J.* 59, 202).—13. *Phosphorus* reacts at 200° to form P_4O, PCl_3, $P_2O_3Cl_4$, and a little P_2O_5 (Reinitzer a. Goldschmidt, *B.* 13, 845).—14. $POCl_3$ is reduced by heating in closed tubes with many finely divided *metals*, *e.g.* Ag, Hg, Fe, Cu, As (Pb is without action); the products are generally PCl_3 and P_2O_5, and oxide, chloride, or phosphate of the metal; sometimes $P_2O_3Cl_4$ is said to be formed (*v.* R. a. G., *l.c.*); Mg, Al, and Zn are said to form red P_4O (R. a. G., *l.c.*). Zinc-dust with a little $POCl_3$ forms Zn phosphide, which evolves inflammable P hydride on addition of a little water (Denigès, *Bl.* [3] 2, 787).—15. With *ammonia* forms various *phosphamic acids* (*q. v.*, p. 105), and also *phosphamides* (*q. v.*, p. 105).—16. *Boric oxide* heated with $POCl_3$ in a sealed tube to 150°–170° for 8 to 10 hours forms $P_2O_5.B_2O_3$ and $POCl_3.BCl_3$ (Gustavson, *B.* 4, 975).

Combinations.—1. With *ammonia* to form a compound not yet examined.—2. With several *metallic chlorides* to form double compounds, *e.g.* with $AlCl_3$, $MgCl_2$, and $SnCl_2$ (Casselmann, *A.* 91, 241; 98, 213). Some of these compounds may be vapourised in absence of moisture; they are decomposed by water.—3. With *boric chloride* to form $POCl_3.BCl_3$, by passing BCl_3 into $POCl_3$; also by heating $POCl_3$ with B_2O_3. This substance is decomposed by heat; with water it gives H_3PO_4Aq, H_3BO_3Aq, and HClAq (Gustavson, *B.* 4, 975).

Constitution of $POCl_3$.—Two isomeric forms of $POCl_3$ are possible: Cl_2POCl and Cl_3PO; but the compounds obtained by different methods are identical. Wichelhaus (*A. Suppl.* 6, 257) thought that $POCl_3$ must have the constitution Cl_2POCl, because of its formation from Cl_2POEt, in which the O atom is in direct union with the P atom ($Cl_2POEt + Cl_2 = Cl_2POCl + EtCl$); but Geuther a. Michaelis (*J. Z.* 6, 242) pointed out that this formation of $POCl_3$ may be interpreted also in favour of the constitution Cl_3PO by supposing that Cl first replaces OEt, forming PCl_3, and that the PCl_3 and EtOCl then react;

(1) $Cl_2POEt + Cl_2 = Cl_3P + EtOCl$,
(2) $Cl_3P + EtOCl = Cl_3PO + EtCl$. The experiments of Reinitzer a. Goldschmidt (*B.* 13, 845) on the action of metals, on $POCl_3$ show that in most cases O is withdrawn, leaving PCl_3; and that in a few cases the 3 Cl atoms are withdrawn with formation of P_2O_5. These results do not indicate any differences between the functions of the Cl atoms, and hence they tend to favour the formula Cl_3PO. Thorpe (*C. J.* 37, 387) arrived at the formula Cl_2POCl from consideration of the specific volumes of $POCl_3$ and PCl_3. Masson a. Ramsay (*C. J.* 39, 50), also from considering the specific volumes of P and P compounds, deduced the formula $OPCl_3$. Although but one $POCl_3$ has been obtained, the isomeric compounds $(C_6H_5)_2POC_6H_5$ and $(C_6H_5)_3PO$ have been isolated (La Coste, *B.* 18, 2118).

Pyrophosphoryl chloride $P_2O_3Cl_4$ (*Phosphorus trioxytetrachloride*). Mol. w. not known. Boils 210°-215°, with partial decomposition. S.G. 1·58 at 7°.

Preparation.—1. 100 g. PCl_3 are placed in a cylinder surrounded by ice and salt, and the vapour from 20 g. liquid NO_2 is passed into the cylinder by a tube which reaches just to the surface of the PCl_3. The action proceeds at once; the products are P_2O_5, $POCl_3$, $P_2O_3Cl_4$, and NOCl. When all the NO_2 has been distilled into the PCl_3, the cylinder is placed in warm water to remove NOCl, and its contents are then fractionated; PCl_3 distils over first, then a considerable quantity of $POCl_3$ between 105° and 110°, and then $P_2O_3Cl_4$ from 200° upwards. It is best to prepare a considerable quantity of the impure product before fractionating; 350 g. PCl_3 yielded 40 g. $P_2O_3Cl_4$ (Geuther a. Michaelis, *B.* 4, 766).—2. The vapour obtained by heating 80 g. starch with 180 g. HNO_3Aq is led into 100 g. PCl_3; the product is fractionated, and that boiling under 100° is again treated as before; finally, the whole is fractionated. About 20 g. $P_2O_3Cl_4$ are obtained from 200 g. PCl_3 (G. a. M., *l.c.*).

Properties.—A colourless liquid, which fumes in the air; the vapour attacks cork. Has not been solidified by cooling. Boils, with partial decomposition into P_2O_5 and $POCl_3$, at 210°-214°.

Reactions.—1. *Heat* produces partial decomposition into $POCl_3$ and P_2O_5.—2. Decomposed by *water* to H_3PO_4Aq and HClAq.—3. *Alcohol* produces $PO.OEt.Cl_2$, $PO.OEt.(OH)_2$, and HCl. 4. *Phosphorus pentachloride* produces $POCl_3$. 5. *Phosphorus pentabromide* forms $POBr_3$ and $POCl_2Br$ (G. a. M., *l.c.*).

Metaphosphoryl chloride PO_2Cl. Gustavson (*B.* 4, 853) said that a compound of this composition is formed by heating P_2O_5 with $POCl_3$; but Michaelis (*G. O.* 2, 396) says that the substance is not a true compound, and this is confirmed by Huntly (*C. J.* 59, 242).

Phosphorus, oxychlorobromides of, *v.* Phosphorus, oxybromochlorides of, p. 142.

Phosphorus, oxyfluoride of, POF_3 (*Phosphoryl fluoride*). Mol. w. 103·92. V.D. 52 (Thorpe, *C. J.* 55, 759; Moissan, *Bl.* [3] 4, 260). A gas which fumes in air and is rapidly absorbed by water. Formed by the reaction of P_2O_5 with fluorides (Schulze, *J. pr.* [2] 21, 438); also by exploding a mixture of 2 vols. PF_3 and 1 vol. O by passing electric sparks (Moissan, *C. R.* 102, 1245); by gently heating an intimate mixture of 2 pts. finely-powdered cryolite with 3 pts. P_2O_5 in a brass tube, and collecting over Hg as soon as the gas which comes off is wholly absorbed by NaOHAq (Thorpe, *l.c.*). Moissan (*l.c.*) prepares POF_3 by heating ZnF_2 with $POCl_3$ in a brass tube, fitted with a leaden delivery tube; he allows the gas to pass through a brass tube cooled to −20°, and then over ZnF_2 to remove traces of $POCl_3$.

POF_3 liquefies at 16° under a pressure of 15 atmos., or at the ordinary pressure by cooling to −50° (M., *C. R.* 102, 1245). When compressed under 50 atmos. and the pressure then suddenly released, it solidifies to a snow-like mass. When quite dry it is without action on glass or Hg; heated in a glass tube SiF_4 and an alkaline phosphate are formed.

Phosphorus, oxyiodide of, $P_3I_6O_8$. Burton (*Am.* 3, 280) obtained a red crystalline compound, to which he gave this composition, as a by-product in preparing C_2H_5I. M.P. c. 140°; sublimable, with partial decomposition; e. sol. water, alcohol, and ether.

Phosphorus, oxynitride of, PON (*Phosphoryl nitride. Phosphoryl nitrile.* Formerly called *Phosphomonamide*). Mol. w. uncertain. A white powder, which melts at red heat to black glass-like mass. Obtained by heating $PO(NH_2)_3$ or $PONHNH_2$, the former of which is formed by the reaction of $POCl_3$ with NH_3, and the latter by the reaction of PCl_5 and NH_3 (Schiff, *A.* 101, 300; *cf.* Phosphamides, p. 105). Gives K_3PO_4 and NH_3 by action of molten KOH (*v.* also Gladstone, *C. J.* [2] 7, 18).

Phosphorus, selenides of. P and Se combine directly to form four compounds: P_4Se, P_2Se, P_2Se_3, and P_2Se_5. P_2Se, P_2Se_3, and P_2Se_5 combine with the selenides of the more positive metals to form compounds $R_2Se.P_2Se$, $(R_2Se)_2.P_2Se_3$, and $(R_2Se)_2.P_2Se_5$. The formulæ are not necessarily molecular.

Phosphorus subselenide P_4Se (*Phosphorus hemiselenide*). Prepared by melting together Se and ordinary P in the ratio Se : 4P(1:1·57) in an atmosphere free from O, and separating from amorphous P by distillation in absence of O. A dark yellow, oily, fetid-smelling liquid, which solidifies at −12°; e. sol. in CS_2, insol. alcohol and ether; takes fire in air; decomposed by water containing air, with formation of H_3PO_4Aq and Se compounds; not acted on by cold alkali solutions, but with boiling alkali solutions gives alkali phosphate and selenite, metallic selenide and P hydride; in solutions of metallic salts becomes covered with a crust of metallic phosphide and selenide (Hahn, *J. pr.* 93, 430).

Diphosphorus selenide P_2Se. (*Phosphorus protoselenide* or *monoselenide*). Prepared by melting together, in absence of O, P, and Se in ratio 2P : Se(1:1·28). A red solid; unchanged in dry air, in moist air gives off H_2Se; insoluble alcohol and ether; P is withdrawn by CS_2; boiling alkali solutions produce H_2Se and a red substance containing Se and P. By heating, in absence of O, with equivalent weights of metallic selenides, compounds $R^I{}_2Se.P_2Se$ and $R^{II}Se.P_2Se$ are formed; R = Ba, Cu, Fe, Mn, K, Ag, Na. The alkali compounds are decomposed by water; the compounds containing heavy metals decompose only at high temperatures, but they generally take fire when rubbed in a mortar; they are slowly decomposed by hot alkali solutions (Hahn, *l.c.*). From their empirical composition, R^IPSe, these compounds might be called *seleno-meta-hypophosphites.*

PHOSPHOROUS SELENIDE P_2Se_3. (*Phosphorus sesquiselenide* or *triselenide*). Prepared by heating together P and Se in ratio 2P:3Se(1:3·82) in absence of O. A dark ruby-red solid; sublimes to yellow vapours when heated out of O; burns when ignited in air. Oxidised slowly in moist air; evolves H_2Se when boiled with water. Insoluble alcohol, ether, and CS_2; easily soluble in potash, less soluble in alkali carbonate solutions. Forms compounds with metallic selenides $(R^I{}_2Se)_2.P_2Se_3$, and $2R^{II}Se.P_2Se_3$ (Hahn, *l.c.*); R = Ba, Cu, Pb, Mn, K, Ag, Na. From their empirical composition, $R^I{}_4P_2Se_5$, these compounds might be called *selenopyrophosphites.*

PHOSPHORIC SELENIDE P_2Se_5 (*Phosphorus pentaselenide*). Prepared by heating together amorphous P and Se in ratio 2P:5Se (1:6·37) in a stream of CO_2. A dark-red, nearly black, glass-like solid; insoluble in CS_2; crystallises from CCl_4 in black needles. In moist air, or water, decomposes slowly to H_2Se and H_3PO_4Aq; in conc. KOHAq quickly forms K_2Se and K_3PO_4Aq; alcohol forms H_2Se and $Et_3PO_2Se_2$ and also $Et_2HPO_2Se_2$. Very unstable compounds probably of the forms $(R^I{}_2Se)_2.P_2Se_5$ and $2R^{II}Se.P_2Se_5$ are obtained by heating P_2Se_5 with metallic selenides; R = Ba, Cu, Pb, Mn, K, Ag, Na. The empirical composition of these compounds would lead to the name *selenopyrophosphates* (Bogen, *A.* 124, 57; Rathke, *A.* 152, 200). Rathke (*l.c.*) supposed that the K salt of a selenophosphoric acid is formed by the reaction of P_2Se_5 with KOHAq.

Phosphorus, selenion acids of, salts of; *v.* DIPHOSPHORUS SELENIDE, PHOSPHOROUS SELENIDE, and PHOSPHORIC SELENIDE (*supra*).

Phosphorus, sulphides of. P and S combine, when heated together, with production of much heat and light; the action is often violently explosive. Four definite compounds seem to exist; the simplest formulæ are P_4S_3, P_2S_3, PS_2, and P_2S_5.

Two compounds containing less S than P_4S_3, viz. P_2S and P_4S, are often described, and substances said to be compounds of P and S in the ratio P : 3S and P : 6S have been mentioned by Dupré and Berzelius.

The substance to which the formula P_4S was given was obtained by heating P and S in the proper proportions (Berzelius, *A.* 46, 129, 255), or by digesting P with an alcoholic solution of K_2S_5 (Böttger, *J. pr.* 12, 357), or according to Wicke (*A.* 86, 115) by contact of P and S at ordinary temperatures; it was described as a colourless, oily liquid. A solid red form of P_4S was said to be formed by heating liquid P_2S with Na_2CO_3 (Berzelius, *l.c.*). The formula P_2S was given to a substance of which two forms were described: a yellow liquid obtained by carefully heating together P and S in the proper ratio, and a dark-red powder obtained by heating the liquid form with dry MnS in H (Berzelius, *l.c.*). Various double compounds of P_2S with metallic sulphides, $R^I{}_2S.P_2S$ and $R^{II}S.P_2S$ (R = Cu, Fe, Mn, Hg, Ag) were described by Berzelius. The composition of these bodies would lead to their being called *thiometahypophosphites.* Isambert (*C. R.* 96, 1771) has shown that when a solution of P in a large excess of S is distilled *in vacuo* the whole of the P passes off and leaves S. Schulze (*J. pr.* [2] 22, 113) found that P separated at 8° from a solution of S in P in the ratio P_4S, and that S separated when the elements were present in the ratio P_2S. Schulze also found that a stream of CO_2 removed P from both solutions at 150°; that heating to this temperature generally produced explosion; that the so-called liquid P_2S was soluble in CS_2, and that most of the S was removed by shaking this solution with alcohol, ether, or $CHCl_3$. Further, Schulze (*B.* 16, 2066) observed that solutions of S in P, in the ratio P_4S and P_2S, did not solidify homogeneously, but that P separated from the first, and S from the second, solution. From these facts Isambert and Schulze concluded that the so-called P_4S and P_2S are merely solutions of S in P. Lemoine (*C. R.* 96, 1630) maintained that these substances were true compounds. According to Mai (*A.* 265, 192), when 67 parts P and 96 parts S are melted together, and the product is distilled at 10–11 mm. pressure, a distillate is obtained which slowly solidifies, and digestion of this solid with CS_2 under pressure gives a solution from which crystals of P_4S_7 separate, and the mother-liquor deposits what seems to be a mixture of P_2S_3 and P_4S_5. The melting-points of mixtures of P and S are much below those of either constituent (Pelletier, *A. Ch.* [2] 4, 1; Faraday, *A. Ch.* [2] 7, 71; Dupré, *A. Ch.* [2] 73, 435). The experiments of Faraday (*l.c.*) and Ramme (*B.* 12, 940, 1350) show that the crystals obtained by dissolving S in liquid P sulphides—to which Berzelius gave the composition PS_{12}, and Dupré the composition PS_6—are merely S with more or less adhering P.

TETRAPHOSPHORUS TRISULPHIDE P_4S_3 (*Sesquisulphide of phosphorus. Hypophosphorous sulphide*). Mol. w. 219·8. Melts at 166° (Ramme *B.* 12, 1350). Boils at 380° (Isambert, *C. R.* 96, 1499). S.G. 2·0 at 11°. V.D. 114·3 (Isambert, *l.c.*; Ramme, *l.c.*). H.F. $[P^4,S^3] = 86,800$ (I., *l.c.*).

Formation.—1. By heating together P and S in the ratio 4P:3S.—2. By heating P_4S_6 with ordinary P to 320° (Ramme, *l.c.*).

Preparation.—A mixture of 1 part S with 1·3 parts amorphous P is placed in a flask with a long wide neck connected with a wide tube dipping beneath the surface of Hg; the mixture is heated towards 260°, when the reaction begins, and proceeds with production of much heat; the product is dissolved in CS_2 and crystallised (Lemoine, *Bl.* [2] 1, 407). Ramme (*B.* 12, 1350) heats the red P and S together in a sealed tube at 260° for eight hours. If ordinary P is used, combination occurs at 130°, with violent explosion. The explosion may be prevented by melting the S and P in the water-bath, and adding twice as much sand from which air has been removed by CO_2 (Isambert, *C. R.* 96, 1499). Ramme (*B.* 12, 1351) obtained P_4S_3 by heating P_4S_6 with ordinary P in a sealed tube, filled with CO_2, to 320°.

Properties.—A yellow crystalline solid, which melts at 167° to a slightly coloured liquid. Boils 230°-240° at 11 mm. pressure, with partial decomposition to red P (Mai, *A.* 265, 192). Crystallises from CS_2, PCl_3, or $PSCl_3$ in rhombic prisms (Lemoine, *Bl.* [2] 1, 407); sublimes under 800°, probably in regular crystals (Isambert, *C. R.* 96, 1499). Very soluble CS_2, $PSCl_3$, and PCl_3; dissolved and decomposed by alcohol (Lemoine, *l.c.*). Burns at c. 100° to P_2O_5 and SO_2; scarcely changed in ordinary air.

Reactions.—1. Burns when *heated in air* to c. 100°, forming P_2O_5 and SO_2.—2. Not acted on by cold *water*; hot water slowly produces H_2S and H_3PO_3Aq.—3. Dissolves in *potash solution*, forming K phosphite and sulphide, and evolving H and P hydride (Lemoine, *l.c.*).—4. *Hydrated lead oxide* reacts at 200° with separation of PbS (L., *l.c.*).—5. Soluble in *potassium sulphide* solution, probably with formation of a double compound (L., *l.c.*).—6. *Chlorine*, when moist, slowly produces H_2SO_4 and H_3PO_4 (L., *l.c.*; I., *l.c.*).—7. Not acted on by cold *sulphuric* or *hydrochloric acid*; *nitric acid* and *aqua regia* oxidise P_4S_3 slowly and regularly on warming.

Phosphorous sulphide P_4S_6 (*Trisulphide of phosphorus. Tetraphosphorus hexasulphide. Thiophosphorous anhydride*). Mol. w. 315·72. Melts at c. 200°, and boils at c. 490°. V.D. 147·5, to 173·6 at lower temperatures (Isambert, *C. R.* 102, 1386).

Formation.—1. By heating red P and S in the ratio 2P:3S in CO_2. Combination occurs without explosion, but so much heat is produced that a part of the product sublimes rapidly (Kekulé, *A.* 90, 310; Michaelis, *A.* 164, 22).—2. By the reaction of PCl_3 with H_2S (Serullas, P. 17, 101). Ramme (*B.* 12, 940) failed to obtain P_4S_6 by heating a solution of P and S in CS_2 in a sealed tube.

Preparation.—A mixture is made of 1 part red P with 1·55 parts S; a small portion of this mixture is heated in a long-necked flask in a stream of CO_2 until combination occurs; the flame is removed, and the rest of the mixture is introduced into the flask in small portions at a time; the heat produced by the combination of one quantity suffices to cause combination of the next quantity. The P_4S_6 is sublimed into the neck of the flask; or it may be dissolved in CS_2 and crystallised (Michaelis, *A.* 164, 22).

Properties.—A greyish-yellow, crystalline, solid (Kekulé, *A.* 90, 310; Isambert, *C. R.* 102, 1386). Tasteless, inodorous; does not fume in air; melts readily (c. 200°), and sublimes more easily than S. Soluble in CS_2. The V.D. shows that the molecular formula is P_4S_6, corresponding with the oxide P_4O_6. P_4S_6 acts as a thio-anhydride, forming compounds with the sulphides of several metals (*v. Reactions*, No. 7). As P_4S_6 is acted on by moist air, it must be kept in sealed tubes.

Reactions.—1. Decomposes rapidly in *moist air* (? to H_2S and H_3PO_3).—2. Decomposed by *water* to H_2S and H_3PO_3Aq.—3. Burns when *heated in air.*—4. Dissolves in *potash, soda, or ammonia solution*, and is reppd. in yellow flocks by addition of acid.—5. Decomposes *carbon compounds containing* OH, forming corresponding SH compounds and H_3PO_3.—6. With *iodine* in CS_2 forms PI_2 (Isambert, *C. R.* 96, 1771).—7. According to Berzelius, P_2S_3 combines with many metallic sulphides forming compounds $2R^I_2S.P_2S_3$ and $2R^{II}S.P_2S_3$ the composition of which would lead to their being calle *thiopyrophosphites*; R = Cu, Fe, Hg, Ag.—8. B dissolving in *caustic soda* solution cooled to 0 Lemoine (*C. R.* 93, 489; 98, 45) obtained th compound $P_2OS_2.2Na_2O.5H_2O$ and the compoun $P_2OS_2.3Na_2O.4H_2O$; and by using *ammoniu* *sulphide* he obtained $P_2OS_2.2(NH_4)_2O.3H_2O$ an $P_2O_2S.2(NH_4)_2O.6H_2O$. These substances evolve H_2S by the action of HClAq; heated to 200°-240° they gave off H_2S, but retained S; the may perhaps be called *thio-oxypyrophosphites.*

Triphosphorus hexasulphide P_3S_6 (*Phosphorus disulphide* [PS_2]. *Phosphorus tetrasulphide* [P_2S_4]). ? Mol. w. 284·8. Melts at 296°-298° (Ramme, *B.* 12, 940); at 248°–249° (Seiler *Dissertation*, Göttingen, 1876). Boils at 335°-340° at pressure of 10–11 mm. (Mai, *A.* 265, 192). V.D. Ramme (*B.* 12, 1350) says that V. D. agrees with formula P_3S_6, but no numbers are given.

Formation.—1. By heating a solution of P and S in CS_2 in sealed tubes to 210°; according to Ramme (*B.* 12, 940), P_3S_6 is produced with P and S in the following ratios:—P:S, P:2S, 2P:S, 3P:S, 4P:S, 6P:S (*v.* also Dervin, *Bl.* [2] 41, 433).—2. By heating together P and S in the ratio P:2S (Seiler, *l.c.*).

Preparation.—P and S are dissolved in CS_2 in the ratio P:2S, the solution is heated in a sealed tube to 210° for 8–10 hours, after cooling the liquid is poured off, and the crystals are recrystallised repeatedly from CS_2 in a sealed tube (Ramme, *l.c.*).

Properties and Reactions.—Long, clear yellow, needle-shaped crystals. Ramme (*l.c.*) says that V.D. corresponds with formula P_3S_6 but he gives no data; the corresponding oxide is generally written P_2O_4, but its molecular weight has not yet been determined. Heated with water in a sealed tube to 150° for some hours, P_3S_6 gave H_2S, H_3PO_3Aq, and H_3PO_4Aq, and an orange-yellow solid insoluble in CS_2 and not melting at 310° (Ramme, *B.* 12, 1350).

Phosphoric sulphide P_2S_5 (*Phosphorus pentasulphide* or *persulphide. Thiophosphoric anhydride*). Mol. w. 221·8. Melts at 274°–276° (V. a. C. Meyer, *B.* 12, 610). Boils at 518°, pressure = 730 mm. (Goldschmidt, *B.* 15, 303); at 520° (Isambert, *C. R.* 102, 1386); at 530° (Hittorf, *P.* 126, 196); at 332°–340°, pressure being 11 mm. (Mai, *A.* 265, 192). V.D. 110·7, at 530° in N (V. a. C. Meyer, *B.* 12, 610).

Formation.—1. By heating a solution of ordinary P and S, in the proper ratio, in CS_2 to 210° for 8–10 hours, and crystallising from CS_2 (Ramme, *B.* 12, 940).—2. By melting together red P and S, in ratio 2P:5S, in CO_2 (Kekulé, *A.* 90, 310); with ordinary P violent explosion occurs.

Preparation.—A mixture of 40 parts S and 18·5 parts red P is melted together, the mass is powdered, placed in a retort filled with CO_2, and distilled to c. ⅓ to ½ (to remove P, S, and more volatile P sulphides); the residue is again powdered and distilled in CO_2; the distillate is pure P_2S_5 (V. a. C. M., *l.c.*).

Properties.—Large, clear, pale-yellow crystals. Vapourises in N or CO_2, without change, to a yellowish gas. Burns when heated in air.

Soluble in CS_2; P_2S_5 seems to react as a thio-anhydride (*v. Reactions*, No. 7).

Reactions.—1. Decomposes in *moist air* or by *water*, to H_2S and H_3PO_4; burns when *heated in air* to P_2O_5 and SO_2.—2. With *phosphorus pentachloride* forms $PSCl_3$ (Weber, *J.* 1859. 80). 3. With *carbon tetrachloride* at 200° produces CS_2 and $PSCl_3$ (Rathke, *Z.* 1870. 57).—4. With *ferric chloride* gives FeS_2 and $PSCl_3$ (Glatzel, *B.* 23, 37).—5. With *sulphonyl chloride*, $PSCl_3$, SO_2, and S are formed (Prinz, *J. Z.* 13, *Supplbd.* 1, 90).—6. With many *carbon compounds containing* O and also with many *inorganic oxides*, P_2S_5 form S compounds, exchanging S for O (Kekulé, *A.* 90, 310; Carius, *A.* 106, 331; 112, 180; *v.* also Prinz, *l.c.*).—7. According to Berzelius (*A.* 46, 129, 255), P_2S_5 combines directly with several metallic sulphides, forming compounds $2R^I_2S.P_2S_5$ and $2R^{II}S.P_2S_5$ (R = Cu, Fe, Mn, Hg, Zn): these compounds may be called *thiopyrophosphates.*

THIO-OXYORTHOPHOSPHATES. Salts of the hypothetical acids H_3PSO_3 (*monothio-oxyorthophosphoric acid*) and $H_3PS_2O_2$ (*dithio-oxyorthophosphoric acid*) have been obtained by the action of alkali solution on P_2S_5 or on $PSCl_3$. Salts of *trithio-oxyphosphoric acid* (H_3PS_3O) have not been isolated.

Monothio-oxyphosphates. The Na salt, $Na_3PSO_3.12H_2O$ was obtained by Wurtz by warming $PSCl_3$ with fairly conc. NaOHAq (*A. Ch.* [3] 20, 472), and by Thorpe a. Rodger by the action of NaOHAq on PSF_3 (*C. J.* 55, 318). Kubierschi (*J. pr.* [2] 31, 93) obtained the salt by adding powdered P_2S_5 to NaOHAq, in ratio P_2S_5:6NaOH, cooling, adding absolute alcohol—which ppd. a mixture of Na_3PSO_3 and $Na_3PS_2O_2$ (leaving Na polysulphides in solution)—dissolving the pp. in water, warming to 90° till H_2S ceased to come off, evaporating, and crystallising. Thin six-sided prisms, melting at 60°. The Mg salt (with $20H_2O$), and the Mg-NH_4 salt (with $9H_2O$) were also obtained.

Dithio-oxyphosphates. The Na salt, $Na_3PS_2O_2.11H_2O$ was obtained (K., *l.c.*) by dissolving in water the pp. obtained as above by alcohol, warming to 50°-55°, ppg. by alcohol, and crystallising from water at 40°. Colourless, lustrous, needles, melting at 45°-46°. The NH_4 salt (with $2H_2O$), Ba salt (with $8H_2O$), and Mg-NH_4 salt (with $6H_2O$) were also obtained in crystalline form.

For reactions of these thio-oxyorthophosphates *v.* Kubierschi, *l.c.* (*cf.* Michaelis, *B.* 5, 5).

Phosphorus, sulphobromides of. Two compounds, corresponding with the two oxychlorides, have been prepared.

THIOPHOSPHORYL BROMIDE $PSBr_3$ (*Sulphophosphoryl bromide. Phosphorus sulphobromide*). Formula probably molecular, from analogy of $POCl_3$.

Formation.—1. By reaction of H_2S with PBr_5 (Gladstone, *P. M.* 35, 345; Baudrimont, *A. Ch.* [4] 2, 58).—2. By distilling PBr_3 with S, or Br with P_2S_3.—3. By the action of Br on a solution of P and S in CS_2.

Preparation.—Equal parts of P and S are dissolved in CS_2, the solution is well cooled, and 8 parts Br are allowed to drop in slowly from a funnel with a stopcock; the CS_2 is removed by warming in a water-bath, and the liquid is then distilled quickly over a large flame. Part of the $PSBr_3$ solidifies in the neck of the retort, and part passes over and remains liquid in the receiver; the contents of the receiver are shaken with fresh quantities of water until the oily liquid solidifies to a yellow crystalline mass which is $PSBr_3.H_2O$; this hydrate is dissolved in CS_2, water is removed by contact with $CaCl_2$, CS_2 is distilled off in a stream of CO_2, and $PSBr_3$ remains as a yellow oil, which solidifies on touching it with a glass rod. The solid may be recrystallised from PBr_3 (Michaelis, *A.* 164, 36).

Properties.—Yellow octahedral crystals, with an aromatic but unpleasant odour; vapour attacks the eyes. Melts at 38°, when molten remains for a long time without solidifying unless touched by a solid (Michaelis, *B.* 4, 777). Easily soluble in ether, CS_2, PBr_3, or PCl_3. Cannot be distilled without decomposition.

Reactions.—1. Decomposed by *heat* to S and a yellow liquid, $PSBr_3.PBr_3$, which is resolved by repeated distillation into S and PBr_3, and by repeated washing with water yields $PSBr_3.H_2O$ (Michaelis, *A.* 164, 36).—2. Decomposed by *water*, slowly when cold, rather more rapidly when boiling, forming H_2S, S, H_3PO_3Aq and H_3PO_4Aq (*v.* Michaelis, *B.* 5, 4).—3. With *alcohol* forms $PS(OEt)_3$.—4. Decomposed by *ammonia solution*, slowly when cold, more rapidly when hot, giving NH_4 phosphite and phosphate, H_2S, S, and NH_4 sulphide (M., *l.c.*). 5. Reacts with *phosphorus pentachloride* to form $PSCl_3$ and PBr_5 (M., *l.c.*).

Combinations.—1. With *water* to form $PSBr_3.H_2O$ (*v. Preparation*). A yellow crystalline solid; melts at 35°, being resolved into H_2O and $PSBr_3$; S.G. 2·7937 at 18°; gradually decomposes in air, giving off HBr (Michaelis, *A.* 164, 36).—2. With *phosphorus bromide* to form $PSBr_3.PBr_3$; obtained by heating $PSBr_3$ (*v. Reactions*, No. 1).

PYROPHOSPHORYL BROMIDE $P_2S_3Br_4$ (*Phosphorus trisulphotetrabromide*). A light-yellow oil, with aromatic and pungent odour; S.G. 2·2621 at 17°; fumes in air, with separation of S. Decomposed by *distillation* into S, P_2S_5, and $PSBr_3.PBr_3$; decomposed by *water*, giving S, $PSBr_3$, H_2S, P, and a substance probably $P_2S_3(OH)_4$; *alkalis* act similarly to, but more violently than, water, but neither S nor $PSBr_3$ is formed; with *absolute alcohol* yields $P_2S_3(OEt)_3Br$, $P_2S_3(OEt)_4$, $P_2S_3(OEt)_2(SEt)_2$; *bromine* reacts, when heated, forming PBr_5 and $PSBr_3$ (Michaelis, *A.* 164, 22). Prepared by moistening 100 g. finely powdered P_2S_3 with CS_2, and adding 200 g. Br diluted with an equal volume of CS_2, shaking thoroughly, distilling off CS_2 in water-bath not above 80°, removing last traces of CS_2 in stream of CO_2, dissolving residue in six times its volume of dry ether, and removing ether by a stream of CO_2 (M., *l.c.*).

Phosphorus, sulphobromochloride of, $PSBrCl_2$ (*Thiophosphoryl bromochloride*). Formula probably molecular, from analogy of $POBrCl_2$ (Michaelis, *B.* 5, 6). A slightly yellow liquid, with aromatic odour; boils c. 150°, but boiling-point soon rises and S separates. Decomposed slowly by *water*, more completely when heated in a sealed tube to 150° for some hours, giving S, H_2S, HClAq, HBrAq, H_3PO_3Aq, and H_3PO_4Aq. Prepared by adding 80 parts Br drop by drop to 168 parts $PCl_2.SEt$ [obtained by action of EtSH on PCl_3; for details *v.* Michaelis, *l.c.*]; much heat is produced; the liquid is distilled, the distillate from 150°–180° is shaken with water so long as any action takes place; water is removed by a separating funnel; the liquid is dried by $CaCl_2$, and HCl and HBr are removed by warming gently (M., *l.c.*).

Phosphorus, sulphochlorides of. But one compound, $PSCl_3$, is known with certainty. It is doubtful whether the substance obtained by Gladstone (*C. J.* 3, 5) by the reaction of S with PCl_3 is a definite compound PS_2Cl_5, or a double compound $PSCl_3.SCl_2$.

THIOPHOSPHORYL CHLORIDE $PSCl_3$ (*Phosphorus sulphochloride*). Mol. w. 169·05. Boils at 125·12° (Thorpe, *C. J.* 37, 341). S.G. $^{0^\circ}_{4^\circ}$ 1·6682 (T., *l.c.*). V.D. 85 at 160°–300° (Cahours, *A. Ch.* [3] 20, 369; Chevrier, *C. R.* 68, 1174). For thermal expansion *v.* Thorpe (*l.c.*). S.V. 116·1.

Formation.—1. By the reaction of H_2S with PCl_5 (Serullas, *A. Ch.* [2] 42, 25).—2. By heating S with PCl_3 to 130° (Henry, *B.* 2, 638).—3. By heating P with S_2Cl_2 (Wöhler a. Hiller, *A.* 93, 274).—4. By heating together P_2S_5 and PCl_5 (Weber a. Thorpe, *Z.* 1871. 467).—5. By the reaction of PCl_3 with SO_2, SO_2Cl_2, or S_2Cl_2; and by the reaction of PCl_5 with CS_2, or with Sb_2S_5 (Michaelis; Cairns, *A.* 112, 190; 119, 291; Rathke, *Z.* 1870. 57; Baudrimont, *J. pr.* 87, 301).

Preparation.—An intimate mixture of P_2S_5 and PCl_5, in the ratio $P_2S_5 : 3PCl_5 (= 1:2·82)$, is heated in a sealed tube to c. 120°; after a short time the liquid which has formed is distilled. Should the product have a yellowish colour, it is shaken with a little water, dried by $CaCl_2$, and distilled. The equation $P_2S_5 + 3PCl_5 = 5PSCl_3$ is realised (Thorpe, *C. J.* 37, 341).

Properties.—A colourless, highly refractive liquid; with an aromatic, somewhat pungent, and very peculiar odour, which becomes very marked on warming. Slowly decomposed by water.

Reactions.—1. Very slowly acted on by *water*, with formation of H_3PO_4Aq, HClAq, and H_2S. When distilled in steam the greater part of the $PSCl_3$ passes over unchanged.—2. Heated with *alcohol* under pressure, $PS(OEt)_3$ is formed.—3. Passed through a hot tube, with excess of *hydrogen sulphide*, P_2S_3 and HCl are formed (Baudrimont, *J. pr.* 87, 301).—4. Decomposed by *chlorine* with formation of S_2Cl_2 and PCl_5.—5. *Silver nitrate* reacts rapidly, producing Ag_3PO_4, AgCl, SO_2, NOCl, and NO_2 (the SO_2 and NO_2 then reacting to form $S_2O_5(NO_2)_2$; Thorpe a. Dyson, *C. J.* 41, 297).—6. *Alkali solutions* form salts of H_3PSO_3 and $H_3PS_2O_2$ (*v.* THIOOXYORTHOPHOSPHATES, p. 147).—7. The prolonged action of *ammonia*—continued until 60 p.c. of the $PSCl_3$ has reacted with the NH_3—produces ***thiophosphamide*** $PS(NH_2)_3(?)$; this compound remains as an amorphous, yellow-white solid on washing the product of the action of NH_3 on $PSCl_3$; S.G. 1·7 at 13°; decomposed at 200°, gives (?)$PS(ONH_4)_3$ with hot water (Chevrier, *C. R.* 66, 748; Schiff, *A.* 101, 292). According to Gladstone a. Holmes (*C. J.* 18, 5), ***thiophosphamic acid*** $PS(NH_2)(OH)_2$ and ***thiophosphodiamic acid*** $PS(NH_2)_2OH$, are produced by the action of ammonia on $PSCl_3$; the former by using fairly dilute NH_3Aq, and the latter by using NH_3 gas—which probably forms $P(NH_2)_2ClS$—and then washing with water. The work of Chevrier (*l.c.*) and Schiff (*l.c.*) makes the isolation of these acids doubtful.

Phosphorus, sulphochlorobromide of; *v.* PHOSPHORUS SULPHOBROMOCHLORIDE, p. 147.

Phosphorus, sulphocyanide of, $P(SCN)_3$ (*Phosphorus thiocyanate. Phosphorus rhodanide*). Mol. w. not determined; formula probably molecular. Prepared by mixing 5 parts $Pb(SCN)_2$ with an equal weight of dry sand, gradually adding 1 part PCl_3, digesting for some time on a water-bath, and then distilling very carefully from a hard glass tube. A liquid which does not solidify at −20°, begins to boil 260°–270°, and decomposes at a higher temperature, giving off CS_2; vapour is spontaneously inflammable; S.G. 1·625 at 18°. Soluble in alcohol, ether, $CHCl_3$, CS_2, and C_6H_6. Slowly decomposed by cold water to H_3PO_3Aq and HSCNAq (Miguel, *A. Ch.* [5] 11, 349).

Phosphorus, sulphofluoride of, PSF_3 (*Thiophosphoryl fluoride*). This compound was prepared and fully described by Thorpe a. Rodgers in 1888 (preliminary notice in *C. J.* 53, 760; fuller account in *C. J.* 55, 306). Mol. w. 119·9. V.D. 59·6 at ordinary temperature.

Formation.—1. By heating a mixture of AsF_3 and $PSCl_3$, in ratio $AsF_3 : 4PSCl_3$, in a sealed tube at 150°.—2. By heating PbF_2 mixed with P_2S_5 to c. 120°–150°; or by using BiF_3 in place of PbF_2 and heating to a higher temperature. A mixture of red P, S, and a large excess of PbF_2 may also be used ($P_2S_5 + 3PbF_2 = 3PbS + 2PSF_3$). 3. By heating S with PF_3Cl_2 to 115° (Poulenc, *C. R.* 113, 75).

Preparation.—A quantity of P_2S_5 (freshly prepared from well-washed and perfectly dry amorphous P and roll S) is quickly mixed with c. $3\frac{1}{3}$ parts of pure freshly fused PbF_2, and the mixture is placed in a thin equal layer in a dry tube of lead or 'composition,' one end of which is fitted with a caoutchouc cork carrying a glass delivery tube dipping under dry Hg, and the other end is connected with an apparatus for supplying pure dry N. A rapid stream of N is passed through till the air is driven out, the tube being gently heated to get rid of traces of H_2S (produced by moisture on P_2S_5); the N is stopped, and the tube is heated from behind forwards by a small flame; reaction begins c. 170°; the temperature should be kept as low as possible, it must not exceed 250°. The gas is collected in a dry glass gas-holder containing a few small pieces of quicklime, the gas being allowed to pass into the holder as soon as a sample is wholly absorbed by dilute potash or ammonia. Before collecting the gas, small quantities of dry N should be passed into the gasholder and repeatedly exhausted by the Sprengel pump (this removes air from the pores of the lime), and when 2 or 3 c.c. of the $PSCl_3$ have passed into the holder the gas should be sucked out by the Sprengel, and this repeated twice or thrice (the traces of N are thus removed). After standing a few days over the lime, which removes PF_3 and any traces of SiF_4, the gas is pure PSF_3.

Properties.—A transparent, colourless gas; liquefied at 7·6 atmos. at 3·8°, 9·4 atmos. at 10°, 10·8 atmos. at 18·6°, and 13 atmos. at 20·3°. PSF_3 is spontaneously inflammable in air or O; it is decomposed easily by heat or electric sparks to S, P, and fluorides of P. Somewhat soluble in ether. Not easily dissolved by H_2O, or by solutions of alkalis. No action on Hg, H_2SO_4, CS_2, or C_6H_6. Neither gaseous nor liquid PSF_3 acts appreciably on glass at ordinary temperatures.

Reactions.—1. A small stream of PSF_3 issuing from a Pt jet into *air* at once takes fire; when mixed with a large volume of air, explosion occurs.—2. Oxidised rapidly and explosively by *oxygen*; probably with formation of PF_3 and SO_2, the PF_3 and O then producing P_2O_5 and also POF_3. The ignition-temperature of PSF_3 is very low, and the flame is a very cold one. (Full details are given by T. a. R., *l.c.*, pp. 312–317.)—3. Slowly decomposed by *water*, thus: $PSF_3 + 4H_2O + Aq = H_2S + H_3PO_4Aq + 3HFAq$. —4. Solution of *potash* or *soda* slowly reacts, forming Na_3PSO_3 and NaF.—4. With *ammonia gas* produces a white, deliquescent solid, probably a mixture of NH_4F and $P(NH_2)_2SF$. For action of water on this substance—perhaps resulting in formation of $PS(NH_2)_2OH$—*v.* T. a. R., *l.c.*, p. 319.—5. *Heated* in a *glass* tube, PSF_3 gives SiF_4, P, and S.—6. PSF_3 is decomposed by *electric sparks* passed from Pt terminals, with separation of S and P, and a gas which is probably PF_5.

Phosphorus, sulphoselenide of. All attempts to prepare this compound have led to negative results. Michaelis heated PCl_3 with Se; Baudrimont (*A. Ch.* [4] 2, 5) tried the reaction of PCl_5 with $SeCl_2$, PCl_5 with P_2Se, Sb_2Se_3, and PbSe, and the action of P on $SeCl_2$ and $SeCl_4$.

Phosphorus, sulphoxide of, $P_4O_6S_4$. Mol. w. 347·52. Melts at 102°, and boils at 295°. V.D. 171·3 at 350°–400°. Formed by heating small quantities P_4O_6 with S in an atmosphere of CO_2 or N at c. 160° (Thorpe a. Tutton, *C. J.* 59, 1022).

Preparation.—A strong glass tube is closed at one end, and filled with dry CO_2 or N; from 3 to 5 g. freshly-distilled P_4O_6 is placed in the bottom of the tube, and 1·74 g. S, best in small crystals, are added for every 3 g. P_4O_6 used (ratio P_4O_6:4S). The tube is sealed, and the lower half is immersed in a glycerin-bath, which is gradually heated. At c. 154°–165° the melted S is suddenly projected to the top of the tube, and in a few seconds the action is complete. The product is transferred to a similar tube, which is exhausted by a Sprengel pump, sealed, and warmed at its lower portion; sublimation begins at c. 90°, and proceeds best at 140°–150°, with formation of long feathery needles; part of the $P_4O_6S_4$ remains as a vitreous or crystalline mass.

Properties and Reactions.—A white solid, occurring in feathery aggregations or a vitreous mass, or as colourless, isolated, tetragonal prisms; melts 102°, and boils 295° (cor.). Very deliquescent, smelling in air of H_2S; quickly dissolved by water, forming H_2S and HPO_3Aq, which soon changes to H_3PO_4Aq. Easily sol. in 2 vols. CS_2, from which it crystallises unchanged. Also sol. benzene, but with decomposition.

Phosphorus, sulphur acids of, salts of; *v.* beginning of article Phosphorus sulphides (p. 145); Phosphorous sulphide, *Reactions* 7 and 8 (p. 146); Phosphoric sulphide, *Reaction* 7 (p. 147); and Thio-oxyorthophosphates (p. 147).

Phosphorus, telluride of. Oppenheim (*J.* 1857. 214) obtained a black amorphous solid, giving off fumes of P_2O_3 in air by heating P with powdered Te.

Phosphorus, thio-acids of, salts of; *v.* beginning of article Phosphorus sulphides (p. 145); Phosphorous sulphide, *Reactions* 7 and 8 (p. 146); Phosphoric sulphide, *Reaction* 7 (p. 147); and Thio-oxyorthophosphates (p. 147).

Phosphorus thio-amic acids of, and thio-amide of; *v.* Thiophosphoryl chloride, *Reaction* 7 (p. 148).

Phosphorus, thiobromides of; *v.* Phosphorus sulphobromides, p. 147.

Phosphorus, thiobromochloride of; *v.* Phosphorus sulphobromochloride, p. 147.

Phosphorus, thiochlorides of; *v.* Phosphorus sulphochlorides, p. 148.

Phosphorus, thiocyanide of; *v.* Phosphorus sulphocyanide, p. 148.

Phosphorus, thioselenide of; *v.* Phosphorus sulphoselenide, *ante.*

M. M. P. M.

PHOSPHORUS, OXYACIDS OF, AND THEIR SALTS. The three phosphoric acids, H_3PO_4, $H_4P_2O_7$, and HPO_3, are described under Phosphoric acids (p. 124); the salts of these acids are described under Phosphates (p. 108); the other oxyacids of P, and their salts, are described in this article.

Besides the phosphoric acids, three oxyacids of P, and some salts of a fourth acid, have been isolated; the acids in question are H_3PO_2, H_3PO_3, H_2PO_3 or $H_4P_2O_6$; and salts of $H_4P_2O_5$. No anhydride of H_3PO_2 is known; the hypothetical anhydride would be P_2O ($P_2O + 3H_2O = 2H_3PO_2$); P_2O_3 is the anhydride of the acid H_3PO_3 ($P_2O_3 + 3H_2O = 2H_3PO_3$), and also the hypothetical anhydride of $H_4P_2O_5$($P_2O_3 + 2H_2O = H_4P_2O_5$); P_2O_4 is the hypothetical anhydride of $H_4P_2O_6$($P_2O_4 + 2H_2O = H_4P_2O_6$), but this oxide gives H_3PO_3Aq and H_3PO_4Aq with water (*v.* Phosphorus tetroxide, p. 141). The oxyacids of P do not correspond in composition with those of N (*v. Table* in Nitrogen group of elements, vol. iii. p. 575).

HYPOPHOSPHOROUS ACID AND SALTS H_3PO_2; $M^IH_2PO_2$ and $M^{II}(H_2PO_2)_2$. Hypophosphites are formed by decomposing phosphide of Ba, Ca, or Sr by water (Dulong, *A. Ch.* [2] 2, 141); by heating P with potash, milk of lime, or BaOAq (H. Rose, *P.* 9, 225, 361; 12, 77, 288); by passing PH_3 into solution of alkalis or alkaline hydrates (Winckler, *P.* 111, 443); and by heating P with syrupy H_3PO_4Aq to 200° (Oppenheim, *Bl.* [2] 1, 163). The acid is monobasic; it may be regarded as derived from the hypothetical anhydride P_2O. There is no acid, nor are there salts, corresponding with hyponitrous acid HNO, but some salts are known of the form MPS; *v. Thiometahypophosphites*, at beginning of Phosphorus, sulphides of (p. 145). *Selenometahypophosphites* M^IPSe have also been isolated (*v.* Diphosphorus selenide, p. 144).

Hypophosphorus acid H_3PO_2. Melts at 17·4° (Thomsen, *B.* 7, 994; ? specimen pure). H.F. $[H^3,P,O^2] = 139,970$ (production of crystallised acid); 187,660 (production of acid in liquid state); $[H^3,P,O^2,Aq]$ = 139,800 (*Th.* 2, 225).

Preparation.—$Ba(H_2PO_2)_2.H_2O$ is prepared by warming water with BaO and P (in small pieces) in a basin till inflammable P hydride ceases to come off, filtering, removing excess of BaO by passing in CO_2, filtering again, and crystallising. 285 g. pure $Ba(H_2PO_2).H_2O$ are dissolved in c. 5 litres water, 98 g. H_2SO_4 (c. 101·5 g. ordinary conc. acid), diluted with 3 to 4 times its weight of water, are added; after shaking for some time the pp. of $BaSO_4$ is allowed to settle, and the clear liquid is syphoned off, and evaporated in a porcelain dish, by boiling, till it is c. $\frac{1}{10}$ of the original volume, when it is placed in a Pt dish; a thermometer is immersed in the liquid, evaporation is continued, the temperature being allowed to rise gradually to 110°; any solid which separates is filtered off while the liquid is hot, and the filtrate is evaporated, without being allowed to boil, at c. 110°. Thomsen (*B.* 7, 994) finally heats for 10 mins. to 130° or 138°, filters into a stoppered bottle, and cools below 0°; Geuther a. Ponndorff (*J. Z.* 10, *Supplbd.* 2, 45, 49) say that heating above 110° decomposes H_3PO_2, and that Thomsen's preparation therefore contained H_3PO_3.

Properties.—Large, white, crystalline tablets; melting at 17·4°; remains liquid considerably above m.p. (Thomsen, *l.c.*). Decomposed by heat to PH_3 and H_3PO_4. H_3PO_2Aq is a very energetic reducing agent. The acid is monobasic, forming salts $M^IH_2PO_2$ and $M^{II}(H_2PO_2)_2$.

Reactions.—1. Decomposed by *heat*, giving P hydride and H_3PO_4 (H. Rose, *l.c.*).—2. H_3PO_2Aq is readily changed to H_3PO_3Aq or H_3PO_4Aq by *oxidisers*; Cl, Br, HNO_3Aq, $KMnO_4Aq$, and several metallic oxides produce H_3PO_4Aq (Dulong, *l.c.*; Rose, *l.c.*; P. de St. Gilles, *A. Ch.* [3] 55, 374); PbO_2 forms $PbHPO_3$ (Wurtz, *C. R.* 18, 702); SO_2 forms H_3PO_3Aq and S (Geuther a. Ponndorff, *l.c.*). According to Engel (*C. R.* 110, 786) Pd charged with H oxidises H_3PO_2Aq to H_3PO_3Aq with evolution of H.—3. H_3PO_2Aq reduces *solutions of salts of gold, silver, and mercury*, ppg. the metals; from *copper sulphate solution*, Cu_2H_2 is ppd. at 55°-60° (Wurtz, *l.c.*; Rammelsberg, *l.c.*).—4. Reduced by *nascent hydrogen* to PH_3 (Dusart, *C. R.* 43, 1126; Blondlot, *C. R.* 52, 1197).—5. With *hydriodic acid* forms PH_4I (G. a. P., *l.c.*).—6. Heated with *conc. sulphuric acid*, H_3PO_4, SO_2, and S are produced (Wurtz, *l.c.*). 7. Heated with *phosphorus pentachloride*, $POCl_3$, PCl_3, and HCl are formed; *phosphorus trichloride* produces P, H_3PO_3, and HCl; with *phosphoryl chloride*, P, PCl_3, HPO_3, and HCl are the products (Geuther, *J. pr.* [2] 8, 359).

HYPOPHOSPHITES $M^IH_2PO_2$ and $M^{II}(H_2PO_2)_2$. These salts are formed in several reactions (*v.* beginning of this article); the greater number are prepared by reacting on the salt of Ba with the sulphates of other metals; the salts of Ba, Ca, and Sr are generally prepared by heating BaOAq, CaOAq, and SrOAq with P. The hypophosphites of Cd, Ca, Pb, and Tl crystallise without water; those of Ba, Li, Mn, Na, Sr, and U with one H_2O; those of Co, Mg, Ni, and Zn with $6H_2O$ (Rammelsberg, *C. J.* [2] 11, 12). They are decomposed by heat, evolving P hydride and H, and generally leaving pyro- and meta- phosphate, the Co and Ni salts leave metaphosphate and phosphide, and the U salt leaves pyro- and meta- phosphate and phosphide (R., *l.c.*). The hypophosphites are easily oxidised to phosphites and phosphates, hence they react as reducing agents. Heated in solution with alkalis they give phosphites, and then phosphates, and evolve H (Wurtz; H. Rose, *l.c.*). The chief memoirs on hypophosphites are by H. Rose (*P.* 9, 225, 361; 12, 77, 288); Wurtz (*A. Ch.* [3] 7, 193; 16, 196); and Rammelsberg (*C. J.* [2] 11, 1, 13).

Ammonium hypophosphite $NH_4H_2PO_2$. Hexagonal tablets; by decomposing the Ba salt by $(NH_4)_2SO_4Aq$; easily sol. absolute alcohol (Wurtz, Rose).

Barium hypophosphite $Ba(H_2PO_2)_2.H_2O$. Lustrous monoclinic needles (Rammelsberg; Topsöe, *W. A. B.* 69 [2] 19). By heating BaOAq with P till gas ceases to come off, filtering, removing BaO from the filtrate by CO_2, filtering, and crystallising. Loses H_2O at 100°. Soluble in $3\frac{1}{2}$ parts cold, and 3 parts boiling, water; insol. alcohol. Heated out of air leaves pyro- and meta- phosphate (Wurtz, Rose, Rammelsberg).

Calcium hypophosphite $Ca(H_2PO_2)_2$. Prepared like the Ba salt. Berlandt (*Ar. Ph.* [2] 122, 237) recommends 29 parts P, 47 parts CaO_2H_2, and 24 parts water. Bachmann and Martenson (*J.* 1864. 191) decompose Ca phosphide by boiling water. Thin, monoclinic tablets (Rammelsberg; Schabus, *J.* 1854. 325). Very bitter taste; unchanged in air; does not give off H_2O at 300°; heated to redness gives off H, PH_3, and H_2O, and leaves pyro- and meta- phosphate (Rammelsberg; Michaelis, *J.* 1872. 210). Sol. 6 parts cold water, not much more sol. hot water; insol. strong alcohol (Rose).

Cobalt hypophosphite $Co(H_2PO_2)_2.6H_2O$. Red octahedral crystals, isomorphous with Mg salt (Rose); by decomposing Ba salt by $CoSO_4Aq$, filtering, and evaporating *in vacuo* (Wurtz). Forms a *double salt* with $Ca(H_2PO_2)_2$ (Rose).

Copper hypophosphite $Cu(H_2PO_2)_2$. Obtained with difficulty from Ba salt and $CuSO_4Aq$; solution easily decomposes, giving Cu_2H_2 (Wurtz).

Lead hypophosphite $Pb(H_2PO_2)_2$. By adding PbO or $PbCO_3$ to H_3PO_2Aq (Rose, Wurtz).

Manganese hypophosphite $Mn(H_2PO_2)_2.H_2O$. Small, rose-red crystals; from Ba salt and $MnSO_4Aq$ (Wurtz, Rammelsberg); or by boiling Ca salt with Mn oxalate (Rose).

Potassium hypophosphite KH_2PO_2. Prepared by decomposing the Ba or Ca salt by K_2CO_3Aq, filtering, evaporating to dryness, treating the residue with alcohol, and crystallising the alcoholic solution *in vacuo*; or by dissolving P in boiling KOHAq, evaporating, and dissolving out from the residue by alcohol; also by decomposing the Ba salt by K_2SO_4Aq (Rose, Wurtz). A white, semi-crystalline mass. Easily sol. water and alcohol; very hygroscopic (Dulong, *A. Ch.* [2] 2, 141). Burns when heated in air; oxidised violently by evaporation with HNO_3Aq. Heated out of air evolves inflammable P hydride, and leaves pyro- and meta- phosphate (Rammelsberg).

Sodium hypophosphite $NaH_2PO_2.H_2O$. Prepared like the K salt. Small, rectangular tablets, easily sol. water and absolute alcohol. Evaporation of the solution is attended with explosions (Marquart, *Ar. Ph.* [2] 95, 284; Trommsdorff, *ibid.* 99, 388).

The salts $LiH_2PO_2.H_2O$, $Ni(H_2PO_2)_2.6H_2O$,

$Sr(H_2PO_2)_2$, and $Zn(H_2PO_2)_2$ are also described; and salts of Al, Be, Cd, Cr, and Fe have been obtained, but their compositions are somewhat doubtful.

PHOSPHOROUS ACID AND SALTS H_3PO_3; $M^IH_2PO_3$, $M^I_2HPO_3$, $M^{II}HPO_3$, $M^{III}_2(HPO_3)_3$. P_2O_3 is the anhydride of H_3PO_3; the acid is produced by dissolving the oxide in cold water, but the oxide is not obtained by removing H_2O from the acid. H_3PO_3 is dibasic; the salt Na_3PO_3, said to be formed by adding a large excess of NaOH to H_3PO_3 (Zimmermann), has been shown by Amat (*C. R.* 108, 403) not to exist. The acid is formed by oxidising P slowly in moist air; the salts are obtained by reactions between the acid and metallic hydroxides, or by double decomposition from the alkali salts. Neither the acid nor salts of the acid corresponding with nitrous acid, HNO_2, are known, nor have thio-salts of this form been isolated.

PHOSPHOROUS ACID H_3PO_3. Melts at 74° (Geuther a. Hurtzig, *A.* 111, 159); at 70·1° (Thomsen, *J. pr.* [2] 8, 359). H.F. $[H^3,P,O^3]$ $=227,700$ (crystallised acid); 224,630 (acid in liquid state); 227,570 (acid in aqueous solution) (*Th.* 2, 225). Heat of fusion $= -3070$; one gram-molecule of the liquid acid occupies 49·66 c.c. (*Th.* 2, 224).

Formation.—1. Along with H_3PO_2 and H_3PO_4, by the long-continued oxidation of P in moist air (*v.* J. Corne, *J. Ph.* [5] 6, 123).—2. By dissolving P in dilute HNO_3Aq and allowing to oxidise in air.—3. By the oxidation of H_3PO_2Aq by weak oxidisers.—4. By dissolving P_2O_3 in cold water (Thorpe a. Tutton, *C. J.* 57, 567).—5. By decomposing PCl_3 by H_2O, or by warming with $H_2C_2O_4$ (Hurtzig a. Geuther, *A.* 111, 159); or by leading Cl into warm water in presence of an excess of molten P (Droquet, *P.* 12, 628).

Preparation.—1. A small quantity of PCl_3 is shaken with cold water, the reaction is moderated by plunging the beaker into cold water; when the PCl_3 is all decomposed, a little more is added, and so on ($PCl_3 + 3H_2O + Aq$ $= 3HClAq + H_3PO_3Aq$). The solution is evaporated, the temperature being raised to 180° near the end of the process; the syrupy liquid thus obtained is placed over H_2SO_4, *in vacuo*, till it crystallises; addition of a crystal of H_3PO_3 causes rapid crystallisation (Thomsen, *B.* 7, 996). 2. A stream of dry air is passed through PCl_3 at 60°, and then into two flasks, each containing c. 100 g. water at 0°; after c. 4 hours the first flask is filled with crystals, which are drained under a pump, washed with small quantities of ice-cold water, and dried *in vacuo* (Grosheintz, *Bl.* [2] 27, 433).—3. A mixture of 1 part PCl_3 and 2 parts dry $H_2C_2O_4$ is heated in a flask with a reversed condenser until a clear liquid is obtained; the liquid is evaporated in a stream of CO_2, and the crystals are washed and dried as in 2 (Hurtzig a. Geuther, *A.* 111, 159: $PCl_3 + 3H_2C_2O_4$ $= H_3PO_3 + 3CO + 3CO_2 + 3HCl$).

Properties.—**A colourless, crystalline mass; obtained in transparent crystals by evaporating H_3PO_3Aq *in vacuo* over H_2SO_4. Melts at 74° (H. a. G., *l.c.*); at 70·1° (Thomsen, *l.c.*). Heated above its m.p. decomposes to H_3PO_4 and PH_3. H_3PO_3 is very deliquescent, and oxidises very slowly in air; it acts as an energetic reducing agent. H_3PO_3 is dibasic, forming salts $M^IH_2PO_3$ and $M^I_2HPO_3$.**

Reactions.—1. *Heated* above its m.p., H_3PO_3 decomposes to H_3PO_4 and inflammable P hydride (Vigier, *Bl.* [2] 11, 125; Rose, Davy, *Gm.-K.* 2, 115); according to Hurtzig a. Geuther (*A.* 111, 159) P also separates.—2. Slowly oxidised in *air* to H_3PO_4; dilute solutions of H_3PO_3 are more rapidly oxidised; according to Salzer (*A.* 232, 114), H_3PO_3Aq does not oxidise in air at ordinary temperatures. — 3. Converted into H_3PO_4 by many *oxidisers*, *e.g.* HNO_3Aq, ClAq, BrAq, $KMnO_4Aq$, hypochlorites; with SO_2Aq, H_3PO_4Aq and H_2S are formed along with S (*Gm.-K.* 2, 116).—4. Reduces many *metallic salts in solution*; *e.g.* $AgNO_3Aq$ to Ag, $HgCl_2Aq$ to HgCl and then to Hg, $CuCl_2Aq$ to Cu_2Cl_2 and then to Cu (Rammelsberg, *C. J.* [2] 11, 13).—5. *Nascent hydrogen* forms PH_3 (Dusart, *C. R.* 43, 1126). 6. When crystalline H_3PO_3 is heated with *bromine* to 100° in a sealed tube, H_3PO_4 is formed along with HBr and PBr_3, or the products are HPO_3 and HBr, according to the relative quantity of Br used (Gustavson, *J.* 1867. 139). According to Ordinaire (*C. R.* 64, 363), a crystalline compound is obtained—perhaps bromo-phosphorous acid—by heating H_3PO_3 and Br in the ratio $H_3PO_3 : 4Br$.—7. By heating H_3PO_3 with *iodine* Gustavson (*l.c.*) obtained H_3PO_4, HI, PI_3, and PH_4I.—8. Heated with *phosphorus trichloride* to 170°, P, HCl, and H_3PO_4 or $H_4P_2O_7$ are formed (Geuther, *J. pr.* [2] 8, 359; Kraut, *A.* 158, 332; Gautier, *C. R.* 76, 49). At 79° HCl, $H_4P_2O_7$, and a compound PH_4O are formed, according to Gautier (*l.c.*) (*v.* PHOSPHORUS, COMPOUNDS OF, WITH HYDROGEN AND OXYGEN, p. 134).—9. With *phosphorus pentachloride*, $POCl_3$, HCl, and PCl_3 are produced; and the products of the reaction with *phosphoryl chloride* are PCl_3, HPO_3, and HCl (Geuther, *J. pr.* [2] 8, 359).—10. By *neutralisation with alkalis or alkaline carbonates* salts of the form M_2HPO_3 are produced.

Qualitative distinction between phosphorous and hypophosphorous acids. H_3PO_3Aq reduces $CuSO_4Aq$ to Cu, while the reduction product with H_3PO_2Aq is Cu_2H_2.

PHOSPHITES $M^IH_2PO_3$, $M^I_2HPO_3$, $M^{II}HPO_3$, $M^{III}_2(HPO_3)_3$. These salts are generally obtained by neutralising H_3PO_3Aq by metallic hydroxides or carbonates, or by double decomposition from the alkali salts. They are also formed by the slow oxidation of hypophosphites. Zimmermann's assertion that Na_3PO_3 exists (*A.* 175, 1) has been disproved by Amat (*C. R.* 106, 1351), who has shown that the normal Na salt is Na_2HPO_3. The alkali phosphites are soluble water; most of the others are insoluble. Phosphites are decomposed by heat, generally giving off H or PH_3, and leaving pyrophosphate and phosphide. Solutions of phosphites are scarcely changed in air, but they are readily oxidised to phosphates by energetic oxidisers. The chief memoirs on phosphites are those of H. Rose (*P* 9, 26, 224; 12, 77, 288), Rammelsberg (*P.* 131, 263, 359; 132, 481; *B.* 9, 1577), Kraut (*A.* 177 274), Wurtz (*A.* 58, 65).

Ammonium phosphites $(NH_4)H_2PO_3$ and $(NH_4)_2HPO_3.2H_2O$. The former is obtained by adding NH_3Aq to H_3PO_3Aq till neutral to methyl orange, concentrating, and drying the crystals over H_2SO_4; melts 123°; above 150° gives off

NH_3 and PH_3, and leaves H_3PO_4; absorbs NH_3 at 80°–100°, forming $(NH_4)_2HPO_3$ (Amat, *C. R.* 105, 809). The salt $(NH_4)_2HPO_3.2H_2O$ was obtained by Rose by adding slight excess NH_3Aq to the acid and crystallising; *in vacuo* at ordinary temperature, or at 100° in air, loses NH_3 and gives $NH_4H_2PO_3$ (Amat, *l.c.*).

Barium phosphites. The *normal salt* $BaHPO_3$ is obtained by adding $BaCl_2Aq$ to $(NH_4)_2HPO_3Aq$ (Berzelius, *Gm.-K.* 2, 270), also by boiling $BaHPO_2Aq$ with KOHAq. A crystalline powder; strongly heated gives $Ba_2P_2O_7$, H, and Ba phosphide (*v.* Rammelsberg, *B.* 9, 1577); very slightly sol. water; on boiling with water gives a basic and an acid salt (Dulong, *Gm.-K.* 2. 270). The *acid salts* $BaH_2(HPO_3)_2$, $2BaHPO_3.H_3PO_3.8H_2O$, and $2BaHPO_3.3H_3PO_3.2H_2O$ are said to be formed by the action of H_3PO_3Aq on the normal salt (Rammelsberg, Rose, Wurtz).

Calcium phosphites. $CaHPO_3.xH_2O$; from $CaCl_2Aq$ and $(NH_4)_2HPO_3Aq$ (Wurtz, Rose, Rammelsberg). The *acid salt* $CaH_2(HPO_3)_2.H_2O$ is obtained by dissolving marble in H_3PO_3Aq, and evaporating *in vacuo* (Wurtz).

Cobalt phosphite $CoHPO_3.2H_2O$. A reddish powder, obtained by $CoCl_2Aq + (NH_4)_2HPO_3Aq$, or by dissolving freshly ppd. $CoCO_3$ in H_3PO_3Aq; goes blue at 250° (Rose, Rammelsberg).

Copper phosphite $CuHPO_3.2H_2O$. By double decomposition from $(NH_4)_2HPO_3$ (Rose); also by acting on Cu acetate by H_3PO_3Aq (Wurtz). Unchanged by boiling water (Rammelsberg), but reduced to Cu by boiling with H_3PO_3Aq (Rose).

Lead phosphites. The *normal salt* $PbHPO_3$ is obtained by ppg. Pb acetate by $(NH_4)_2HPO_3Aq$ (Rose). A white powder; heated gives off H and PH_3, leaving $Pb_2P_2O_7$ and Pb phosphide. Insol. water (Amat, *C. R.* 110, 901). By adding NaH_2PO_3Aq to excess of $Pb2NO_3Aq$, the compound $PbHPO_3.Pb(NO_3)_2$ is obtained (Amat, *l.c.*). The *acid salt* $PbH_2(HPO_3)_2$ is formed by dissolving the normal salt in very conc. H_3PO_3Aq, and drying the crystals at 100°; with water gives $PbHPO_3$ and H_3PO_3Aq (Amat, *l.c.*).

Magnesium phosphite $MgHPO_3.xH_2O$. By ppg. boiling $MgSO_4Aq$ by Na_2HPO_3Aq (Rammelsberg). Forms a *double salt* $Mg_3(NH_4)_2(HPO_3)_4.16H_2O$ (Rammelsberg, Rose).

Manganese phosphite $MnHPO_3.H_2O$. A reddish powder; very slightly sol. water, more sol. solutions of Mn salts; loses H_2O at 200°. From NH_4 salt and a Mn salt; or by dissolving $MnCO_3$ in H_3PO_3Aq, and adding Na_2CO_3 till ppn. begins, but not enough to remove acid reaction (Rose, Rammelsberg).

Potassium phosphites. The *normal salt* K_2HPO_3 is formed from H_3PO_3Aq and KOHAq or K_2CO_3Aq; semi-crystalline, syrup-like mass; very hygroscopic; insol. alcohol (Wurtz, Rose). The *acid salt* $K_2HPO_3.2H_3PO_3$ was obtained by Wurtz (*A.* 58, 63). Amat (*C. R.* 106, 1351) obtained the *acid salt* KH_2PO_3 by adding KOHAq or K_2CO_3Aq to H_3PO_3Aq till neutral to methyl orange, concentrating, and cooling.

Sodium phosphites. The *normal salt* $Na_2HPO_3.5H_2O$ is obtained by dissolving H_3PO_3 in an excess of NaOHAq, and evaporating *in vacuo* (Amat, *C. R.* 108, 403). Zimmermann (*A.* 175, 1) supposed that Na_3PO_3 is formed under these conditions. Na_2HPO_3 melts at 53°; heat of solution at 13·5° = −4600 (Amat, *C. R.* 110, 191). Dehydrated by drying *in vacuo*, and then at 150° (A., *l.c.*). The *acid salt* $2NaH_2PO_3.5H_2O$ is produced by making H_3PO_3Aq neutral to methyl orange by NaOHAq or Na_2CO_3Aq, concentrating, and cooling. Melts 42°; dehydrated by long heating at 100°; heated above 130° forms $Na_4P_2O_5$; very sol. water; heat of solution at 15° = −10,600 (Amat, *C. R.* 106, 1351).

Zinc phosphite $2ZnHPO_3.5H_2O$; from $ZnSO_4Aq$ and ammoniacal solution of PCl_3 (Rose); also from PCl_3Aq and ZnO (Rammelsberg).

The following phosphites have also been described:—$Di_2(HPO_3)_3$ (Frerichs a. Smith, *A.* 191, 331); $Fe_2(HPO_3)_3.9H_2O$ (Rose, Rammelsberg); $La_2(HPO_3)_3$ (F. a. S., *l.c.*); $SnHPO_3$ (Rose). Phosphites of Al, Be, Bi, Cd, Cr, ferrous Fe, Hg, Ni, and Sr have also been prepared, but their compositions are somewhat doubtful (*v.* especially Rose, *l.c.*).

HYPOPHOSPHORIC ACID AND SALTS $H_4P_2O_6$; $M^IH_3P_2O_6$, $M^I_2H_2P_2O_6$, $M^I_3HP_2O_6$, $M^I_4P_2O_6$, $M^{II}H_2P_2O_6$, $M^{II}_2P_2O_6$. When sticks of P are partly covered with water and left for some time in a large vessel, an acid liquid is obtained; this liquid was formerly called Pelletier's phosphatic acid (P., *Crell. Ann.* 1796 [2] 447). Dulong (*A. Ch.* [2] 2, 141) found 47·8 p.c. P and 52·2 p.c. O in this substance, and supposed it to be P_2O_9. In 1856 Pagel (*J. pr.* 69, 24) showed that the acid liquid contained phosphoric and phosphorous acids; and in 1877 Salzer (*A.* 187, 322) proved the presence of small quantities of a new acid to which he gave the composition nH_2PO_3 and the name *hypophosphoric acid.* The acid has been found to be tetrabasic, hence the formula is written $H_4P_2O_6$. The hypophosphates are generally formed directly from the acid, or by double decomposition from the alkali salts. The hypophosphates are more stable than the hypophosphites and phosphites; normal salts pass into phosphates by taking up O; they are decomposed by heating strongly, giving of PH_3 or H, and leaving phosphate and phosphide.

HYPOPHOSPHORIC ACID $H_4P_2O_6$. Melts at c. 55° (Joly, *C. R.* 102, 110). Heat of solution = 3,850 (J., *l.c.*).

Formation.—1. Along with H_3PO_3 and H_3PO_4, by the slow oxidation of P in moist air (Salzer, *A.* 187, 322; 194, 28; 211, 1; 232, 114, 271).—2. The Ag salt is formed by oxidising P by dilute HNO_3Aq in presence of $AgNO_3$ (Philipp, *B.* 18, 749); also by reacting on H_3PO_3Aq with $AgNO_3Aq$ (Sänger, *A.* 232, 1); and the Cu salt by reacting on P with $Cu(NO_3)_2Aq$ (Corne, *J. Ph.* [5] 6, 123).

Preparation.—Sticks of P are placed in glass tubes narrowed at the lower end; these are arranged inside a funnel, which is placed in the mouth of a bottle containing a little water; the bottle is set in a basin, and the whole is covered with a large bell-jar open at the top. The apparatus is placed in a cool place (best in a cellar) for some weeks or months; according to Joly (*C. R.* 101, 1058), from $\frac{1}{7}$ to $\frac{1}{5}$ of the P is oxidised to $H_4P_2O_6$ if the process is conducted in winter, and not more than $\frac{1}{10}$ in summer.

The acid liquid is mixed with a cold conc. solution of Na acetate, the ppd. $Na_2H_2P_2O_6.6H_2O$ is collected, washed with a *very little* cold water, then dissolved in water (sol. in c. 45 parts cold water), and ppd. by Pb acetate; the $Pb_2P_2O_6$ is collected, washed with cold water, suspended in water, and decomposed by H_2S; the filtrate is evaporated at a low temperature—not exceeding 30°—or *in vacuo* over H_2SO_4, until crystals of $H_4P_2O_6$ are deposited. Joly (*C. R.* 101, 1058, 1148) heats to boiling the acid liquid obtained by oxidising P, as described above, adds Na_2CO_3 till nearly neutral to methyl orange, and crystallises by concentration; he washes the crystals of $Na_2H_2P_2O_6.6H_2O$ with cold water, and recrystallises from hot water, dissolves in hot water, adds an equivalent of $BaCl_2$ in hot water, washes the ppd. $BaH_2P_2O_6$, decomposes it by an equivalent of H_2SO_4 diluted with its own weight of water, filters after two or three days, and evaporates *in vacuo* over H_2SO_4. Drawe (*B.* 21, 3401) carries out the oxidation of P in presence of Na acetate solution.

Properties.—Small colourless crystals, which melt at c. 55° (Joly, *C. R.* 102, 110); very hygroscopic; solution is unchanged in air at ordinary temperatures. Heated to c. 70° suddenly decomposes to H_3PO_3 and HPO_3 (J., *l.c.*); at c. 120° gives $H_4P_2O_7$ and P hydride (J., *C. R.* 102, 760).

Reactions and Combination.—1. *Heat* decomposes $H_4P_2O_6$ (*v. supra*).—2. *Not oxidised* by such *oxidisers* as H_2O_2Aq, ClAq, CrO_3Aq, $HgCl_2Aq$, &c.—3. *Not reduced* by such *reducers* as SO_2Aq, H_2S, or Zn and H_2SO_4Aq.—4. *Potassium permanganate* is slowly reduced in the cold, quickly on heating, by $H_4P_2O_6Aq$ to which H_2SO_4Aq has been added.—5. Heated with *nitric acid*, H_3PO_4Aq is formed.—6. Heated with *dilute sulphuric acid*, H_3PO_3Aq and H_3PO_4Aq are produced.—7. *Silver nitrate* solution gives a white pp., which does not blacken in light and is soluble in warm HNO_3Aq (1:1).—8. By evaporating $H_4P_2O_6Aq$ till the liquid had the composition $P_2O_4.6H_2O$, and then placing over H_2SO_4 *in vacuo*, Joly (*C. R.* 101, 1058; 102, 110) obtained crystals of the *hydrate* $H_4P_2O_6.2H_2O$, melting at 62°–62·5°.

HYPOPHOSPHATES. $M^IH_3P_2O_6$, $M^I_2H_2P_2O_6$, $M^I_3HP_2O_6$, $M^I_4P_2O_6$, $M^{II}H_2P_2O_6$, $M^{II}_2P_2O_6$. These salts have been examined chiefly by Salzer (*A.* 187, 322; 194, 28; 211, 1; 232, 114, 271), and crystallographically by Haushofer a. Fresenius (*Z. K.* 1, 257, 620; 3, 605; 6, 113; 9, 254). The hypophosphates are much more stable towards oxidisers than the hypophosphites or phosphites. They reduce $KMnO_4Aq$ very slowly in the cold after addition of H_2SO_4Aq, and give white pp. with $AgNO_3Aq$ unchanged in light.

Ammonium hypophosphates. The *normal salt* $(NH_4)_4P_2O_6.xH_2O$ is obtained by adding excess of NH_3Aq to the acid; on drying, loses NH_3 and effloresces. The *acid salts* $(NH_4)_2H_2P_2O_6$ and $(NH_4)_3HP_2O_6$ are formed, the former by boiling a solution of the normal salt, the latter by adding the proper quantity of $H_4P_2O_6$ to the former salt.

Barium hypophosphates. The *normal salt* $Ba_2P_2O_6$ is obtained from $BaCl_2Aq$ and $Na_4P_2O_6Aq$; the *acid salt* $BaH_2P_2O_6.2H_2O$ is formed from $NaH_2P_2O_6Aq$ and $BaCl_2Aq$ (*v.* Joly, *C. R.* 101, 1058).

Cadmium hypophosphate $Cd_2P_2O_6.2H_2O$; and the *double salt* $CdNa_2P_2O_6.6H_2O$ (Drawe, *B.* 21, 3401).

Calcium hypophosphates $Ca_2P_2O_6$ and $CaH_2P_2O_6.6H_2O$.

Cobalt hypophosphate $Co_2P_2O_6.8H_2O$; and the *double salt* $2CoNa_2P_2O_6.3H_2O$ (Drawe, *l.c.*).

Copper hypophosphate $Cu_2P_2O_6.6H_2O$ (Drawe, *l.c.*).

Lead hypophosphate $Pb_2P_2O_6$.

Magnesium hypophosphates $Mg_2P_2O_6.12H_2O$ and $MgH_2P_2O_6.4H_2O$; and the *double salt* $Mg(NH_4)_2P_2O_6.6H_2O$.

Nickel hypophosphate $Ni_2P_2O_6.12H_2O$; and the *double salt* $NiNa_2P_2O_6.12H_2O$ (Drawe, *l.c.*).

Potassium hypophosphates $K_4P_2O_6.8H_2O$, $K_3HP_2O_6.3H_2O$, $K_2H_2P_2O_6$, and $KH_3P_2O_6$.

Silver hypophosphate $Ag_4P_2O_6$ (*v.* Philipp, *B.* 14, 749).

Sodium hypophosphates. The *acid salt* $Na_2H_2P_2O_6.6H_2O$ is obtained by slowly oxidising P in moist air, and adding Na acetate solution as described under *Preparation of hypophosphoric acid* (p. 154); sol. 45 parts cold, or 5 parts boiling, water; insol. alcohol; on strongly heating gives off H and P hydride and leaves $NaPO_3$. The *normal salt* $Na_4P_2O_6.10H_2O$ is obtained by adding an equivalent of Na_2CO_3 to $Na_2H_2P_2O_6Aq$; sol. c. 30 parts cold water, much more sol. hot water; solution reacts alkaline, and gives a mixture of salts on evaporation. The *acid salt* $Na_3HP_2O_6.9H_2O$ is formed by mixing the Na_2 and Na_4 salts in the ratio $Na_2H_2P_2O_6 : Na_4P_2O_6$. The *acid salt* $NaH_3P_2O_6.2H_2O$ is formed by adding the proper quantity of $H_4P_2O_6Aq$ to $Na_2H_2P_2O_6$. For reaction of the Na salts with different indicators *v.* Joly, *C. R.* 101, 1058.

Another *acid salt* $Na_5H_3(P_2O_6)_2.20H_2O$ is said to be formed by adding rather more than one molecular weight NaOH to $4Na_2H_2P_2O_6.6H_2O$.

Zinc hypophosphate $Zn_2P_2O_6.2H_2O$ (Drawe, *l.c.*).

PYROPHOSPHITES. In 1887 Amat (*C. R.* 106, 1400) showed that when $2NaH_2PO_3.5H_2O$ is heated to 160° it loses $6H_2O$ and gives the salt $Na_2H_2P_2O_5$. A few other salts of the form $M_2H_2P_2O_5$ have been obtained, but the acid has not been isolated. When the Ba salt is decomposed by an equivalent of H_2SO_4Aq, the solution shows the reactions of pyrophosphites, but the pyrophosphite gradually changes to phosphite (Amat, *C. R.* 108, 1056). The pyrophosphites in solution slowly change to phosphites, the more rapidly the more conc. the solution and the higher the temperature; the presence of an acid, *e.g.* H_2SO_4, greatly quickens the rate of change (A., *l.c.*). Addition of NaOHAq to a boiling solution of the Na salt produces Na_2HPO_3 (A., *C. R.* 106, 1400). Pyrophosphites in very dilute solutions give no pp. with $Pb(NO_3)_2Aq$ until boiled; phosphites give an immediate white pp.; this reaction serves as a qualitative test for the two classes of salts (A., *C. R.* 110, 901).

Lead pyrophosphite $PbH_2P_2O_5$ is obtained by heating $PbH_2(HPO_3)_2$ in a dry vacuum to c. 140°

It is insol. water, but is gradually changed by water to H_3PO_3Aq and $PbHPO_3$ (A., *C. R.* 110, 901).

Sodium pyrophosphite $Na_2H_2P_2O_5$ is formed by heating $2NaH_2PO_3.5H_2O$, which has been partially dehydrated *in vacuo*, to c. 160°. V. sol. water; solution changes to NaH_2PO_3Aq, but by careful evaporation *in vacuo* over H_2SO_4 crystals of $Na_2H_2P_2O_5$ can be again obtained (A., *C. R.* 108, 1056). Presence of acid hastens the change to NaH_2PO_3Aq; this change is also effected by adding NaOHAq to boiling $Na_2H_2P_2O_5Aq$. Heat of solution of $Na_2H_2P_2O_5 = 300$ (A., *C. R.* 110, 191).

For *thiopyrophosphites* $M_4P_2S_5$ and *thio-oxy-pyrophosphites* $M_4P_2O_3S_2$ and $M_4P_2O_4S$ *v.* Phosphorous sulphide, *Reactions* 7 and 8, p. 146; and for *selenopyrophosphites* $M_4P_2Se_5$ *v.* Phosphorous selenide, p. 145). M. M. P. M.

PHOSPHORYL COMPOUNDS. Compounds of the radicle PO are generally called *phosphoryl compounds*; and compounds of the radicle PS are often called *thio-phosphoryl compounds.* These compounds are described in this Dictionary as *phosphorus oxychloride, oxyfluoride, sulphochloride*, &c. The phosphoryl compounds are $PO(NH_2)_3$, $POCl_3$, $POBr_3$, $POBrCl_2$ and $POBr_2Cl$, POF_3, $PO.NH.NH_2$, PON. The thiophosphoryl compounds are $PS(NH_2)_3$, $PSCl_3$, $PSBr_3$, $PSBrCl_2$, PSF_3. The compounds $P_2O_3Cl_4$ and $P_2S_3Br_4$ are sometimes called *pyrophosphoryl chloride* and *pyrothiophosphoryl bromide*, respectively.

M. M. P. M.

(α)-PHOSPHOTOLUIC ACID

$C_6H_3Me(PO_3H_2).CO_2H$ [3:4:1]. *Toluphosphinic acid.* [262°]. Formed by oxidising *m*-xylene phosphonic acid with hot alkaline $KMnO_4$ (Weller, *B.* 20, 1723; 21, 1492). Prisms, v. sol. hot water, v. e. sol. alcohol. Yields HPO_3 and *m*-toluic acid when heated.—PCl_5 yields oily $C_6H_3Me(POCl_2).COCl$. — PbHA‴ aq: needles (from dilute HOAc).—Ag_3A'''.

(β)-Phosphotoluic acid

$C_6H_3Me(PO_3H_2).CO_2H$ [5:3:1]. [220°]. Formed by oxidising *s-m*-xylene phosphonic acid (Weller). Yields HPO_3 and *m*-toluic acid on heating. —Ag_3A''': amorphous pp.

Chloride $C_6H_3Me(POCl_2).COCl$. (249° at 147 mm.). Oil.

Phosphotoluic acid

$C_6H_3Me(PO_3H_2).CO_2H$ [4:*x*:1]. [278°]. Formed by oxidising *p*-xylene phosphonic acid. Needles, decomposed by heat into HPO_3 and *p*-toluic acid.

Chloride $C_6H_3Me(POCl_2).COCl$. [62°]. Crystalline mass.

PHOTO-CHEMISTRY *v. Influence of light on chemical change*, under Chemical change, vol. i. p. 748; also next article (Photographic chemistry); also *Optical methods*, a section of Physical methods, in this volume, p. 221.

PHOTOGRAPHIC CHEMISTRY. The photographic processes at present in use depend primarily upon the photo-chemical decomposition of certain metallic compounds in the presence of suitable oxidisable substances known as sensitisers. Broadly speaking, the photo-decomposable compound may be regarded from a chemical point of view as an oxidising agent, of which the oxidising power is only brought into action under the stimulus of light, th associated compound or sensitiser being at th same time oxidised by the oxygen or halogen thus liberated. Very many metallic compounds are thus susceptible to the influence of light, although only a few of these have up to the present time found practical application. The nature of the chemical change undergone in such cases may be well illustrated by the action of light upon ferric salts. An aqueous solution of ferric chloride, for example, is not acted upon by light because the associated substance (water) is not capable of reacting with the liberated chlorine with sufficient rapidity; in other words, water is incapable of acting as a sensitiser towards ferric chloride. But if some oxidisable organic compound is present, light then reduces the ferric to the ferrous salt. Thus an alcoholic solution of ferric chloride exposed for a few minutes to sunlight gives a blue colouration with potassium ferricyanide, indicating the presence of a ferrous salt, probably formed according to the equation: $Fe_2Cl_6 + C_2H_6O = Fe_2Cl_4 + C_2H_4O + 2HCl$. In a similar way paper coated with a solution of ferric chloride can be used to obtain prints, because the paper (or the size contained in it) plays the part of a sensitiser, and the exposed portions of the surface thus become covered with a ferrous instead of a ferric compound, and on brushing over with a solution of ferricyanide the print is developed in blue. In practice ferric oxalate is found to be the most sensitive ferric compound, the organic acid being the sensitiser: $Fe_2(C_2O_4)_3 = Fe_2(C_2O_4)_2 + 2CO_2$.

Although the chemical action of light upon metallic compounds generally is of the nature of reduction, and is accompanied by the simultaneous oxidation of the compound which plays the part of a sensitiser, there are many instances in which light promotes the action of atmospheric oxygen or other oxidising agent. Thus potassium iodide may be kept in a dry atmosphere in the dark for any length of time without undergoing change, but in the presence of light and moisture photo-chemical oxidation takes place, and the salt becomes alkaline:

$$4KI + 2H_2O + O_2 = 4KOH + 2I_2.$$

Action of light upon silver salts. Of all known metallic compounds the salts of silver are the most sensitive to the action of light, and these salts accordingly form the basis of all existing photographic processes. The most familiar instance of the photo-decomposition of a silver salt is the well-known change in colour experienced by silver chloride on exposure to light, a phenomenon which has been familiar since the sixteenth century. The other silver haloids, viz. the bromide and iodide, are also decomposed by light, the latter only in the presence of some sensitiser capable of rapidly absorbing iodine. The absolute sensitiveness of the silver haloids cannot be estimated by the degree of darkening on exposure, because the product of photo-decomposition is of a darker colour in the case of the chloride than in the case of the bromide, and the product is darker in the case of the bromide than in that of the iodide. The sensitiveness is actually determined by two conditions, viz. the nature of the sensitiser and the state of molecular aggregation of the silver haloid. In most of the negative processes ow in use, the bromide or iodide, or a mixture f the two, forms the sensitive surface.

The nature of the chemical change undergone n exposure to light has not yet been completely lucidated for all the silver haloids. It is known hat the chloride loses chlorine on exposure, and hat the darkened product contains less chlorine han the unaltered haloid. It is as yet uncerain whether the halogen which is given off is lways evolved in the free state or not; it has been hown, however, that silver chloride on exposure o light gives off a gas which rapidly turns potasium iodide and starch paper blue (Meldola, *Chemistry of Photography*, p. 66). It is stated y many writers that the darkened product is a ubchloride formed according to the equation: $AgCl = 2Ag_2Cl + Cl_2$. There is, however, no satisactory evidence of the existence of such a subalt, and it seems more probable that the dark roduct consists of an oxychloride, in combinaion, or admixture, with unaltered chloride. According to some analyses by Hodgkinson, the xychloride has the formula Ag_4OCl_2. In support f this conclusion it is found that the chloride loes not darken in absolutely dry air, unless apour of mercury is present (Abney), thus naking it appear that moisture is essential for he decomposition. The latest investigation of he action of light on AgCl by Baker (*C. J.* 61, 28) confirms the view that the darkened product ontains an oxychloride; Baker gives the formula Ag_2ClO. A second, white, oxychloride also robably exists (Richardson, *C. J.* 59, 536). Silver chloride is thus analogous to cuprous or hallous chloride, which also darken under the nfluence of light, with the formation of what are believed to be oxychlorides. Whatever may be the chemical composition of the darkened product, it is probable that the bromide and iodide give rise to the formation of analogous compounds, and that the invisible picture in the older processes is formed of these products on a background of unaltered haloid. The undeveloped image on modern dry plates, coated with gelatin emulsion, may, however, have a different composition, owing to the presence of the organic sensitiser.

Photosalts of silver. These are coloured forms of the silver haloids prepared by the action of certain reducing agents upon silver compounds, and the subsequent conversion of the partially reduced products into the haloids by treatment with the necessary acids. These compounds are of a red or purple colour, and have been shown to contain less halogen than the unaltered haloids. It is probable that they consist of physical combinations of the oxyhaloid or hydrated oxyhaloid with the unaltered haloid; their discoverer (Carey Lea) has shown that they closely resemble, if they are not actually identical with, the products of the photo-chemical reduction of the silver haloids. If this be admitted, it follows that the product which forms the photographic image can be prepared by purely chemical methods (*Am. S.* 1887).

Photographic processes. In all photographic processes the first operation is the exposure of a surface coated with a uniform film of the silver haloid to the image formed by a lens in a camera. The image thus depicted on the film is invisible, in the first place because of the very slight difference in colour between the product of photo-reduction and the unaltered haloid, and in the next place because the short period of exposure does not produce a sufficient quantity of the product of reduction to render the latter visible. The invisible image thus consists of a layer of reduction-product of infinitesimal thinness, and the picture is afterwards made visible by the deposition of metallic silver on this reduction-product by the application of certain solutions known as 'developers,' the chemical action of which will be described subsequently.

Daguerreotype. This process is historically interesting as having been the first method of photography with a silver salt successfully applied to the production of a picture from the image formed in a camera. It takes its name from Daguerre, who announced the discovery in 1839. The process is no longer used; it has been superseded by more rapid methods. In order to prepare a Daguerreotype plate, a plate of copper is silvered, and the polished surface is exposed to the vapour of iodine and bromine alternately. The sensitive film is therefore a mixture of silver iodide and bromide. Silver iodide can act to some extent as its own sensitiser, but the substratum of metallic silver is chiefly effective in this capacity as it is capable of rapidly absorbing the halogen liberated by the action of light upon the sensitive surface. The invisible image is developed by exposure to the vapour of mercury, which condenses on the product of reduction but not on the unaltered haloid.

Collodion processes. In these processes the sensitive film consists of a silver haloid formed by double decomposition in collodion as a vehicle. Collodion is a solution of the tri- and tetranitrate of cellulose (collodion pyroxyline) in alcohol and ether (*v.* vol. i. p. 716), and on coating a glass plate with this solution the solvents evaporate and leave a uniform layer of the pyroxyline attached to the plate. Some soluble iodide, NH_4I or CdI_2, sometimes mixed with a small quantity of a bromide, is first dissolved in the collodion, the plate is coated with this salted collodion, and when dry is sensitised by immersion in a silver nitrate solution. The sensitive surface in this process is therefore a silver haloid wetted with a film of silver nitrate solution, the latter playing the part of a sensitiser by absorbing the liberated halogen: $3I_2 + 6AgNO_3 + 3H_2O = 5AgI + AgIO_3 + 6HNO_3$. By washing out the soluble salts after the plate has been removed from the silver solution the sensitiveness is practically destroyed, because the pyroxyline by itself has no halogen-absorbing power. On drying such a washed plate, and then coating it with a solution of tannin or some organic sensitiser, the sensitiveness is partially restored. Plates thus treated can be used in the dry state, and dry-plate photography by this method was made practically successful in 1861 by Colonel Russell.

Emulsion processes. All the photographic methods at present in vogue are comprised in this group. The silver haloid is precipitated in a finely divided state in some vehicle, usually gelatin, and the plates coated with this emulsion are allowed to dry and are then ready for use. A brief description of a method for preparing a gelatin emulsion will suffice to make clear the general mode of procedure. The soluble bromide (potassium or ammonium), sometimes mixed with a little iodide, is dissolved in water, together with a certain quantity of the gelatin, and to this solution the calculated quantity of silver nitrate (previously dissolved in water) is added little by little with constant agitation. The quantities are so adjusted as to leave no excess of silver nitrate. The silver haloid is by this means precipitated in an extremely fine state of division in the viscid gelatin solution, with which it forms an emulsion. A stronger solution of gelatin is then mixed intimately with the first dilute emulsion, and the whole is heated on a water-bath for about an hour to become 'ripened.' When cold, the semi-solid emulsion is washed by immersion in a fine state of division in cold water, so as to remove all soluble salts (nitrates formed by double decomposition, excess of soluble haloids, &c.). The washed emulsion is then mixed with the necessary quantity of strong gelatin solution to reduce it to the required consistency, and the plates are coated and allowed to dry. Many variations in the details of mixing have been introduced, but these involve no change in principle. Ripening can also be effected at ordinary temperatures by the action of ammonia.

Ripening of emulsions. The process of ripening above referred to is necessary in order to increase the sensitiveness of the silver haloid, since the latter when first precipitated is comparatively insensitive. The increase of sensitiveness is no doubt due, partially if not wholly, to a physical change in the state of molecular aggregation of the silver haloid, as it is accompanied by a growth in the size of the particles and by a change in the absorption spectrum, the unripened emulsion transmitting more of the red rays, and, therefore, absorbing less of this part of the spectrum, than the ripened emulsion. The extreme sensitiveness of the emulsions at present in use is thus due in great measure to the circumstance that the haloid is rendered sensitive to a much wider range of spectral colours than is the case with ordinary silver bromide precipitated in a non-emulsifying medium. The increased sensitiveness of a ripened emulsion may also be ascribed, in part, to the formation of an actual compound of the silver haloid with the gelatin or some constituent thereof (Meldola, *Cantor Lectures on Photographic Chemistry*, 1891. 20, 21).

Development of the photographic image. *Acid development.* In the wet collodion process the image is developed by the application of a solution of ferrous sulphate mixed with acetic acid and alcohol (to insure uniformity of flow). The film being already wet with silver nitrate solution, the action of the developer is simply to reduce this salt according to the reaction: $6AgNO_3 + 6FeSO_4 = 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6 + 6Ag$. Metallic silver is thus contained as a potential deposit in the mixed solutions, but its precipitation is retarded by the acetic acid, which plays the part of what is technically called a 'restrainer.' The finely-divided metal is deposited only on the product of photo-decomposition (the invisible picture), the density of the deposit being proportional to the amount of decomposition on each portion of the sensitive surface. The image thus continues to gain in density as long as there is silver to feed it, so that the picture is built up by accretion and is raised in relief on the surface of the film. If the film is treated with dilute nitric acid after development, the picture is dissolved off, leaving the film in the same condition as before exposure, thus proving that the image is purely superficial. The ferrous sulphate developer, which acts in the manner described, is a type of the class of acid developers.

Alkaline development. Gelatin emulsions contain no excess of silver nitrate, so that the foregoing process of development is inapplicable. The gelatin itself, being a bromine absorbent, is in this case the sensitiser. Development is effected in modern processes by means of an alkaline or neutral solution of some reducing agent, usually an easily oxidisable organic compound, such as ammonium pyrogallate, first introduced by Colonel Russell in 1862. In this method the developer acts directly as a reducing agent upon the product of photo-reduction, replacing the latter by its equivalent of metallic silver. The image at the same time gains in density by the further reduction of those portions of the unaltered silver haloid which are in immediate contact with the nascent silver being generated by the developer; the action is probably electrolytic, since the image goes on increasing in density as long as the developer can exert a reducing action. A very small amount of the silver deposit may also be due to the reduction of the minute quantity of silver actually dissolved out of the film by the ammonia or other solvent in the developer. In alkaline development the main portion of the silver image is therefore built up by growth from the silver haloid in the film, and after development the image can be dissolved out by dilute nitric acid, leaving its impression sunk in the gelatin, instead of leaving a plane surface, as in the case of a collodion picture similarly treated.[1] The developers belonging to this class are all strong reducing agents capable of directly reducing the silver haloids, so that the action has to be moderated by means of restrainers, potassium bromide being generally employed for this purpose. The restraining action of this salt is probably due to its tendency to form a double potassio-silver bromide, which is more stable than the silver bromide itself. In addition to ammonium pyrogallate several other developers acting in a similar manner have come into use. Of these may be mentioned potassio-ferrous oxalate (Carey Lea, 1877), which acts according to the equation: $3Br_2 + 6FeC_2O_4 + 3K_2C_2O_4 = 3Fe_2(C_2O_4)_3 + 6KBr$. The bromine in this case is derived primarily from the reduction-product. Other developers coming under this category are an alkaline solution of hydroquinone (quinol), hydroxylamine, phenylhydrazine, and an alkaline salt of amido-β-naphthol-monosulphonic acid (Meldola, *C. J.* 39, 47), introduced by Andresen (*Eikonogen*). Among the most recently introduced developers are certain amido-phenols, amido-phenols and carboxylic acids, and their alkyl derivatives, known as '*amidol*,' '*metol*,' &c. Those which contain the basic and hydroxyl substituents in the para- position seem to be the most effective (Hauff, *Engl. Patents* [1891] 15, 431; 20, 690).

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[1] An able investigation of the connection between the density of the deposit of reduced silver and the period of exposure, &c., is published by Harter a. Driffield (*S. C. I.* 9, 455; 10, 100; *v.* also other papers in same volume; also Armstrong, *Conference No. of Journ. of the Camera Club*, 1892, and discussion in same journal, July 1892).

In the processes of alkaline development the gelatin itself also acts the part of a restrainer by preventing too intimate a contact between the reducing solution and the silver haloid. Any viscous substance exerts this protecting influence (sugar, glycerin, &c.), and such compounds are sometimes called *physical restrainers*, to distinguish them from chemical restrainers, such as the acid in the ferrous sulphate developer or the potassium bromide in alkaline developers. A developer of very great reducing power is for this reason available in dry plate photography, and upon this fact largely depends the extreme sensitiveness of modern processes.

Development by vapour. The Daguerreotype picture was developed by exposure to mercury vapour, this metal having the property of condensing on the product of photo-reduction (the invisible image) but not on the unaltered silver haloid. It is not known whether the combination of the mercury with the reduction-product is of a chemical or physical nature. This method of development is at present the sole representative of its class.

Fixing the picture. The image developed by the foregoing methods is always on a background of unchanged silver haloid, which must obviously be removed before the picture can be exposed to white light. In the early days of photography strong solutions of potassium, sodium, or ammonium chloride were used as fixing agents, these salts having the property of forming soluble double salts with the silver haloids. The action of these salts was, however, very imperfect, and a certain amount of undissolved silver haloid was always left in the film, which led on exposure to the gradual darkening and obliteration of the whole picture. Potassium cyanide has since been employed, this salt forming with the silver haloid an extremely soluble double cyanide: $AgBr + 2KCN = AgK(CN)_2 + KBr$. The fixing agent now generally preferred is sodium thiosulphate (Sir J. Herschel, 1839); this salt, if used in excess, forming the extremely soluble sodio-silver thiosulphate $Ag_2Na_4(S_2O_3)_3, 2aq$: $2AgBr + 3Na_2S_2O_3 = Ag_2Na_4(S_2O_3)_3 + 2NaBr$. If the fixing solution is dilute, the insoluble $NaAgS_2O_3$ is formed, which remains in the film and spoils the picture: $AgBr + Na_2S_2O_3 = AgNaS_2O_3 + NaBr$. After immersion in the fixing bath, the soluble salts are removed by thorough washing in a stream of water.

Intensification, and reduction, of density. In cases where the image is wanting in density through under-exposure, bad light, insufficient development, &c., a process of intensification is resorted to. The process as applied to modern dry plates consists in substituting for the silver, of which the image is composed, some denser deposit. Thus, by immersing a negative in a solution of mercuric chloride, the image is bleached by conversion into a mixture of mercurous and silver chlorides: $2Ag + 2HgCl_2 = 2AgCl + Hg_2Cl_2$. By treating this mixture with a solution of potassio-ferrous oxalate the image is restored in silver and mercury, and thus in a condition of increased density: $2AgCl + Hg_2Cl_2 + 4FeC_2O_4 + 2K_2C_2O_4 = 2Ag + 2Hg + 2Fe_2(C_2O_4)_3 + 4KCl$. Many other intensifiers are known, some acting by simple substitution, such as auric or platinic chloride: $6Ag + 2AuCl_3 = 2Au + 6AgCl$, or $4Ag + PtCl_4 = Pt + 4AgCl$; others giving rise to a mixture of products together denser than the original deposit, e.g. lead or uranium ferricyanide: $4Ag + 2Pb_3Fe_2(CN)_{12} = Ag_4Fe(CN)_6 + 3Pb_2Fe(CN)_6$. In cases where too dense an image has been obtained, and it is desired to thin it down, a reducing solution is applied; the chemical principle may be described as a conversion of the metallic silver into some compound which can be simultaneously removed by a solvent such as sodium thiosulphate. Thus a mixture of potassium ferricyanide with thiosulphate is often used for gelatino-bromide plates: $4Ag + 2K_6Fe_2(CN)_{12} = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6$. The silver ferro-cyanide is dissolved off by the thiosulphate, as fast as formed: $Ag_4Fe(CN)_6 + 6Na_2S_2O_3 = 2Ag_2Na_4(S_2O_3)_3 + Na_4Fe(CN)_6$. When the necessary reduction of density has been attained, the action of the solution is stopped by washing the film with water.

Reversal of the photographic image and allied phenomena. Any influence which affects a sensitive film in a way similar to the action of light gives rise to a developable image. Thus mechanical pressure-marks produced by rubbing a film with a glass rod can be developed by ferrous oxalate &c., so as to show a corresponding set of dark streaks. It is probable that the friction in this case induces a minute amount of chemical change between the sensitive haloid and its associated sensitiser (gelatin, &c.), this small quantity of reduction-product being afterwards exaggerated by the cumulative action of the developer. Whether the compound resulting from this mechanical action is identical with that produced by the action of light is at present uncertain, but the associated sensitiser appears to be as essential to the success of the phenomenon in this case as in the ordinary formation of the invisible picture by the action of light. The sensitiser, as has already been explained, is an *essential* part of any photographic system, and this is best shown by the so-called 'reversal' of the photographic image by over-exposure or other means. It has been found that a very strong light allowed to act on a sensitive film for too long a period gives a weaker image on development than is produced with a shorter exposure, and that under some circumstances the image is even 'reversed,' *i.e.* the high lights come out lighter, on development, than the shadows. The explanation of this phenomenon is probably to be found in the circumstance that while the silver haloid is losing halogen under the influence of light, the sensitiser is simultaneously becoming halogenised, so that when the charge of halogen in the latter exceeds a certain amount the chemical change sets in in a reversed direction, *i.e.* the halogenised sensitiser begins to re-halogenise the product of photo-decomposition and thus to destroy the invisible image. That this explanation is, in the main, correct in principle, is shown by the fact that the most sensitive processes are just those which are most prone to give rise to reversal, because it is in such films that the sensitiser becomes most rapidly halogenised. A preliminary exposure to diffused light also promotes reversal, because this imparts a certain initial charge of halogen to the sensitiser. Then, again, oxidising agents favour reversal, because these lessen the halogen-absorbing power of the sensitiser; on the other hand, reducing agents prevent reversal, because they retard or prevent the halogenation of the sensitiser. Thus plates exposed in ozone or in solutions of $K_2Cr_2O_7$ and $K_2Mn_2O_8$ are easily reversed, while nitrites, sulphites, &c., prevent reversal (Abney). Atmospheric oxygen in many cases probably plays a part in the process by assisting in the liberation of halogen from the sensitiser. Thus, by way of illustration, if a plate be given a preliminary exposure to diffused light, and be then coated with a solution of potassium iodide, a completely reversed image can be obtained on exposure in the camera and development. The chemical reaction is in this case: $4KI + 2H_2O + O_2 = 2I_2 + 4KOH$. The iodine is here absorbed by the reduction-product, and thus reverses the picture; the surface of the film is in fact the sensitiser in this case, and the potassium iodide is the photo-sensitive compound.[1]

Waterhouse has recently found that a small quantity of a thio-carbamide added to the developer produces a 'reversed' image (*Photo. News*, 1890. 727, 743, 804; *v.* also *Journ. of Camera Club*, July 1892; also Rawlins, *S. C. I.* 10, 18).

Printing processes. It is obvious that the photographic image, after normal development, represents the object with its lights and shadows reversed, *i.e.* the picture is a negative one. A positive print is obtained by exposing suitable sensitive surfaces under such a negative.

Silver prints. A very general method of obtaining silver prints depends upon the use of a sensitive surface (usually paper) consisting of a mixture of silver chloride and an organic compound of silver with albumen, this surface being obtained by first coating the substratum with a solution of albumen containing ammonium chloride, and then (when dry) floating on a solution of silver nitrate. The printing is carried on to the required depth of colour, and the visible print consists of the reduction-products of silver chloride, and of the organic silver compound, which is also susceptible of photo-reduction. To correct the reddish colour of these mixed reduction-products the print is 'toned' by immersion in a solution of auric chloride, kept neutral by the addition of sodium carbonate, acetate, or phosphate, chalk, borax, &c. The function of these salts is to neutralise the hydrogen chloride liberated by the reduction of the auric chloride by the reducing compounds which constitute the picture. The gold is thus precipitated in a state of fine division only on the products of photo-decomposition (the picture), and imparts the desired tone. The accumulation of acid in the toning bath retards the precipitation of gold, and the deposit is not of a good tone; hence the necessity for the presence of one of the salts referred to. The unaltered silver chloride &c. is removed by fixing with thiosulphate, and washing. In some recent processes the albumenised silver paper is replaced by paper coated with gelatino-bromide or chloride emulsion, a short exposure being given, and the invisible (positive) picture being developed in the usual manner.

Printing with iron and uranium salts. Ferric and uranic salts in the presence of organic sensitisers become reduced on exposure to light, and the ferrous or uranous compounds thus formed can be developed by treatment with potassium ferricyanide or other salts which give coloured products with the ferrous or uranous, but not with the unreduced, salts. Thus paper coated with ferric oxalate gives a faint image of the ferrous salt, which comes out as a deep-blue print on development with ferricyanide: $6FeC_2O_4 + 2K_6Fe_2Cy_{12} = 2Fe_3(Fe_2Cy_{12}) + 6K_2C_2O_4$. Many printing processes depending upon the foregoing principles have come into use, and will be found described in works on practical photography.

Platinotype. Prints in finely-divided platinum can be obtained by exposing a surface coated with a mixture of ferric oxalate and potassium chloroplatinite under a negative. The ferrous salt thus produced does not react with the chloroplatinite till the picture is developed by immersion in a solution of potassium oxalate, which dissolves the ferrous oxalate, with the formation of a double salt, which simultaneously reduces the chloroplatinite:
$3K_2PtCl_4 + 6FeC_2O_4$
$= 3Pt + 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl$. The soluble salts are then removed by washing with dilute hydrochloric acid, and finally with water.

Pigment printing. A mixture of gelatin with potassium dichromate undergoes a chemical change on exposure to light, in the course of which the dichromate is reduced and the gelatin at the same time becomes insoluble in water. The chemical composition of this insoluble gelatin is unknown, but it appears to contain an oxide of chromium as an essential constituent (Eder). Many printing processes are based upon this property of gelatin, such, for example, as the so-called carbon and pigment prints, in which the finely divided carbon or pigment is intimately mixed with the gelatin solution and the mixture sensitised by the addition of dichromate. After exposure under a negative the picture is developed by warm water, which dissolves away those portions of the tissue unacted upon by light. Many of the photo-mechanical printing processes depend also on this property of gelatin.

Photo-etching processes. When a layer of asphalt or bitumen is spread over a surface and exposed under a design, those portions of the film which are acted on by light become insoluble in hydrocarbon oils, so that the design can be developed by such solvents, and the surface, if of metal, can be converted into a printing block by etching with acid. The change experienced by the bitumen is probably the result of photo-chemical oxidation. The processes based on this property are much in vogue at the present time under various modifications. This action of light upon bitumen furnished the earliest successful permanent reproduction of the camera picture (Joseph Nicephore Niepce, 1824).

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[1] Potassium bromide similarly acts as a reversing agent though to a less extent. It is for this reason that every trace of this salt has to be washed out of a gelatino-bromide emulsion after the process of ripening, since the presence of the soluble bromide materially diminishes the sensitiveness of the emulsion.

Bibliography.—It has not been considered advisable in the present article to give the authority for every statement, as most of the results achieved by photographers are to be found in publications rarely consulted by chemists. The following general works contain practically all that is known of photographic chemistry at the present time:—Robert Hunt, *Researches on Light*, 2nd edit., 1854; E. Becquerel, *La Lumière*, Paris, 1867; J. W. Draper, *Scientific Memoirs*, a collection of reprints, 1878; J. M. Eder, *Ueber die Reactionen der Chromsäure u. der Chromate auf Gelatine, Gummi, Zucker, &c.* Wien, 1878; J. M. Eder, *Ausführliches Handbuch der Photographie*, Halle, 1884 9; H. W. Vogel, *La Photographie des Objets Colorés avec leurs Valeurs Réelles*, Paris, 1887; Pizzighelli and Hübl, *La Platinotypie*, Paris, 1887; W. de W. Abney, *Treatise on Photography*, 5th edit., 1888; by the same author, *Instructions in Photography*, and *Photography with Emulsions*; Chapman Jones, *Introduction to the Science and Practice of Photography*, 1888; R. Meldola, *The Chemistry of Photography*, 1889; H. W. Vogel, *Handbuch der Photographie*, Berlin, 1890-1. R. M.

PHOTOSANTONIN *v.* SANTONIN.

PHRENOSIN $C_{41}H_{79}NO_8$. A substance occurring, according to Thudichum (*J. pr.* [2] 25, 19), in the brain.

PHTHALACENE $C_{21}H_{16}$. [173°]. Formed by reduction of phthalacone carboxylic ether with HI and P at 170° (Gabriel, *B.* 17, 1390). Crystals (from HOAc). Yields $C_{21}H_{15}Br$ [184°], which is oxidised by $K_2Cr_2O_7$ and HOAc to $C_{21}H_{13}BrO$ [c. 200°]. Fuming HNO_3 and HOAc yield di-nitro-phthalacene, which separates from hot nitro-benzene in yellow needles. $K_2Cr_2O_7$ and HOAc oxidise phthalacene to 'phthalacene oxide' $C_{21}H_{14}O$ [211°-214°], which yields an oxim $C_{21}H_{14}(NOH)$ [266°].

PHTHALACENIC ACID $C_{20}H_{15}.CO_2H$. [247°]. Formed by heating phthalacene-oxide with soda-lime (Gabriel, *B.* 17, 1399). Crystals.—A'Ag.

PHTHALACONE CARBOXYLIC ACID $C_{21}H_{11}O_2(CO_2H)$. [281°]. Formed by dissolving its ether in conc. H_2SO_4 and pouring into water (Gabriel, *B.* 17, 1389). Minute yellow needles, sol. hot alcohol. The acid yields a dioxim $C_{21}H_{11}(NOH)_2CO_2H$ [273°] and the salts KA'aq and NaA'aq. Zinc-dust and NaOHAq yield a tetrahydride $C_{22}H_{16}O_4$, melting above 280°, which gives AgA', crystallising in needles.

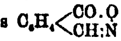
Ethyl ether EtA'. [211°]. A product of the action of phthalic anhydride and NaOAc on acetoacetic ether at 140°. Yellow needles, sol. hot HOAc. Yields a di-nitro- derivative [above 280°] and a dioxim $C_{21}H_{11}(NOH)_2CO_2Et$ [264°]. Zinc-dust and HOAc reduce it to the white tetrahydride $C_{21}H_{13}(OH)_2CO_2Et$ [213°].

PHTHAL-ALCOHOL *v.* DI-OXY-XYLENE.

PHTHALALDEHYDIC ACID $C_8H_6O_3$ *i.e.* $CHO.C_6H_4.CO_2H$ [1:2]. [97°]. Formed, together with $C_{16}H_{10}O_5$ [221°], by heating α-bromo-phthalide with water (Racine, *B*, 19, 778; *A.* 239, 78; *C. R.* 106, 947). Formed also by boiling penta-ω-chloro-*o*-xylene with water (Colson a. Gautier, *Bl.* [2] 45, 509). V. sol. water, alcohol, and ether. Reduces ammoniacal $AgNO_3$. Phenyl-hydrazine yields $C_{14}H_{10}N_2O$ [105°]. Alcoholic NH_3 forms $C_{24}H_{18}N_2O_6$ [187°], while an alcoholic solution of aniline gives $C_{14}H_{11}NO_2$ [174°]. Ac_2O at 200° forms $CHO.C_6H_4.CO_2Ac$ [60°-63°]. Urea forms $NH_2.CO.N:CH.C_6H_4.CO_2H$ [240°].—CaA'_2 2aq.—AgA': slender needles.

Ethers MeA'. [44°].—EtA'. [66°].

Anhydride $C_{16}H_{10}O_5$. [221°]. Got by heating the acid with bromo-phthalide.

Oxim $CH(NOH).C_6H_4.CO_2H$. [120°]. Formed by adding hydroxylamine hydrochloride to a cold aqueous solution of the acid. In an alcoholic solution the product is  $C_6H_4\langle\begin{smallmatrix}CO.O\\CH:N\end{smallmatrix}$ [120°], which is converted by heat first into $CN.C_6H_4.CO_2H$ and then into phthalimide (Allendorff, *B.* 24, 2346, 3264).

Isomeride *v. p*-ALDEHYDO-BENZOIC ACID.

Diphthalaldehydic acid *v.* DI-PHTHALYL-LACTONIC ACID.

PHTHALAMIC ACID *v.* PHTHALIC ACID.

PHTHALAMIDE *v.* PHTHALIC ACID.

ISOPHTHALAMIDINE $C_8H_{10}N_4$ *i.e.* $C_6H_4(C(NH).NH_2)_2$ [1:3]. Formed from $C_6H_4(C(NH).OEt)_2$ and alcoholic NH_3 (Luckenbach, *B.* 17, 1432). Small needles, insol. benzene and ether, v. sol. alcohol and water. Its aqueous solution soon decomposes, giving off NH_3.—$B''H_2Cl_2$: needles, v. sol. water.—$B''H_2PtCl_6$.—$B''H_2SO_4$.—$B''2HNO_3$.—$B'HNO_3$: needles (Grabowski, *A.* 265, 168).—$C_6H_4(NAg.NH_2)_2$.

ISOPHTHALAMIDOXIM $C_8H_{10}N_4O_2$ *i.e.* $C_6H_4(C(NOH).NH_2)_2$. [193°]. Formed from $C_6H_4Cy_2$ [1:3] and hydroxylamine (Goldberg, *B.* 22, 2976). Prisms (from alcohol) containing ½aq ?, v. sol. hot water.

Phthalanil *v. Phenylimide* of PHTHALIC ACID.

PHTHALBENZO-TOLUIDE *v. Phthalyl*-AMIDO-TOLYL PHENYL KETONE.

PHTHAL-*o*-CYANO-BENZYL-IMIDE *v.* *o*-CYANO-BENZYL-PHTHALIMIDE.

PHTHALEÏNS. Colouring-matters obtained by condensation of phthalic anhydride with phenols (*e.g.* PHENOL-PHTHALEÏN and FLUORESCEÏN). They may be reduced to colourless 'phthalins,' which are re-oxidised by air to phthaleïns.

PHTHALIC ACID $C_8H_6O_4$ *i.e.* [1:2] $C_6H_4(CO_2H)_2$. Mol. w. 166. [184°] (Lossen, *A.* 144, 76); [203°] (Ador, *A.* 164, 230; Baeyer, *A.* 269, 184). S. ·54 at 14°; 18 at 99° (Graebe, *A.* 238, 321); S. (alcohol) 10 at 15° (Bourgoin, *Bl.* [2] 29, 247); S. (ether) ·684 at 15°. H.C. 771,600. H.F. 187,400 (Stohmann, *J. pr.* [2] 43, 540); 153,000 (von Rechenberg). S.H. (from 75° to 119°) ·256 (Hess, *A. Ch.* [2] 35, 410).

Formation.—1. By the action of nitric acid on naphthalene, naphthalene dichloride, alizarin, purpurin, munjistin, naphthoquinone, *o*-toluic acid (Laurent, *A. Ch.* [2] 61, 113; Marignac, *A.* 42, 215; Schunck, *A.* 66, 197; Wolff a. Strecker, *A.* 75, 12, 25; Stenhouse, *A.* 130, 334; Liebermann a. Dittler, *B.* 6, 94 ; Piccard, *B.* 12, 579; Beilstein a. Kurbatoff, *A.* 202, 215).—2. By the action of various oxidising agents on naphthalene (Lossen, *A.* 144, 71; Hermann, *Z.* [2] 4, 551; Depouilly, *C. R.* 56, 82; Häussermann, *D. P. J.* 223, 310).—3. A product of the action of MnO_2 and H_2SO_4 on benzene (Carius, *Z.* [2] 4, 705; *A.* 148, 60).—4. By oxidising *o*-toluic acid with $KMnO_4$ (Weith, *B.* 7, 1057).—5. By oxidising isoquinoline with alkaline $KMnO_4$ (Hoogewerff a. Van Dorp, *R. T. C.* 4, 285).—6. By heating salicylic acid with H_2SO_4 and K_4FeCy_6 (Guyard, *Bl.* [2] 29, 247).—7. By heating resorcin or salicylic acid with formic acid and H_2SO_4 (G.).—8. By the action of a hot solution of cuprous potassium cyanide upon *o*-diazobenzoic chloride (from anthranilic acid), and subsequent saponification of the product (Sandmeyer, *B.* 18, 1499).

Properties.—Trimetric plates. Yields an anhydride when heated. Insol. chloroform.

Reactions.—1. Distillation with *lime* yields benzoic acid and benzene.—2. *Sodium-amalgam* reduces it to a dihydride.—3. *Chromic acid mixture* oxidises it to CO_2 (Fittig, *A.* 156, 242).—4. The acid aniline salt $A''H(NH_3Ph)$ of *ortho*-phthalic acid loses H_2O when its aqueous solution is boiled, phenyl-phthalimide crystallising out. The *para-* and *meta-* phthalic acids do not react in this way; the reaction therefore serves as a means of separating ordinary phthalic acid from its isomers (Michael a. Palmer, *B.* 19, 1376; *Am.* 9, 202).

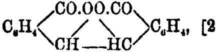
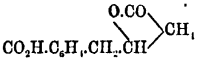
Salts.—$(NH_4)HA''$: prisms, v. sol. water.—$NaHA''2aq$: prisms (Wislicenus, *A.* 242, 89).—Na_2A'': pearly plates.—K_2A''.—$CaA''aq$.—$BaH_2A''_2$: prisms (Hermann, *A.* 151, 78).—BaA'': v. sl. sol. water (Carius, *A.* 148, 64).—$Ba_4A''_3O$: monoclinic prisms.—$CuA''aq$.—PbA''.—Ag_2A'': crystalline pp.—Aniline salt: needles [146°] (Clarke, *B.* 12, 1066).

Di-methyl ether Me_2A'' (280° i.V.) at 734 mm. (Graebe, *B.* 16, 860). H.F. 164,600 (Stohmann, *J. pr.* [2] 40, 353).

Mono-ethyl ether $EtHA''$. Formed by heating phthalic anhydride with absolute alcohol at 100° (Michael, *Am.* 1, 413). Liquid, m. sol. water. Decomposed by heat into phthalic anhydride and alcohol.—$Ba(EtA'')_2$.—$AgEtA''$.

Di-ethyl ether Et_2A''. (295° cor.). Got by passing HCl into an alcoholic solution of phthalic acid (Graebe a. Born, *J.* 1866, 411). Formed also from phthalyl chloride and alcohol. Liquid. Not attacked by hydroxylamine (Jeaurenaud, *B.* 22, 1273). When warmed with NaOEt and EtOAc it yields the compound $C_6H_4<\substack{CO\\CO}>CH.CO_2Et$ [75°-78°] (Wislicenus, *A.* 246, 349). PCl_3 followed by sodium malonic ether forms the acid $C_{21}H_{16}O_{10}$ [c. 180°] (Zelinsky, *B.* 20, 1010).

Phenyl ether Ph_2A''. [70°]. Formed by heating phthalyl chloride with phenol (Schreder, *B.* 7, 704; von Gerichten, *B.* 13, 419). Colourless crystals.

Anhydride $C_8H_4O_3$ *i.e.* $C_6H_4<\substack{CO\\CO}>O$. Mol. w. 148. V.D. 5·26 (calc. 5·13) (Troost, *C. R.* 89, 351). [128°]. (284·5° i.V.). H.C.p. 784,000. H.F. 106,000 (Stohmann, *J. pr.* [2] 40, 139). Formed by heating phthalic acid alone or with AcCl (Laurent; Anschütz, *B.* 10, 326). Formed also by the action of lead nitrate on phthalyl chloride (Lachovitch, *B.* 17, 1283). Long needles, v. sol. alcohol and ether, sl. sol. cold water. *Reactions.*—1. When heated with *phenols* it yields phthaleïns, with elimination of water (Baeyer, *B.* 7, 968).—2. Heated with NaOAc and HOAc it yields phthalyl-acetic acid $C_{10}H_6O_4$, while *phenyl-acetic acid* gives benzylidene-phthalide. Phenyl-acetonitrile gives rise to $C_6H_4<\substack{CO.O\\C:CPh.CN}$ [165°], and *isobutyric acid* and $ZnCl_2$ at 250° give a ketone $C_{11}H_{10}O_2$ [96°]. 3. Boiling with NaOAc and *phenoxyacetic acid* yields $C_6H_4:C_2O_2:CH.OPh$ [143°] while *p-tolyl-oxy-acetic acid* and sodium acetate give rise to $C_6H_4:C_2O_2:CH.OC_6H_4Me$ [174°] (Gabriel, *B.* 14, 922).—4. *Acetoacetic ether* gives $C_6H_3Bz_3$ and phthalacone carboxylic ether.—5. On heating with *succinic acid* and *sodium succinate* it yields CO_2 and $C_{18}H_{10}O_4$ [above 300°].—6. *Di methyl-quinoline* and zinc chloride at 200° give $C_6H_4:C_2O_2:C_{11}H_9N$ [238°] (Beyer, *J. pr.* [2] 33, 407).—7. *Ethenyl-amido-phenyl-mercaptan* and $ZnCl_2$ at 200° give $C_6H_4<\substack{N\\S}>C.CH<\substack{CO\\CO}>C_6H_4$ crystallising in yellow needles [above 320°] (Jacobson, *B.* 21, 2630).—8. *Cyanethine* forms, on heating, $C_9H_{13}N_2.N:C_2O_2:C_6H_4$ [128°] (E. von Meyer, *J. pr.* [2] 39, 262).—9. Coal-tar *picoline* and zinc chloride at 200° form pyrophthalone $C_8H_4O_2:CH.C_5H_4N$ [above 260°] (Jacobsen a. Reimer, *B.* 16, 2604) crystallising from alcohol in yellow plates.—10. *Benzene* and $AlCl_3$ yield *o*-benzoyl-benzoic acid, and other aromatic hydrocarbons act in like manner (Friedel a. Crafts, *C. R.* 92, 833).—11. *Benzyl chloride* and *zinc-dust* at 75° yield $C_{50}H_{46}$ (?) [73°] (Wislicenus, *A.* 248, 68).—12. On heating with *amines* and *amides*, phthalic anhydride yields derivatives of the imide and amide of phthalic acid; thus acetamide yields phthalimide and HOAc, while ethylamine yields ethyl-phthalimide. Secondary amines form derivatives of the amic acid and of the amide (Piutti, *A.* 227, 181; *G.* 16, 1, 251).—13. *Amido-acids* are converted by phthalic anhydride into their phthalyl derivatives (Reese, *A.* 242, 1).—14. On fusion with *zinc-dust* phthalic anhydride gives diphthalyl. Zinc-dust and HOAc yield a mixture of phthalide, diphthalyl dihydride  $C_6H_4<\substack{CO.OO.CO\\CH—HC}>C_6H_4$, [229°] and  $\substack{O.CO\\CO_2H.C_6H_4.CH_2.CH}>CH_4$ [199°], which is reduced by HIAq to $C_2H_4(C_6H_4.CO_2H)_2$ (Wislicenus, *B.* 17, 2178).—15. *Tri-amido-phenol* (picramic acid) forms $(C_8H_4O_2:N)_3C_6H_2.OH$ [above 300°] converted by potash into the compound $(CO_2H.C_6H_4.CO.NH)_3C_6H_2OH$ [above 300°], from which nitric acid produces the quinone $(C_8H_4O_2:N)_2C_6H_2O_2$ [277°] reduced by SO_2 to $(C_8H_4O_2:N)_2C_6H_2(OH)_2$ [above 310°] (Piutti, *G.* 16, 254).

Chloride $C_6H_4<\substack{CCl_2\\CO}>O$. *Phthalyl chloride.* [0°] (Wischin, *A.* 143, 259). (275°) at 726 mm. S.G. $\frac{20}{4}$ 1·4089. $\mu_a = 1·569$ (Brühl, *A.* 235, 14). Formed by heating phthalic acid with PCl_5 for 2 hours at 190° (H. Müller, *Z.* 1863, 257; Graebe, *A.* 238, 320). Oil, absorbs moisture from the air, forming phthalic anhydride. Slowly converted into phthalic acid by water or Na_2CO_3Aq. Reduced by zinc and HClAq to phthalide. Sodium-amalgam and HOAc form $C_6H_4(CH_2.OH)_2$. PCl_5 forms two isomeric chlorides $C_6H_4<\substack{CCl_2\\CCl_2}>O$ and $C_6H_4<\substack{CCl_3\\COCl}$, one melting at 88° and boiling at 275°, the other melting at 47° and boiling at 262°; both are converted by aniline into $C_6H_4<\genfrac{}{}{0pt}{}{C(NPh)}{CO}>NPh$ [153°] (von Gerichten, *B.* 13, 417; Claus, *B.* 19, 1188). Excess of PCl_5 yields chloro-benzoic acid, CCl_4, and other products (Claus). Aqueous NH_3 forms $C_8H_4O_2(NH_2)_2$ [90°] not identical with phthalamide, but converted by HClAq into $C_8H_4O_2(NH)$ [145°] which is changed by fusion into the isomeric phthalimide [228°] (Auger, *A. Ch.* [6] 22, 303; *cf.* Kuhara, *Am.* 3, 26). Dry NH_3 acting on the benzene solution behaves in like manner. Hydroxylamine yields $C_6H_4{:}C_2O_2{:}NOH$ [230°] (*v.* vol. ii. p. 738). *o*-Amido-phenyl mercaptan hydrochloride forms $C_{20}H_{12}N_2S_2$ [112°] (Hofmann, *B.* 13, 1233). $ZnMe_2$ forms $C_{10}H_{10}O_2$ [68°] (240°) (Rjasantzeff, *Bl.* [3] 1, 166). $ZnEt_2$ followed by water gives, in like manner, $C_{12}H_{14}O_2$ [54°] (250°).

Semi-nitrile v. o-CYANO-BENZOIC ACID.

Amic acid $C_6H_4(CO.NH_2).CO_2H$. *Phthalamic acid.* [c. 140°] (Auger); [149°] (Aschan, *B.* 19, 1401). Formed by heating phthalic anhydride with alcoholic NH_3 or phthalimide with baryta-water. Prepared by evaporating phthalic anhydride with NH_3Aq, and decomposing the resulting ammonium salt by HCl (Auger, *Bl.* [2] 49, 349). Prisms, sl. sol. water, v. sol. alcohol. Converted by heat into phthalimide, and by hot water into hydrogen ammonium phthalate. Excess of HClAq forms phthalic acid.—NH_4A'.—KA'.—BaA'_2.—BaA'_2 aq.—AgA': needles, v. sl. sol. water (Landsberg, *A.* 215, 197).

Isoamyl-amic acid
$C_6H_4(CO_2H).CO.NHC_5H_{11}$. *Isoamyl-phthalamic acid.* [115°]. Formed by warming isoamyl-phthalimide with KOHAq (Neumann, *B.* 23, 998). Crystalline pp.—AgA'.

Phenyl-amic acid
$C_6H_4(CO_2H).CO.NHPh$. *Phenyl-phthalamic acid. Phthalanilic acid.* [192°]. Got by boiling phenyl-phthalimide with NH_3Aq and some alcohol (Laurent a. Gerhardt, *A. Ch.* [3] 24, 188). Plates, sl. sol. cold water, v. sol. alcohol.

Phenyl-ethyl-amic acid $C_{16}H_{15}NO_3$ *i.e.* $C_6H_4(CO_2H).CONPhEt$. *Phenyl-ethyl-phthalamic acid.* Got by dissolving phthalic anhydride in ethyl-aniline (Piutti, *G.* 13, 545; *A.* 227, 185). Heavy oil, v. sl. sol. water.

Di-phenyl-amic acid
$C_6H_4(CO_2H).CONPh_2$. *Di-phenyl-phthalamic acid.* [148°]. Made from diphenylamine and phthalic anhydride (P.). Hard prisms, sl. sol. ether, v. sol. alcohol.—AgA'.

o-Tolyl-amic acid
$C_6H_4(CO_2H).CONHC_6H_4Me$. Got by boiling *o*-tolyl-phthalimide with NH_3Aq (Kuhara, *Am.* 9, 51). Needles.—$Ag_2C_{15}H_{11}NO_3$: pp.

m-Methyl-benzyl-amic acid
$C_6H_4(CO_2H).CO.NHCH_2C_6H_4Me$. [131°]. Got from *m*-xylyl-phthalimide and caustic soda (Brömme, *B.* 21, 2700). Needles, sol. alcohol.—AgA': white pp.

ψ-Cumyl-amic acid
$C_6H_4(CO_2H).CO.NHC_6H_2Me_3$. *Phthal-ψ-cumidic acid.* [179°]. Needles, v. sol. alcohol, sl. sol. ether (Fröhlich, *B.* 17, 1808).

Naphthyl-amic acids
$C_6H_4(CO_2H).CO.NHC_{10}H_7$. The (α)- acid [185°] is got from (α)-naphthyl-phthalimide. The (β)-acid crystallises from alcohol in tables (Piutti, *G.* 15, 480).

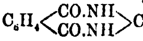
Phenyl-oxy-ethyl-amic acid
$C_6H_4(CO_2H).CO.NH.C_2H_4.OPh$. [125°]. Formed by warming phenyl-oxyethyl-phthalimide with KOHAq (Schmidt, *B.* 22, 3255).

p-Tolyl-oxy-ethyl-amic acid
$C_6H_4(CO_2H).CO.NH.CH_2.CH_2.O.C_6H_4Me$. [137°]. Formed from the corresponding imide which is got by heating potassium phthalimide with $C_6H_4Me.OC_2H_4Br$ (Schreiber, *B.* 24, 191).

Phenyl-amido-phenyl-amic acid
$C_6H_4(CO_2H).CO.NH.C_6H_4.NHPh$. [120°-130°]. Powder (Gabriel, *B.* 22, 2223).

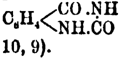
Benzoylethyl-amic acid
$C_6H_4(CO_2H).CO.NH.CH_2.CH_2Bz$. *Propiophenone-phthalamic acid.* [140°]. Made from the imide (Schmidt, *B.* 22, 3251). Needles.—AgA': pp.

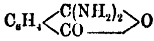
Di-sulphido-di-ethyl-amic acid
$(C_6H_4(CO_2H).CO.NH.CH_2.CH_2)_2S_2$. [130°]. Formed from sulphocyano-ethyl-phthalimide and (10 p.c.) KOHAq (Coblenz, *B.* 24, 2131). Scales. HClAq at 180° forms $S_2(C_2H_4NH_2)_2$.

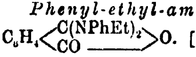
Uramic acid $C_6H_4(CO_2H).CONH.CO.NH_2$. *Phthaluric acid.* S. 3·5 at 99°. Formed by heating phthalic anhydride with urea at 115° (Piutti, *A.* 214, 19; *G.* 12, 173). Silvery scales, sol. alcohol. May be converted by $POCl_3$ into  $C_6H_4<\genfrac{}{}{0pt}{}{CO.NH}{CO.NH}>CO$, which yields $AgC_9H_5N_2O_3$.

Salts.—NaA' 2aq.—BaA'_2.—AgA': needles.

Thio-uramic acid
$C_6H_4(CO_2H).CO.NH.CSNH_2$. [172°]. Got by heating phthalic anhydride with thio-urea (P.). Silvery needles (from alcohol).—BaA'_2 7aq.

s-Amide $C_6H_4(CO.NH_2)_2$. *Phthalamide.* [220°] (Bülow, *A.* 236, 188 Formed from phthalimide and cold NH_3Aq (Aschan, *B.* 19, 1399). Minute crystals, insol. cold water, alcohol, and ether. Boiling water converts it into phthalimide. Alkaline KOBr at 80° forms  $C_6H_4<\genfrac{}{}{0pt}{}{CO.NH}{NH.CO}$ (Hoogewerf a. Van Dorp, *R. T. C.* 10, 9).

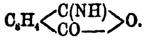
u-Amide  $C_6H_4<\genfrac{}{}{0pt}{}{C(NH_2)_2}{CO}>O$. [c. 90]. Formed from phthalyl chloride and NH_3Aq (Auger, *A. Ch.* [6] 22, 304). Long transparent prisms, v. sol. water, sol. hot alcohol. $AgNO_3$ ppts. $C_8H_4O_2NAg$ in white lustrous scales, NH_3 being eliminated.

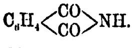
Phenyl-ethyl-amide
 $C_6H_4<\genfrac{}{}{0pt}{}{C(NPhEt)_2}{CO}>O$. [141°]. Formed by heating the ethyl-aniline salt of phenyl-ethyl-phthalamic acid above 200° (Piutti, *G.* 13, 547; *A.* 227, 187). Prisms, insol. water, sol. alcohol and ether. Not attacked by KOHAq, but split up by potash-fusion into phthalic acid and ethyl-aniline.

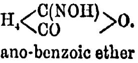
Di-phenyl-amide $C_6H_4{:}C_2O_2(NPh_2)_2$. '*Di-phenylamine-phthaleïn.*' [288°]. Formed from phthalyl chloride and diphenylamine (Lellmann, *B.* 15, 830). Formed also by boiling phthalic anhydride with diphenylamine (P.). Needles (from alcohol). H_2SO_4 containing HNO_3 forms an intense violet solution.

m-Phenylene-diamide
$C_8H_4O_2{:}N_2H_2{:}C_6H_4$. [179°]. Formed, together with $(C_8H_4O_2{:}N)_2C_6H_4$ [252°], by fusing *m*-phenylene-diamine with phthalic anhydride (Biedermann, *B.* 10, 1160). Nodules.

p-Phenylene-diamide $C_6H_4:C_2O_2:N_2H_2:C_6H_4$. [182°]. Converted by warming with dilute HClAq into a base $C_{31}H_{28}N_6O_4$ and $(C_6H_4:C_2O_2:N)_2C_6H_4$ [295°] (Biedermann, *B.* 10, 1163).

u-Imide  $C_6H_4{<}\substack{C(NH)\\CO—}{>}O$. *u-Phthalimide.* [c. 145°]. Formed by the action of HClAq on the *u*-amide (Auger). Slender needles, exactly resembling the *s*-imide, into which it changes when heated. Differs from the *s*-imide by decomposing moist $BaCO_3$ in the cold, hence it may possibly be *o*-cyano-benzoic acid.

s-Imide  $C_6H_4{<}\substack{CO\\CO}{>}NH$. *Phthalimide.* [228°]. Formed by heating $C_6H_4(CO_2H)(CO_2NH_4)$ or $C_6H_4(CO_2H).CONH_2$ (Laurent, *A.* 41, 110; *A. Ch.* [2] 61, 121; [3] 23, 119; Lansberg, *A.* 215, 181). Got also by heating the *u*-imide, and by the action of $CuCy_2$ and KCy on *o*-diazobenzoic acid (Sandmeyer, *B.* 18, 1499). Six-sided prisms (from ether). May be sublimed. Reduced by tin and HCl to phthalidine $C_8H_6O(NH)$ (Graebe, *B.* 17, 2598). When distilled with steam over heated zinc-dust it yields $C_{15}H_{11}N$ [100°] (Gabriel, *B.* 13, 1684). Boiling Ac_2O forms $C_6H_4:C_2O_2:NAc$ [132°–135°] (Aschan, *B.* 19, 1398). Amyl alcohol and Na reduce phthalimide to *o*-methyl-benzyl-amine (Bamberger, *B.* 21, 1888). Yields benzonitrile when distilled with lime (Reese, *A.* 242, 5). Alkaline KOBr at 80° forms *o*-amido-benzoic acid (Hoogewerff a. Van Dorp, *R. T. C.* 10, 8) $C_8H_4O_2NK$. Formed from phthalimide and alcoholic potash (Cohn, *A.* 205, 301; Gabriel, *B.* 20, 2225). Plates, converted into potassium phthalamate by boiling water. Converted by alkyl iodides into alkylphthalimides. [1:2]$C_6H_4(CH_2Br)_2$ gives rise to $C_6H_4(CH_2.N:C_8H_4O_2)_2$ [253], while the *m*-isomeride melts at 237°. Reacts with epichlorhydrin, forming $C_8H_4O_2N.C_3H_5O$ [204°] (Goedeckemeyer, *B.* 21, 2689) with (α)-dichlorhydrin, forming $(C_8H_4O_2:N.CH_2)_2CH.OH$ [204°], and with γ-bromobutyronitrile, forming $C_8H_4O_2N.CH_2.CH_2.CH_2.CN$ [81·5°] (Gabriel, *B.* 22, 224, 3337; 23, 1771).—$C_8H_4O_2NNa$. — $(C_8H_4O_2N)_2Mg$: white pp. — $(C_8H_4O_2N)_2Ba$ 4aq: plates. — $(C_8H_4O_2N)_2Hg$. — $(C_8H_4O_2N)_2Cu$ aq. — $(C_8H_4O_2N)_2Cu$ 4aq. — $C_8H_4O_2NAg$ ½aq: cheesy pp.

Imidoxim $C_8H_6N_2O_2$ *i.e.*  $C_6H_4{<}\substack{C(NOH)\\CO}{>}O$. [250°]. Formed by heating *o*-cyano-benzoic ether with an alcoholic solution of hydroxylamine at 90° for a long time (Müller, *B.* 19, 1498). Needles (from dilute alcohol), insol. benzene. Boiling with HClAq and $FeCl_3$ converts it into phthalimide.

Methyl-imide $C_8H_4O_2:NMe$. [132°]. (286°). Formed from potassium-phthalimide and MeI at 150° (Graebe, *B.* 17, 1174; *A.* 247, 302). Needles, reduced by tin and HCl to C_9H_9NO [120°] (300°), which yields a gold salt [196°].

Ethyl-imide $C_6H_4:C_2O_2:NEt$. *Ethylphthalimide.* [79°]. (282°) at 726 mm. Formed by distilling a solution of phthalic anhydride in aqueous ethylamine; and formed also from potassium phthalimide and EtI (Michael, *B.* 10, 1645; Graebe, *A.* 247, 302; Wallach a. Kamenski, *B.* 14, 171). Needles. Br at 140° forms $C_{10}H_6Br_3NO_2$ [c. 189°].

Bromo-ethyl-imide $C_8H_4O_2:N.CH_2.CH_2Br$. [83°]. Formed from potassium phthalimide and $C_2H_4Br_2$ (Gabriel, *B.* 20, 2225; 21, 566; 22, 1137). Needles. Converted by aniline into phenyl-amido-ethyl-phthalimide [100°], and by *p*-toluidine into both $(C_8H_4O_2:N.C_2H_4)_2NC_6H_4Me$ [200°] and $C_8H_4O_2:N.C_2H_4.NHC_6H_4Me$ [96°]. ψ-Cumidine forms $C_8H_4O_2:N.C_2H_4.NHC_6H_2Me_3$ [146°], while (α)- and (β)-naphthylamines form compounds $C_8H_4O_2:N.C_2H_4.NHC_{10}H_7$ [158°] and [141°] respectively (Newman, *B.* 24, 2196). Potassium sulphocyanide forms $C_8H_4O_2:N.C_2H_4SCy$ [108°] (Coblenz, *B.* 24, 2131).

Sulphydro-ethyl-imide $C_8H_4O_2:N.C_2H_4SH$. [77°]. Formed from the bromo-ethyl-imide and KSH at 100°. Converted by NaOEt and glycollic chlorhydrin into syrupy $C_8H_4O_2:N.C_2H_4.S.C_2H_4OH$, whence $POCl_3$ forms $C_8H_4O_2:N.C_2H_4.S.C_2H_4Cl$ [77°], while $POBr_3$ forms $C_8H_4O_2:N.C_2H_4.S.C_2H_4Br$ [90°]. Reacts with $C_8H_4O_2:N.C_2H_4Br$ and NaOEt, forming $(C_8H_4O_2:N.C_2H_4)_2S$ [129°], which is oxidised by bromine water to the corresponding sulphoxide [191°], and by chromic acid to the sulphone [256°]. Iodine in alcoholic solution forms $(C_8H_4O_2:N.C_2H_4)_2S_2$ [139°], whence $B''H_2Cl_2$ [203°] (Gabriel, *B.* 24, 1122, 3098).

n-Propyl-imide $C_8H_4O_2:NPr$. [66°]. (283°). Crystals (Gabriel, *B.* 24, 3105).

Isopropyl-imide [85°]. (273°).

β-Bromo-propyl-imide $C_8H_4O_2:N.CH_2.CHBr.CH_3$. [105°]. Formed from the allylimide and HBr (Seitz, *B.* 24, 2627). Converted by KSH into $C_8H_4O_2:N.CH_2.CHMe.SH$ [88°], which is oxidised in alcoholic solution by I to $(C_8H_4O_2:N.CH_2.CHMe)_2S$ [161°]. Potassium sulphocyanide forms $C_8H_4O_2:N.CH_2.CHMe.SCy$ [89°–93°].

γ-Bromo-propyl-imide $C_8H_4O_2:N.CH_2.CH_2.CH_2Br$. [73°]. Got from trimethylene bromide and potassium phthalimide (Gabriel, *B.* 21, 2671; 23, 90). Needles (from ligroïn). Converted by sodium ethyl-malonic ether into $C_8H_4O_2:N.C_3H_6.CEt(CO_2Et)_2$ [62°], and by sodium benzyl-malonic ether into $C_8H_4O_2:N.C_3H_6.C(CH_2Ph)(CO_2Et)_2$ [c. 110°] (Aschan, *B.* 23, 3692). Potassium sulphocyanide forms $C_8H_4O_2:NC_3H_6SCy$ [98°].

Ethylene-di-imide $(C_8H_4O_2.N)_2C_2H_4$. [232°]. Formed by heating potassium phthalimide with ethylene bromide at 200° (G.).

Butyl-imide $C_8H_4O_2:NC_4H_9$. [65°]. Formed by distilling cupric phthalyl-amido-hexoate (Reese, *A.* 242, 16). Tables (from dilute alcohol).

Isobutyl-imide $C_8H_4O_2:N.CH_2Pr$. [93°]. Formed from isobutyl bromide and potassium phthalimide (Neumann, *B.* 23, 999). Plates.

Isoamyl-imide $C_8H_4O_2:N.C_5H_{11}$. (308°). Solidifies when strongly cooled (N.).

Allyl-imide $C_8H_4O_2:NC_3H_5$. *Allyl-phthalimide.* [71°]. (295°). Tables. Yields a dichloride $C_8H_4O_2:NC_3H_5Cl_2$ [93°], and a dibromide [114°]. When nitrous acid is passed into its solution in cold benzene, and the product heated to 145°, there is formed $C_8H_4O_2:NC_3H_4NO_2$, crystallising in plates [178°] (Neumann, *B.* 23, 1000).

Acetonyl-imide $C_8H_4O_2:N.CH_2Ac$. [117°] Made by heating potassium phthalimide with chloro-acetone at 120° (Goedeckemeyer, *B.* 21, 2684). Plates and needles. Gives rise to an oxim [172°] and also to a phenyl-hydrazide $CH_3.C(N_2HPh).CH_2N:C_8H_4O_2$ [152°].

Desyl-imide $C_8H_4O_2:N.CHPhBz$. [158°]. Formed from phenyl bromo-benzyl ketone and potassium phthalimide (Neumann, *B.* 23, 994). Yellowish crystals, v. sl. sol. alcohol.

Phenyl-imide $C_6H_4<^{CO}_{CO}>NPh$. *Phthalanil.* [205°]. Formed by distilling phthalic acid (1 mol.) with aniline (1 mol.), and by heating phthalimide with aniline (Laurent; Doebner, *A.* 210, 267; Piutti, *B.* 16, 1322); Michael a. Palmer, *Am.* 9, 202). Needles (from alcohol), insol. water. Converted by heating with BzCl and $ZnCl_2$ into $C_8H_4O_2:N.C_6H_4Bz$ [183°] (Doebner, *A.* 210, 267). The *p*-chloro-, *p*-bromo-, *p*-iodo-, and *m*-nitro- phenyl-imides of phthalic acid melt at 195°, 204°, 228°, and 243° respectively (Gabriel, *B.* 11, 2260).

Benzyl-imide $C_8H_4O_2:NCH_2Ph$. [116°]. Formed from potassium-phthalimide and benzyl chloride (Gabriel, *B.* 20, 2227). Needles (from alcohol). The *o*- and *m*- nitro-benzylimides melt at 219° and 155° respectively.

o-Cyano-benzyl-imide $C_6H_4:C_2O_2:NCH_2.C_6H_4.CN$. [182°]. Prisms (from HOAc) (G.). The *p*- isomeride [184°] is converted into $CO_2H.C_6H_4.CO.NH.CH_2.C_6H_4.CO_2H$ [255°] by NaOHAq (Günther, *B.* 23, 1059).

Tolyl-imides $C_6H_4:C_2O_2:NC_6H_4Me$. The *o*-, *m*-, and *p*- compounds melt at 182°, 153°, and 204° respectively (Michael, *B.* 10, 579; Piutti, *A.* 227, 205; Fröhlich, *B.* 17, 2679; Kuhara, *Am.* 9, 52).

m-Methyl-benzyl-imide $C_6H_4:C_2O_2:N.CH_2C_6H_4Me$. [118°]. Formed by heating potassium phthalimide with $C_6H_4Me.CH_2Br$ at 200° (Brömme, *B.* 21, 2700). White needles, v. sol. alcohol. The compound $(C_6H_4:C_2O_2:N.CH_2)_2C_6H_4$ [237°] is formed by using [1:3] $C_6H_4(CH_2Br)_2$.

ψ-Cumyl-imide $C_{17}H_{15}NO_2$ *i.e.* $C_6H_4:C_2O_2:NC_6H_2Me_3$. [148°]. (above 360°). Formed by heating phthalic anhydride with ψ-cumidine (Fröhlich, *B.* 17, 1802). Trimetric crystals. Converted by ammonia into the compound $C_6H_4(CONH_2).CONHC_6H_2Me_3$ [218°], crystallising in needles, while methylamine and allyl-amine yield the corresponding compounds $C_6H_4(CONHMe).CONHC_6H_2Me_3$ [215°] and $C_6H_4(CONHC_3H_5).CONHC_6H_2Me_3$ [179°].

s-Tri-methyl-phenyl-imide $C_6H_4:C_2O_2:NC_6H_2Me_3$. *Phthalmesidil.* [171°]. Got by boiling mesidine with phthalic anhydride (Eisenberg, *B.* 15, 1017). Silky needles (from alcohol), insol. water. Yields, on nitration, the compounds $C_8H_4O_2:NC_6HMe_3(NO_2)$ [210°] and $C_8H_4O_2:NC_6Me_3(NO_2)_2$ [242°].

Isocymyl-imide $C_8H_4O_2:NC_{10}H_{13}$. [145°]. Formed by heating the anhydride with *m*-isocymidine (Kelbe a. Warth, *A.* 221, 169). Yields $C_8H_4O_2:NC_{10}H_{12}NO_2$ [167°] on nitration.

Naphthyl-imides $C_6H_4:C_2O_2:NC_{10}H_7$. The (α)- compound [166°] (P.); [182°] (M.) and its (β)- isomeride [216°] are got by heating the corresponding naphthylamines with phthalic anhydride (Piutti, *G.* 15, 479; Maschke, *C. C.* 1886, 824).

Tri-nitro-phenyl-imide $C_8H_4O_2:N.C_6H_2(NO_2)_3$. [259°]. From potassium phthalimide and picryl chloride (Schmidt, *B.* 22, 3257). Stair-like groups of crystals.

o-Oxy-phenyl-imide $C_6H_4:C_2O_2:NC_6H_4OH$. *Oxyphthalanil.* [220°]. Formed by heating phthalic anhydride with *o*-amido-phenol (Ladenburg, *B.* 9, 1528). Converted by sodium carbonate solution into $CO_2H.C_6H_4.CO.NH.C_6H_4OH$ [223°].

p-Oxy-phenyl-imide. [288°]. Got in like manner from *p*-amido-phenol (Piutti, *G.* 16, 252). Yields $C_6H_4:C_2O_2:N.C_6H_4OAc$ [239°] and $CO_2H.C_6H_4.CO.NH.C_6H_4OH$ [289°]. HNO_3 forms $C_6H_4:C_2O_2:NC_6H(NO_2)_2OH$ [210°], which yields an acetyl derivative [177°].

m-Nitro-phenacyl-imide $C_8H_4O_2:N.CH_2.CO.C_6H_4NO_2$. [204°]. Formed from ω-bromo-*m*-nitro-acetophenone and potassium phthalimide (Schmidt, *B.* 22, 3249). Pointed crystals (from HOAc).

Phenyl hydrazide $C_6H_4:C_2O_2:N_2HPh$. [178°]. Formed from phthalyl chloride and phenyl-hydrazine in ethereal solution (Pickel, *A.* 232, 233). Yellow needles, insol. water, sol. hot alcohol and chloroform.

Hydrides of phthalic acid. When reduced by sodium-amalgam in a solution kept acid by HOAc phthalic acid yields *trans* (1, 2)-dihydride. Neutral sodium phthalate reduced by sodium-amalgam without addition of acid yields the stable (4,5)-dihydride (Baeyer, *A.* 269, 154; cf. Graebe a. Born, *A.* 142, 330). Phthalic acid, suspended in water, is reduced by sodium-amalgam to a lactonic acid which yields a crystalline lactone [255°]; phthalide, and the (1,2)-dihydride are also formed. Both the (1,2)-dihydrides reduce aqueous $AgNO_3$ (*sic*) on warming, forming at once a black pp. Boiling aqueous cupric acetate gives off CO_2 and forms a white pp. which on addition of HOAc deposits Cu_2O. The liquid contains benzoic acid (Baeyer, *A.* 269, 151). None of the other dihydrides of phthalic acid are attacked by cupric acetate. Boiling *ammoniacal* $AgNO_3$ gives with: the (1,2)-dihydride a black pp.; the (4,5)- and (1,6)- dihydrides a brown pp.; the (3,6)- dihydride a white pp. not turning brown. The (1,2)- (1,6)- and (4,5)- dihydrides give benzoic acid and CO_2 when feebly oxidised. The (3,6)- dihydride gives phthalic acid (Baeyer, *A.* 269, 179). The hexahydrides are most stable, the tetra-hydrides next, and the dihydrides least stable (Baeyer, *A.* 269, 169). The *cis* anhydrides are more stable than the *trans* anhydrides. The *trans* acids are more stable than the *cis* acids. The anhydrides of the dihydrides are well crystallised, and yield the corresponding acids when boiled with water. The anhydrides are got by means of AcCl or Ac_2O. The (1,2)- dihydride will not stand AcCl. The (4,5)- dihydride needs long boiling with AcCl. Boiling Ac_2O often changes the *trans* to the *cis* variety. The anhydrides of the *cis* melt at lower temperatures than their *trans* isomerides (Baeyer, *A.* 269, 161).

In the following hydrides the two carboxyls are in the positions 1 and 2. The small numbers following Δ indicate the position of C atoms supposed doubly united to the adjacent C atoms.

Trans- $\Delta^{3,5}$ or (1,2)- *di-hydride.* $\begin{array}{l}\text{CH:CH.CH.CO}_2\text{H}\\ \text{CH:CH.CH.CO}_2\text{H}\end{array}$. [210°]. S. ·16 at 10°; 6 at 100°. Formed by reducing phthalic acid (20 g.) dissolved in NaOAc (32·8 g.) and water 200 c.c. at 0° by adding successive quantities of 3 p.c. sodium-amalgam (40 g.) and 50 p.c. acetic acid (6 c.c.), and finally adding H_2SO_4 (Baeyer, *A.* 269, 189). Prisms (from hot water). Not reduced by sodium-amalgam in the cold. Lead acetate gives a flocculent pp., sol. HOAc.

Reactions.—1. Boiling NaOHAq changes it entirely to the (4,5)-isomeride. Nine hours boiling with water does the same.—2. $KMnO_4$, hot ammoniacal $AgNO_3$, and aqueous $AgNO_3$ at 100° are at once reduced.—3. Aqueous *cupric acetate* forms a green pp., which gives off CO_2. On adding HOAc the liquid becomes clear and contains benzoic acid, Cu_2O being ppd.—4. Oxidised by boiling $CuSO_4$ to benzoic acid (Baeyer, *A.* 269, 191).—5. The acid takes up Br (4 at.) and the product is reduced by zinc-dust and HOAc to the original dihydride.—6. Combines with HCl, hence cannot be etherified by alcohol and HCl.—7. Combines with HBr (2 mols.) in aqueous solution at 100°. The product could not be crystallised, is reduced by sodium-amalgam to a hexahydride, while zinc and HOAc do not form an unsaturated acid.

Cis (1,2)-*dihydride.* [175°]. S. 1·8 at 10°. Does not accompany the *trans* form in the product of reduction of phthalic acid (Baeyer, *A.* 269, 192). The *trans* acid boiled with Ac_2O (but not AcCl) for 7 minutes is changed to the anhydride of the *cis* isomeride. The lead salt of the *cis* acid is insol. HOAc, while that of the *trans* acid is soluble therein. Large colourless many-faced prisms. Readily converted into anhydride by warming with Ac_2O. The anhydride [100°] crystallises from ether in colourless needles, and is re-converted into the acid by boiling water. The *cis* acid is converted into the (4,5)- dihydride by boiling NaOHAq, by 9 hours' boiling with water, and even (unlike the *trans* isomeride) by standing for 2 days with 15 p.c. NaOHAq. Reacts with silver and copper salts like the *trans* acid.

$\Delta^{2,6}$ or (4,5)-*Dihydride.* $\begin{array}{l}\text{CH}_2\text{.CH:C.CO}_2\text{H}\\ \text{CH}_2\text{.CH:C.CO}_2\text{H}\end{array}$ [215°]. S. ·3 at 25°; ·2 at 10°. Got by reducing phthalic acid (60 g.) with sodium-amalgam (1200 g.) (Baeyer, *A.* 269, 195; *cf.* Astié, *A.* 258, 187). Lustrous triclinic crystals.

Reactions.—1. Not affected by evaporating with boiling NaOHAq, but by long warming with very conc. aqueous or alcoholic KOH it is partially changed to the $\Delta^{2,4}$ or (1,6)- dihydride.—2. Reduced by sodium-amalgam in a current of CO_2 at 100° to Δ^2 or (1,4,5,6)- and *cis* and *trans* Δ^4 or (1,2,3,6)-tetrahydrides.—3. $KMnO_4$ oxidises it to oxalic and phthalic acids (no succinic acid).—4. Alkaline K_3FeCy_6 on boiling forms benzoic acid. Cold dilute H_2SO_4 and MnO_2 also form benzoic acid.—5. PCl_5 gives phthalic anhydride.—6. Br in the dark forms $C_8H_8Br_2O_4$ [185°].—7. With HBr (2 mols.) it combines forming crystalline di-bromo-phthalic acid hexahydride (Baeyer, *A.* 269, 198), which is reduced by sodium amalgam to phthalic acid *trans*-hexahydride. AcCl converts the acid into an anhydride [157°]. The silver salt boiled with water is reconverted into the (4,5)- dihydride. Alcoholic potash converts dibromophthalic acid hexahydride into the $\Delta^{2,4}$ or (1,6)- dihydride.

Methyl ether MeA′. (250°).

Anhydride [84°]. Got by boiling the (4,5) acid with AcCl (Baeyer, *A.* 269, 196). The product is evaporated over soda-lime and H_2SO_4 *in vacuo*, when the anhydride separates in large tables or prisms, sl. sol. ether, v. sol. chloroform. Hot water readily dissolves the anhydride, converting it into the parent acid. Na_2CO_3Aq forms an orange-red solution, which bleaches litmus as long as any anhydride is undissolved, the blue colour afterwards returning when all is dissolved. On adding H_2SO_4 to the solution a resin is ppd. Heating on the water-bath resinifies the anhydride, forming some phthalic anhydride.

$\Delta^{2,4}$ or (1,6)-*dihydride.* $\begin{array}{l}\text{CH CH}_2\text{.CH.CO}_2\text{H}\\ \text{CH.CH :C . CO}_2\text{H}\end{array}$ [180°]. Formed by boiling the di-hydro-dibromide of the (4,5)- dihydride of phthalic acid $\begin{array}{l}\text{CH}_2\text{.CHBr.CH.CO}_2\text{H}\\ \text{CH}_2\text{.CHBr.CH.CO}_2\text{H}\end{array}$ with a solution of KOH (1 pt.) in MeOH (2 pts.) for 1½ hours (Baeyer, *A.* 269, 199). Formed also in small quantity by heating the (4,5)- acid with conc. aqueous or alcoholic KOH or NaOH. Rosettes of prisms (from water). More soluble in water than the (4,5)- dihydride. Hot cupric acetate forms a white pp. which dissolves on cooling.

Reactions.—1. $KMnO_4$ and Na_2CO_3Aq form oxalic acid in the cold, and some phthalic acid. 2. Ammoniacal $AgNO_3$ forms a white pp. turning brown on warming.—3. Cold dilute H_2SO_4 and MnO_2 form benzoic acid and CO_2.—4. Boiling alkaline K_3FeCy_6 also forms benzoic acid.—5. Converted by Ac_2O in the cold into the anhydride which crystallises from chloroform in cubes [104°] and is reconverted into the acid by warm water. The anhydride dissolves in Na_2CO_3Aq and bleaches litmus meanwhile. The anhydride is converted by heat into the anhydride of the (3,6)- dihydride. — 6. *Sodium-amalgam* reduces it in the cold (difference from isomerides) to the *cis*-(1,2,3,6)- tetrahydride.—7. Combines with HBr (2 mols.) when heated at 100° with a solution of HBr in HOAc (Baeyer, *A.* 269, 200). The product [190°] crystallises from ether in plates, and is reduced by sodium-amalgam to the *trans* hexahydride.

$\Delta^{1,4}$ or (3,6)-*dihydride* $\begin{array}{l}\text{CH.CH}_2\text{.C.CO}_2\text{H}\\ \text{CH.CH}_2\text{.C.CO}_2\text{H}\end{array}$. [153°]. S. 1·7 at 6°. Formed by boiling the $\Delta^{2,4}$ or (1,6)- dihydride (1 pt.) with Ac_2O (2 pts.) for 6 minutes, and allowing the product to evaporate over soda-lime and H_2SO_4. The anhydride which separates is boiled with water (Baeyer, *A.* 269, 204). Large crystals with many facets. The Pb salt is sl. sol. HOAc. Cupric acetate gives a green pp., sl. sol. HOAc. The Ag salt is not reduced by boiling, even in presence of ammonia (unlike any of its isomerides).

Reactions.—1. When heated at 100° for a long time it is partially converted into anhydride. Evaporation of its aqueous solution also partially converts it into anhydride. The anhydride [185°] is also got by heating the acid with Ac_2O. It crystallises in plates.

Readily sublimes in feathery plates. Does not bleach litmus.—2. *Sodium-amalgam* does not reduce it even when gently warmed (Baeyer, *A.* 269, 205).—3. Dilute H_2SO_4 and MnO_2 oxidise it to phthalic acid. Boiling alkaline K_3FeCy_6 also forms phthalic acid.—4. $KMnO_4$ is at once decolourised.—5. Boiling (10 p.c.) NaOHAq forms (4,5) and (1,6)- isomerides.

Δ^1 or (3,4,5,6)-*Tetrahydride* $\begin{array}{l}CH_2.CH_2.C.CO_2H\\ CH_2.CH_2.C.CO_2H\end{array}$. [120°]. Formed by dissolving its anhydride in boiling water (Baeyer a. Astié, *A.* 258, 203; 269, 176). Got also by distilling the tetrahydride of pyromellitic acid (Baeyer, *A.* 166, 346). Monoclinic leaflets (containing aq). When heated at 100° for some time it melts, forming the anhydride. $KMnO_4$ oxidises it to adipic acid. Boiling conc. KOHAq changes it to the Δ^2 acid. Oxidised by Br and alkalis to di-oxy-phthalic acid hexahydride (tartrophthalic acid).—BaA″ aq: crystalline pp.

Methyl ether Me_2A''. Combines with Br, forming two dibromides [84°] and [124°].

Anhydride $C_8H_8O_3$. [74°]. Formed by heating the Δ^2 acid or its anhydride at 215° for some time. Plates (from ether), v. sol. ether.

Δ^2 or (1,4,5,6)-*Tetrahydride* $\begin{array}{l}CH_2.CH_2.CH.CO_2H\\ CH_2.CH:C\ .\ CO_2H\end{array}$. [215°]. S. ·88 at 10° H.C.p. 881,600. H.F. 215,400 (Stohmann, *J. pr.* [2] 43, 540). Got by reducing a boiling solution of sodium phthalate with sodium-amalgam (Baeyer, *A.* 258, 175). Formed also, together with the *trans* Δ^4 isomeride, by reducing the (4,5)-dihydride in the same way. Prisms (from water). Bromine vapour yields a dibromide [225°]. MeOH and HCl form an oily methyl ether, which yields a crystalline dibromide [74°]. $KMnO_4$ oxidises it to oxalic and succinic acids.

Anhydride $C_8H_8O_3$. [79°]. Formed from the acid and AcCl. Prisms. Changed by heat into the anhydride of the Δ^1 acid.

Trans-Δ^4 or (1,2,3,6)-*Tetrahydride* $\begin{array}{l}CH.CH_2.CH.CO_2H\\ CH.CH_2.CH.CO_2H\end{array}$. [218°]. S. ·145 at 6°. Formed, together with the (1,4,5,6)-tetrahydride, by reducing the (4,5)-dihydride in boiling solution by sodium-amalgam (Baeyer, *A.* 258, 210; 269, 161). Leaflets (from water). Decolourises $KMnO_4$ at once. Yields a methyl ether Me_2A'' [40°], which forms a dibromide [117°]. Anhydride $C_8H_8O_3$. [140°]. Got from the acid and AcCl. Needles (from ether). Changed by heat into the *cis*- isomeride.

Cis-Δ^4 or (1,2,3,6)-*Tetrahydride* [174°]. S. ·9 at 6°. Formed by adding sodium-amalgam at 0° to a solution of the Na salt of the (1,6)-dihydride in a current of CO_2 (Baeyer, *A.* 269, 202). Formed also by boiling the *trans* Δ^4 tetrahydride with Ac_2O for 15 minutes. Large prisms. Boiling Ac_2O forms the anhydride, which crystallises from ether in tables [59°].

Trans- (or fumaroid) *hexahydride* $C_6H_{10}(CO_2H)_2$. [221°]. S. ·23 at 20°. Formed by reducing the hydrobromides of the di- and tetra- hydrides with sodium-amalgam or with zinc-dust and HOAc (Baeyer, *A.* 166, 350; 258, 214; 269, 161; *cf.* Mizerski, *B.* 4, 558). By reducing the (3,4,5,6)-tetrahydride in a hot solution a mixture of *trans*- and *cis*- hexahydrides is obtained. Leaflets (from water). May be distilled unchanged if quickly heated, but yields the *cis*- anhydride when slowly heated. Not oxidised by cold aqueous $KMnO_4$. Yields a dimethyl ether [83°], m. sol. ligroïn.—PbA″ aq: plates.

Anhydride. [140°]. Formed from the acid and AcCl. Long needles (from ether). Changes when heated into the *cis*-isomeride.

Cis- (or maleoid) *hexahydride.* [c. 192°]. Got from its anhydride, which is formed by heating the anhydride of the *trans*- isomeride at 220° for eight hours. Short four-sided prisms, more soluble than the trans- isomeride. Not attacked by cold aqueous $KMnO_4$. Conc. HClAq at 180° changes it to the *trans*- variety. The Ba and Zn salts are less sol. hot than cold water.

Anhydride. [32°].

Isophthalic acid [1:3] $C_6H_4(CO_2H)_2$. [c. 300°]. S. ·013 at 25°; ·22 at 100°. H.C.v. 769,100. H.C.p. 768,800. H.F. 190,200 (Stohmann, *J. pr.* [2] 40, 138).

Formation.—1. By oxidising *m*-xylene with $K_2Cr_2O_7$ and H_2SO_4 (Fittig a. Velguth, *Z.* [2] 3, 526; *A.* 148, 11; 153, 268).—2. By fusing sodium formate with potassium *m*-sulpho-benzoate (V. Meyer, *A.* 156, 265; 159, 1).—3. The ether is formed by the action of $ClCO_2Et$ and sodium-amalgam on *m*-di-bromo-benzene (Wurster, *A.* 176, 149).—4. By fusing potassium formate with potassium benzoate (Richter, *B.* 6, 876), *m*-bromo-benzoate (Ador a. Meyer, *A.* 159, 16), or di-sulpho-benzoate (Barth a. Senhofer, *A.* 159, 228).—5. By oxidation of *m*-toluic acid (Weith a. Landolt, *B.* 8, 715).—6. By saponification of its nitrile.—7. By heating the hydrides of prehnitic and pyromellitic acids with H_2SO_4 (Baeyer, *A.* 166, 334; *Suppl.* 7, 4).—8. By strongly heating NaOBz (Conrad, *B.* 6, 1395).—9. By oxidation of colophony with dilute nitric acid (Schreder, *A.* 172, 93).—10. By the action of a hot aqueous solution of cuprous potassium cyanide upon *m*-diazo-benzoic chloride, and saponification of the resulting nitrile (Sandmeyer, *B.* 18, 1498).

Preparation.—*m*-Xylene is converted, by heating with bromine at 125°, into $C_6H_4(CH_2Br)_2$, which is boiled with alcoholic potash, and the resulting $C_6H_4(CH_2OEt)_2$ oxidised with chromic acid mixture (Kipping, *B.* 21, 46).

Properties.—Long slender needles (from water), m. sol. alcohol. May be sublimed.

Salts.—K_2A''.—BaA″ 6aq. Triclinic crystals (by spontaneous evaporation) (Lossen, *A.* 266, 30). V. sol. water.—BaA″ 4aq? Needles (by cooling hot saturated solutions).—CaA″ 2½aq: needles.—Ag_2A'': amorphous pp.

Methyl ether Me_2A''. [65°]. Needles (from dilute alcohol). H.F. 173,300 (Stohmann, *J. pr.* [2] 40, 353).

Di-ethyl ether Et_2A''. [0°]. (285°).

Di-phenyl ether Ph_2A''. [120°]. Got by boiling the chloride with phenol. Long needles.

Chloride $C_6H_4(COCl)_2$. [41°]. (276°). Formed by heating the acid with PCl_5 at 200° (Schreder, *B.* 7 708; Münchmeyer, *B.* 19, 1849).

Amide $C_6H_4(CO.NH_2)_2$. [265°] (B. Beyer, *J. pr.* [2] 22, 351); [above 270°] (Luckenbach, *B.* 17, 1431). Got from the chloride and NH_3. Plates, sl. sol. water and alcohol.

Nitrile $C_6H_4Cy_2$. [158°]. Formed by distilling potassium cyanide with potassium benzene *m*-disulphonate (Barth a. Senhofer, *A.* 174, 236; Meyer a. Michler, *B.* 8, 672; Nölting, *B.* 8, 1112; Luckenbach, *B.* 17, 1428), or with potassium *m*-chloro- or bromo- benzene sulphonate (Meyer a. Stüber, *A.* 165, 165; Limpricht, *A.* 180, 92). Formed also by heating the oxim of isophthalic aldehyde $C_6H_4(CH{:}NOH)_2$ with excess of AcCl at 100° for a long time (Münchmeyer, *B.* 20, 508), by the dry distillation of calcium *m*-cyano-benzoate (Brömme, *B.* 20, 521), and by boiling an alcoholic solution of $C_6H_4(CS.NH_2)_2$ with an aqueous solution of lead acetate (Luckenbach). Small needles (from alcohol), insol. water, m. sol. ether. Converted by alcohol and dry HCl into phthalimido-ethyl ether $C_6H_4(C(NH).OEt)_2$ [66°]. MeOH and HCl yield $C_6H_4(C(NH).OMe)_2$ [c. 62°]; while mercaptan and HCl form $C_6H_4(C(NH).SEt)_2$, which, like the two preceding bodies, forms a crystalline hydrochloride (Luckenbach).

Semi-nitrile v. *m*-CYANO-BENZOIC ACID.

Tetrahydride of Isophthalic acid $C_6H_8(CO_2H)_2$. [199°]. Formed by reduction of isophthalic acid by boiling its alkaline solution with sodium-amalgam (Baeyer, *B.* 19, 1806). Needles, v. sol. hot water.—Ag_2A'': white pp.

Methyl ether Me_2A''. Oil.

Isomeride *v.* TEREPHTHALIC ACID.

References.—AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, IODO-, NITRO-, OXY-, and OXY-AMIDO-PHTHALIC ACIDS.

Homo-phthalic acid *v.* CARBOXY-PHENYL-ACETIC ACID.

Diphthalic acid *v.* DIPHTHALYLIC ACID.

PHTHALIC ALCOHOL *v.* DI-OXY-XYLENE.

PHTHALIC ALDEHYDE $C_8H_6O_2$ *i.e.* $C_6H_4(CHO)_2$ [1:2]. Mol. w. 134. [52°]. Formed by boiling $C_6H_4(CHCl_2)_2$ (1 mol.) with NaOHAq (4 mols.) (Colson a. Gautier, *Bl.* [2] 45, 509; *A. Ch.* [6] 11, 29). Formed also by oxidising $C_6H_4(CH_2.OH)_2$ (Hjelt, *B.* 19, 411). Solid, v. sl. sol. water. Coloured blue by NH_3Aq. Slowly oxidised by air.

Oxim $C_6H_4(CH{:}NOH)_2$. [215°]. Small needles (Münchmeyer, *B.* 20, 509).

Isophthalic aldehyde $C_6H_4(CHO)_2$ [1:3]. [90°]. Formed by boiling $C_6H_4(CHCl_2)_2$ [1:3] with water (Colson a. Gautier, *Bl.* [2] 45, 509; V. Meyer, *B.* 20, 2005). Needles. Reduces silver solution with difficulty. Gives a violet-red tint with rosaniline reduced by SO_2. Oxidised by $KMnO_4$ to isophthalic acid.

Oxim $C_6H_4(CH{:}NOH)_2$. [212°] (Münchmeyer); [180°] (Meyer). Plates (from hot alcohol). Converted by AcCl at 100° into $C_6H_4Cy_2$. Yields the ethers $C_6H_4(CH{:}NOMe)_2$ [77°] and $C_6H_4(CH{:}NOEt)_2$ [165°].

Reference.—OXY-ISOPHTHALIC ALDEHYDE.

Isomerides.—TEREPHTHALIC ALDEHYDE and PHTHALIDE.

PHTHALIC ALDEHYDE ACID *v.* ALDEHYDO-BENZOIC ACID and PHTHALALDEHYDIC ACID.

PHTHALIDE $C_8H_6O_2$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$. *Lactone of ω-Oxy-o-toluic acid.* [73°]. (290° i.V.).

Formation.—1. By reducing phthalyl chloride with zinc and HClAq (Kolbe a. Wischin, *C. J.* 19, 339), or with Mg and HOAc (Baeyer, *Z.* [2] 5, 399; 10, 123, 1445; 11, 637).—2. Occurs among the products of reduction of phthalic anhydride by zinc-dust and HOAc (Wislicenus, *B.* 17, 2178).—3. By passing bromine-vapour over *o*-toluic acid at 140° (Hjelt, *B.* 19, 412).

Preparation.—Phthalimide (1 pt.) is reduced to phthalidene by means of tin ($1\frac{3}{4}$ pts.) and HCl. The tin is ppd. by zinc, and sodium nitrate added to the filtrate. The yellow pp. of the nitrosamine of phthalidine is filtered off, washed, and heated with dilute NaOH. The phthalide is ppd. by HCl and distilled. Yield on the phthalic anhydride – 70 p.c. of the theoretical (Graebe, *B.* 17, 2599).

Properties.—Needles (from hot water), sl. sol. cold water, v. sol. alcohol and ether. Does not combine with $NaHSO_3$ (Hessert, *B.* 11, 238), or reduce ammoniacal $AgNO_3$. Does not react with hydroxylamine.

Reactions.—1. Oxidised by alkaline $KMnO_4$ to phthalic acid.—2. *Alkalis* and *alkaline carbonates* form ω-oxy-*o*-toluic acid, *v.* vol. iii. p. 781.—3. *Sodium-amalgam* forms hydrophthalide $C_8H_8O_2$, a viscid mass, v. sol. alcohol and ether, and also 'phthalylpinacone' $C_{16}H_{18}O_4$ [197°].—4. *Ammonia* on heating forms phthalimidine.—5. *Aniline* at 210° forms phenyl-phthalimidine.—6. *Phthalic anhydride* on heating forms diphthalyl.—7. KCy at 185° forms $C_6H_4(CH_2.CN).CO_2H$ [116°], which forms CaA'_2 2aq, and yields carboxy-phenyl-acetic acid on saponification (Wislicenus, *B.* 18, 172; 233, 112). KCy at 200° yields $C_{18}H_{11}N_2O_3$ (?) [240°–245°].—8. Boiling HIAq forms *o*-toluic acid. 9. Br at 140° forms *exo*-bromo-phthalide. Cl at 160° yields phthalyl chloride (Racine, *A.* 239, 79).—10. NaOEt acting on an ethereal solution of oxalic ether and phthalide forms an ether $C_{12}H_{10}O_5$ [122°] crystallising from alcohol in needles, and forming with phenyl-hydrazine the compound $C_{18}H_{16}N_2O_4$ [159°] (Wislicenus, *B.* 20, 2062; *A.* 246, 342).

Phenyl-hydrazine compound $C_{14}H_{14}N_2O_2$ *i.e.* $CH_2(OH).C_6H_4.CO.N_2H_2Ph$. [174°]. Readily formed by warming phthalide with phenyl-hydrazine for a few hours (Meyer a. Münchmeyer, *B.* 19, 1707, 2132; Wislicenus, *B.* 20, 401). Sol. hot water and alcohol, sl. sol. ether. Silvery needles. Partially resolved into the parent substances by fusion. Very unstable towards acids and alkalis. H_2SO_4 forms a colourless solution, turned reddish-violet by $FeCl_3$.

References.—AMIDO-, BROMO-, CHLORO-, NITRO-, and OXY-PHTHALIDE.

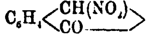
PHTHALIDE CARBOXYLIC ACID *v.* OXY-CARBOXYL-PHENYL-ACETIC ACID.

PHTHALIDE SULPHONIC ACID $SO_3H.C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>O$. Formed by warming phthalide with fuming H_2SO_4 (20 p.c. SO_3 extra) (Hoenig, *B.* 18, 3453). Needles, v. sol. alcohol, insol. ether.—BaA'_2.—CuA'_2 2aq: light-blue prisms.

PHTHALIDINE is PHTHALIMIDINE.

PHTHALIMIDINE C_8H_7NO *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>NH$. [150°]. (337°) at 730 mm. Formed by reducing phthalimide with tin and HCl, and by heating phthalide in a current of NH_3 (Graebe, *B.* 17, 2598; 18, 1408; *A.* 247, 290; Barbier, *C. R.* 107, 918). Needles or prisms, sl. sol. cold water, v. e. sol. alcohol and ether. Not volatile with steam. Oxidised by

$KMnO_4$ to phthalimide. Bromine forms $C_{16}H_9N_2O_2Br_3$ [150°]. Distillation over zinc-dust forms phenyl-isoquinoline. Yields a nitro-derivative



$C_6H_4{<}\begin{matrix}CH(NO_2)\\CO\end{matrix}{>}NH$

[210°], converted by oxidation into phthalide. Yields also a di-nitro- derivative [195°].

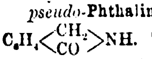
Salts. — B'HCl. [150°]. Thin white needles, v. sol. water.—$B'_2H_2PtCl_6$.—B'_2HAuCl_4. [176°].—$B'C_6H_2(NO_2)_3OH$. [140°].—C_8H_6AgNO.

Acetyl derivative C_8H_6AcNO. [151°]. Needles (from dilute HOAc).

Nitrosamine $C_8H_6(NO)NO$. [156°]. Yellow needles (from water or alcohol). Converted by NaOHAq into ω-oxy-*o*-toluic acid, and by NaSH into thio-phthalide C_8H_6OS [60°].

Reference.—DI-CHLORO-PHTHALIMIDINE.

pseudo-**Phthalimidine** C_8H_7NO probably



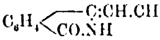
$C_6H_4{<}\begin{matrix}CH_2\\CO\end{matrix}{>}NH$.

This compound is formed, as hydrochloride, by heating ω-chloro-*o*-toluylamide $C_6H_4(CH_2Cl).CO.NH_2$ to 150°-160°. The picrate $B'C_6H_2(NO_2)_3OH$ forms a crystalline yellow pp.; the salt $B'_2H_2Cl_2PtCl_4$ 2aq forms flat orange-yellow needles (Gabriel, *B.* 20, 2234).

ISO-PHTHALIMIDO-ETHYL ETHER $C_6H_4(C(NH).OEt)_2$ [1:3]. [66°]. The hydrochloride is got by passing dry HCl into a mixture of isophthalic nitrile (1 mol.) and absolute alcohol (2 mols.) dissolved in benzene (Luckenbach, *B.* 17, 1431). The free base crystallises in small needles, v. sol. alcohol and ether. It decomposes on heating into alcohol and isophthalic nitrile.—$B''H_2Cl_2$. [270°]. Crystalline.

PHTHALIMIDYL-BENZYL *v.* BENZYLIDENE-PHTHALIMIDINE.

PHTHALIMIDYL PROPIONIC ACID $C_{11}H_9NO_3$ *i.e.*



$C_6H_4{<}\begin{matrix}C{:}CH.CH_2.CO_2H\\CO.NH\end{matrix}$.

[225°]. Formed by dissolving the dilactone of phenyl ethyl ketone dicarboxylic acid in NH_3Aq (Roser, *B.* 18, 3119). Long yellowish needles, v. sol. hot alcohol.—BaA'_2.—CaA'_2 aq.—AgA'.

Lactone $C_{11}H_9NO_3$. [c. 205°]. Formed by evaporating the dilactone mentioned above with conc. NH_3Aq on the water-bath. Small tables, v. sol. alcohol, sl. sol. cold water. Reconverted by boiling HClAq into the dilactone. Dissolves easily in cold aqueous alkalis, forming salts of a dibasic acid $C_{11}H_{11}NO_4$.

PHTHALONITRILE *v. Nitrile* of PHTHALIC ACID.

PHTHALOPHENONE *v.* DI-PHENYL-PHTHALIDE.

o-**Phthalophenone** $C_6H_4Bz_2$ [1:2]. [146°]. Got by oxidising *o*-di-benzyl-benzene (Zincke, *B.* 9, 31). Tables (from alcohol).

Isophthalophenone $C_6H_4Bz_2$ [1:3]. *Phenylene di-phenyl diketone.* [100°]. Formed by the action of benzene and $AlCl_3$ on isophthalyl chloride (Ador, *B.* 13, 320). Plates (from alcohol). Yields two dinitro- derivatives [200°] and [100°]?

Mono-oxim $C_6H_5.C(NOH).C_6H_4Bz$. [201°] (Nölting, *B.* 19, 146). Nodules, v. sol. alcohol.

Di-oxim $(C_6H_5.C(NOH))_2C_6H_4$. [70°-75°] (Münchmeyer, *B.* 19, 1849). Small crystals.

p-**Phthalophenone** $C_6H_4Bz_2$ [1:4]. *Terephthalophenone. (a)-Di-benzoyl-benzene.* [160°]. Formed by oxidising *p*-di-benzyl-benzene with CrO_3 and HOAc (Zincke, *B.* 9, 31; Wehnen, *B.* 9, 309). Got also from terephthalyl chloride, benzene, and $AlCl_3$ (N.). Plates (from benzene). PCl_5 yields $C_{20}H_{14}Cl_4$ [92°]. Sodium-amalgam forms di-oxy-di-benzyl-benzene [171°].

Mono-oxim. [213°]. Nodules.

Di-oxim. [235°]. Crystals.

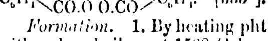
PHTHALOXYL-AMIDO-ACETIC ACID $C_{10}H_9NO_5$ *i.e.* $CO_2H.C_6H_4.CO.NH.CH_2.CO_2H$. *Glycocoll-phthaloylic acid.* [106°]. Formed by the action of alkalis on phthalyl-amido-acetic acid (Reese, *A.* 242, 6; Gabriel a. Kroseberg, *B.* 22, 426). Six-sided plates (containing aq).—Na_2A''. K_2A'': hygroscopic needles.—BaA''.—Ag_2A'': plates, sl. sol. hot water.

PHTHALOXYL-AMIDO-BENZOIC ACID $CO_2H.C_6H_4.CO.NH.C_6H_4.CO_2H$. [277°]. Formed by oxidation of the *p*-tolylimide of phthalic acid with $KMnO_4$ (Michael, *B.* 10, 576).

PHTHALOXYL-AMIDO-HEXOIC ACID $CO_2H.C_6H_4.CO.NH.C_4H_7Me.CO_2H$. Occurs in two varieties, the active [132°] and inactive [1[illegible]3°], which are got by boiling the corresponding phthalyl-amido-hexoic acids with NaOHAq (Reese, *A.* 242, 20). Both acids are decomposed by boiling water into leucine and phthalic acid.

PHTHALURIC ACID *v. Uramic acid* of PHTHALIC ACID.

DIPHTHALYL $C_{16}H_8O_4$ *i.e.*



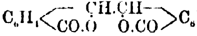
$C_6H_4{<}\begin{matrix}C{:}C\\CO.O\quad O.CO\end{matrix}{>}C_6H_4$.

[335°].

Formation. 1. By heating phthalyl chloride with reduced silver at 150° (Ador, *A.* 164, 229). 2. By fusing phthalic anhydride with zinc-dust; and, together with other products, by reducing phthalic anhydride with zinc-dust and HOAc (Wislicenus, *B.* 17, 2178).—3. By heating phthalide with NaOAc and phthalic anhydride or thio-phthalic anhydride (Graebe a. Guye, *B.* 17, 2851; *A.* 228, 126; 233, 241).—4. By boiling phthalaldehydic ether with alcoholic KCN (Goldschmidt a. Egger, *M.* 12, 60).

Properties.—Needles, insol. water, v. sl. sol. alcohol and ether. May be sublimed in a current of CO_2. Combines with Br forming $C_{16}H_8Br_2O_4$ [c. 225]. PCl_5 at 160° forms the chloride $C_{16}H_8Cl_2O_4$ [245°]. Bromine and water at 100° form bromo-diphthalyl, which crystallises from benzene. Alkalis form diphthalyl-lactonic acid.

Hydride $C_{16}H_{10}O_4$ *i.e.*

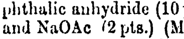


$C_6H_4{<}\begin{matrix}CH.CH\\CO.O\quad O.CO\end{matrix}{>}C_6H_4$

[229°] (W.); [250°] (Hasselbach, *A.* 243, 249), a product of the action of zinc-dust and HOAc on phthalic anhydride (Wislicenus). Needles (from alcohol), v. sol. HOAc. Potash forms di-oxy-di-phenyl-ethane dicarboxylic acid.

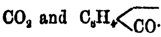
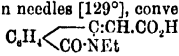
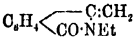
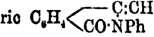
References.—TETRA-CHLORO-, NITRO-, and OXY- DIPHTHALYL.

PHTHALYL-ACETIC ACID $C_{10}H_6O_4$ *i.e.*



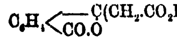
$C_6H_4{<}\begin{matrix}C{:}CH.CO_2H\\CO.O\end{matrix}$.

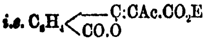
[c. 246°] (G.); [above 260°] (Roser, *B.* 17, 2620). Formed by boiling phthalic anhydride (10 pts.) with Ac_2O (20 pts.) and NaOAc (2 pts.) (Michael a. Gabriel, *B.* 10, 391, 1551, 2199). Formed also by dissolving acetophenone oω-dicarboxylic acid in H_2SO_4 (Gabriel, *B.* 17, 2521). Needles (from nitrobenzene), insol. water, v. sl. sol. hot alcohol.

Reactions.—1. Aqueous NaOH (1 mol.) forms a solution of its Na salt, but *excess of alkali* converts it into acetophenone *oω*-dicarboxylic acid. 2. *Distillation in vacuo* splits it up into CO_2 and methylene-phthalide.—3. *Bromine* in HOAc gives $CBr_2.CO.C_6H_4.CO_2H$ [160°]. Dry Br gives $C_8H_4O_2:CBr.CO_2H$ [c. 235°].—4. *Chlorine* acting on the HOAc solution forms $CCl_3.CO.C_6H_4.CO_2H$ [144°].—5. H_2SO_4 at 100° forms tri-benzoylene-benzene (*v.* vol. i. p. 485).—6. *Ammonia* gives rise to phthalimidyl-acetic acid $C_{10}H_7NO_3$ *i.e.* $C_6H_4<\begin{matrix}C:CH.CO_2H\\CO.NH\end{matrix}$ (?) which crystallises from water in needles [c. 200°] and yields CaA'_2aq, $BaA'_2 4aq$, and AgA' (Roser, *B.* 17, 2623; Gabriel, *B.* 18, 2451).—7. $NMeH_2Aq$ at 0° forms $NHMe.CO.C_6H_4.CO.CH_2.CO_2H$ [145°], which is converted by concentrated H_2SO_4 into $C_6H_4<\begin{matrix}C:CH.CO_2H\\CO.NMe\end{matrix}$ [c. 212°], crystallising from alcohol in silky needles, split up by heat into CO_2 and  $C_6H_4<\begin{matrix}C:CH_2\\CO{\cdot}NMe\end{matrix}$, a crystalline mass which is converted by bromine-water into $C_{10}H_{10}BrNO_2$ [126°] (Gabriel, *B.* 18, 2453).—8. Aqueous *ethylamine* forms $C_{23}H_{24}O_5N_2$ crystallising from ether in needles [129°], converted by cold H_2SO_4 into  $C_6H_4<\begin{matrix}C:CH.CO_2H\\CO{\cdot}NEt\end{matrix}$ [180°] and by heat into liquid  $C_6H_4<\begin{matrix}C:CH_2\\CO{\cdot}NEt\end{matrix}$ (Mertens, *B.* 19, 2368).—9. *Propylamine* forms, in the cold, $C_{25}H_{28}N_2O_5$ [103°], crystallising in prisms (M.).—10. *Aniline* at 100° forms $C_{15}H_{13}NO_2$ [192°], crystallising from benzene in cubes, converted by cold H_2SO_4 into $C_{15}H_{11}NO$ [265°] and by heating at 204°–230° into the isomeric  $C_6H_4<\begin{matrix}C:CH_2\\CO{\cdot}NPh\end{matrix}$ [100°] (Mertens, *B.* 19, 2371).—11. *Secondary* and *tertiary amines* have no action.—12. *Sodium-amalgam* forms the lactone of oxy-carboxy-phenyl-propionic acid (*q.v.*).

Salt.—$AgC_{10}H_5O_4$: amorphous pp.

PHTHALYL-DIACETIC ACID


$C_6H_4<\begin{matrix}C(CH_2.CO_2H)_2.\\CO.O\end{matrix}$ [158°]. Formed by saponifying phthalyl-di-malonic ether with KOHAq (Wislicenus, *A.* 242, 80). Prisms.—$BaA''2aq$: prisms, v. sol. water.—Ag_2A''.

PHTHALYL-ACETOACETIC ETHER $C_{11}H_{12}O_5$ *i.e.*  $C_6H_4<\begin{matrix}C:CAc.CO_2Et.\\CO.O\end{matrix}$ [124°]. Formed from sodium acetoacetic ether and phthalyl chloride (Fischer a. Koch, *B.* 16, 651; Bülow, *A.* 236, 185). Prisms (from alcohol). Decomposed by H_2SO_4 at 65° into HOAc and phthalyl-acetic acid. Alcoholic KOH forms deliquescent crystalline $K_2C_{14}H_{14}O_7$. Phenyl-hydrazine acetate forms $C_{20}H_{18}N_2O_4$ [238°], which is reduced by zinc-dust and HOAc to carboxy-benzyl-acetoacetic ether [92°].

PHTHALYL ALCOHOL *v.* DI-ω-OXY-*o*-XYLENE.

PHTHALYL-AMIDO-ACETIC ACID $C_{10}H_7NO_4$ *i.e.* $C_8H_4:C_2O_2:N.CH_2.CO_2H$. *Phthalyl glycocoll.* [192°]. Formed by heating phthalic anhydride (2 pts.) with glycocoll (1 pt.) (Drechsel, *J. pr.* [2] 27, 418; Reese, *A.* 242, 1). Crystals (from water), decomposed by boiling HClAq into phthalic acid and glycocoll. Cold NaOHAq forms phthaloxy-amido-acetic acid (*q. v.*).—NaA'aq.—NH_4A'. [206°].—$CaA'_2 2aq$.—$CuA'_2 3aq$.—AgA'.—$Pt(N_2H_6A')_2$. Colourless prisms; got by evaporating a solution of the acid with oxide of plato-diammonium.

Ethyl ether EtA'. [105°] (R.); [113°] (G.). (above 300°). Formed from Ag_2A'' and EtI (R.), and also by heating potassium phthalimide with $CH_2Cl.CO_2Et$ (Goedeckemeyer, *B.* 21, 2688; Gabriel, *B.* 22, 426). Needles, v. sol. benzene.

PHTHALYL-*p*-AMIDO-BENZENE SULPHONIC ACID $C_6H_4:C_2O_2:N.C_6H_4.SO_3H$. The Na salt, got by heating phthalic anhydride with sodium *p*-amido benzene sulphonic acid at 250°, crystallises from water in silky needles (Pellizzari, *A.* 248, 153; *G.* 18, 314). It is converted by boiling ammonia into phthalimide and sodium *p*-amido-benzene sulphonate. The Ba and NH_4 salts are also crystalline.

PHTHALYL-*o*-AMIDO-BENZOIC ACID $C_6H_4:C_2O_2:NC_6H_4.CO_2H$. [217°]. Formed by heating anthranilic acid with phthalic anhydride (Gabriel, *B.* 11, 2261). Prisms, sol. HOAc.

Phthalyl-*m*-amido-benzoic acid. [276°] (G.); [282°] (P.). Formed from phthalic anhydride and *m*-amido-benzoic acid, and also by saponifying its ether [152°], which is formed by heating phthalic ether with *m*-amido-benzoic acid (Pellizzari, *B.* 18, 216; *A.* 232, 147). Needles. The amide is described in vol. i. p. 158.

Anilide. [209°]. Prisms (Piutti, *B.* 16, 1322).

PHTHALYL-AMIDO-ETHANE SULPHONIC ACID $C_8H_4O_2:N.C_2H_4.SO_3H$. **Salt.**—$KA'\frac{1}{2}aq$. Formed by heating potassium amido-ethane sulphonate with phthalic anhydride (Pellizzari, *G.* 18, 324). Monoclinic crystals; *a:b:c* = 7·908:1:2·594; β = 60° 42'. Decomposed by alcoholic NH_3 into phthalimide and taurine.

PHTHALYL-AMIDO-HEXOIC ACID $C_{14}H_{15}NO_4$ *i.e.* $C_8H_4O_2:N.CH(C_4H_9).CO_2H$. [116°]. $[\alpha]_D = -21{\cdot}87°$ in a 5 p.c. alcoholic solution at 22°. Formed by fusing leucine with phthalic anhydride (Reese, *A.* 242, 9). Needles, v. sl. sol. hot water. Lævorotatory. Converted by distillation into an inactive variety [142°], which yields $PtN_2H_6A'_2 3\frac{1}{2}aq$. Conc. HClAq at 150° forms leucine and phthalic acid. NaOHAq forms phthaloxy-amido-hexoic acid (*q. v.*).—NaA'.—NH_4A'. [160°–165°].—$PtN_2H_6A'_2 3aq$.

PHTHALYL-AMIDO-NAPHTHALENE SULPHONIC ACID $C_8H_4:C_2O_2:N.C_{10}H_6.SO_3H$. The salt KA'3aq is got by heating sodium (α)-naphthylamine sulphonate with phthalic anhydride (Pellizzari a. Matteuci, *G.* 18, 321). It crystallises in needles, sol. water.

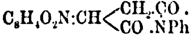
PHTHALYL-γ-AMIDO-*n*-PROPYL-MALONIC ETHER $C_6H_4:C_2O_2:N.CH_2.CH_2.CH_2.CH(CO_2Et)_2$. [48°]. Formed by the action of sodium malonic ether on the γ-bromo-propyl-imide of phthalic acid (Gabriel, *B.* 23, 1767). Monoclinic plates (from ligroïn); *a:b:c* = 3·260:1:1·644; β = 81° 4'. Converted into δ-amido-valeric acid by heating with HClAq at 190°.

Phthalyl-amido-di-propyl-malonic ether $C_8H_4O_2:N.CH_2.CH_2.CH_2.CPr(CO_2Et)_2$. [57°]. Formed in like manner from propyl-malonic ether (Aschan, *B.* 23, 3698). Prisms, insol. water, v. sol. alcohol and ether.

DI-PHTHALYL-DI-AMIDO-QUINONE $C_{22}H_{10}N_2O_6$ *i.e.* $C_6H_2O_2(N:C_2O_2:C_6H_4)_2$ [1:2:4:6]. [277°]. Prepared by heating tri-amido-phenol hydrochloride with phthalic anhydride, dissolving the resulting $C_6H_2(OH)(N{:}C_2O_2{:}C_6H_4)_2$ [above 300°] in potash, and treating the product $C_6H_2(OH)(NH.CO.C_6H_4.CO_2H)_2$ [above 300°] with nitric acid (S.G. 1·48) (Piutti, *G.* 16, 254). Yellow needles (from HNO_3). Forms a compound [174°] with phenyl-hydrazine. H_2S passed into its solution in dilute HOAc forms crystalline $C_6H_2(OH)_2(N{:}C_2O_2{:}C_6H_4)_2$, not melted at 310°.

PHTHALYL-AMIDO-SUCCINIC ACID $C_{12}H_9NO_6$ *i.e.* $C_8H_4O_2{:}N.CH(CO_2H).CH_2.CO_2H$. [225°]. Formed by heating aspartic acid with phthalic anhydride for 1 hour at 180° (Piutti, *G.* 14, 473; 16, 2). Tufts of prisms (from water). Decomposed into phthalic and aspartic acids by heating with HClAq. Boiling aniline forms aspartic acid and the phenylimides of phthalic and phthalyl-amido-succinic acids. Diphenylamine forms three di-phenyl-amic acids $C_8H_4O_2{:}N.C_2H_3(CONPh_2)(CO_2H)$ [180°], [204°], and [194°]; the first and third crystallises with aq, and all three yield a salt AgA′ and are decomposed by potash-fusion into aspartic acid, phthalic acid, and diphenylamine.

Salt.—CuA'_2 4aq: blue prisms.

Phenylimide 

$C_8H_4O_2N{:}CH\left<\begin{array}{l}CH_2.CO\ .\\CO\ .NPh\end{array}\right.$

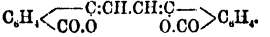
[264°]. Formed from the acid and aniline. Small needles (from HOAc), nearly insol. alcohol.

Tetra-phenyl-diamide $C_8H_4O_2{:}N.C_2H_3{:}C_2O_2(NPh_2)_2$. Two isomerides, [273°] and [286°], are got by heating the acid with diphenylamine for 5 hours at 190°. Both are split up by HClAq at 200° into phthalic acid, diphenylamine, and aspartic acid.

PHTHALYL CHLORIDE *v.* *Chloride* of PHTHALIC ACID.

PHTHALYL-ETHANE *v.* *Anhydride* of PHENYL-ETHYL KETONE *o*-CARBOXYLIC ACID.

Di-phthalyl-ethane $C_{18}H_{10}O_4$ *i.e.*



$C_6H_4\left<\begin{array}{l}\text{—}C{:}CH.CH{:}C\text{—}\\CO.O\qquad\quad O.CO\end{array}\right>C_6H_4$.

Ethine-diphthalyl. [above 350°].

Formation.—1. Together with other products by the condensation of phthalic anhydride with succinic acid (Gabriel, *B.* 10, 1559; 19, 837).—2. By the action of conc. H_2SO_4 upon di-phenyl ethylene diketone di-*o*-carboxylic acid $C_6H_4(CO_2H).CO.CH_2.CH_2.CO.C_6H_4(CO_2H)$, or its ether.—3. By further elimination of H_2O from the (α) or (β) anhydrides $C_{18}H_{12}O_5$ of the latter acid (Roser, *B.* 17, 2770; 18, 3115).

Properties.—Yellow needles (from nitrobenzene), insol. water and alcohol. By boiling with alkalis it is converted into di-phenyl ethylene diketone di-*o*-carboxylic acid. Nitrous acid forms $C_{18}H_{10}N_2O_8$ a crystalline body decomposing at 160°, and converted by boiling HOAc into $C_{18}H_9NO_6$ [c. 240°].

Isomeride $C_{18}H_{10}O_4$. Formed as a by-product in preparing the preceding body by heating phthalic anhydride with succinic acid and NaOAc. Red needles with green lustre, not melted at 280°. Insol. water and alcohol, v. sol. hot aniline and nitrobenzene. Weak acid, forming unstable violet salts.

PHTHALYL-ETHYL-HYDROXYLAMINE *v.* vol. ii. p. 740.

PHTHALYL-HYDROXYLAMINE *v.* vol. ii. p. 738.

DI-PHTHALYLIC ACID $C_{16}H_{10}O_6$ *i.e.* $CO_2H.C_6H_4.CO.CO.C_6H_4.CO_2H$ (?) *Diphthalic acid.* [272°]. Formed by oxidation of diphthalyl (Ador, *A.* 164, 236), of (β)-dinaphthyl-diquinone $C_{20}H_{10}O_4$ (Korn, *B.* 17, 3021), and of di-phenyl-ethane dicarboxylic acid (Dobreff, *A.* 239, 68). Formed also by the action of alcoholic potash on diphthalyl dibromide (Graebe, *A.* 228, 132; 242, 221). Minute tables, almost insol. water, alcohol, and ether. Converted by boiling conc. KOHAq into phthalic acid. Dilute NaOHAq at 110° forms di-phenyl-carbinol tricarboxylic acid. Reduced by HI to $(CO_2H.C_6H_4)_2C_2H_4$. Alcoholic hydroxylamine hydrochloride forms, on heating, $C_{16}H_{13}NO_5$ [152°] and $C_{16}H_8N_2O_4$ [286°].

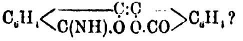
Salts: BaA″ 2aq: plates.—Ag_2A''.

Methyl ether Me_2A''. [192°]. Formed from Ag_2A'' and MeI. Lemon-yellow plates. By passing HCl into a hot solution of the acid in MeOH there is formed a colourless isomeric body [278°], partially converted into the methyl ether by heating with MeOH at 200°, and split up by HClAq at 150° into diphthalylic acid and MeCl.

Ethyl ether Et_2A''. [155°]. Got from Ag_2A'' and EtI. Lemon-yellow needles. The colourless isomeride [174°] is formed by ethylation with alcohol and HCl.

Anhydride $C_{16}H_8O_5$. [165°]. Formed by heating the acid with Ac_2O at 200°. Crystals (from HOAc), v. sol. chloroform.

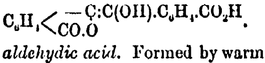
DIPHTHALYLIMIDE $C_{16}H_9NO_3$ *i.e.*



$C_6H_4\left<\begin{array}{l}\text{———}C{:}C\text{—}\\C(NH).O\ O.CO\end{array}\right>C_6H_4$?

[above 360°]. Got by warming di-phthalyl-lactonic acid with NH_3Aq and by heating phthalimidine with NaOAc and phthalic anhydride or phthalimide at 220° (Graebe, *A.* 228, 137; 233, 246). Needles (from HOAc) forming a yellow solution in NaOHAq.

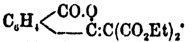
DIPHTHALYL-LACTONIC ACID $C_{16}H_{12}O_6$ *i.e.*



$C_6H_4\left<\begin{array}{l}\text{—}C{:}C(OH).C_6H_4.CO_2H\\CO.O\end{array}\right.$.

Diphthalaldehydic acid. Formed by warming diphthalyl, in an atmosphere of H, with alcoholic potash (Graebe a. Schmälzigang, *A.* 228, 126; *cf.* Ador, *A.* 164, 229). Crystals (from alcohol). When heated for some time at 220° it splits up into water and diphthalyl, which then melts above 300°. When quickly heated it decomposes at 235°–240° with partial fusion. Conc. H_2SO_4 converts it into diphthalyl. Its alkaline solution is yellow, but becomes colourless through absorption of atmospheric oxygen, yielding diphthalic acid.

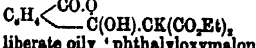
PHTHALYL-MALONIC ETHER $C_{15}H_{14}O_6$, *i.e.*



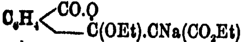
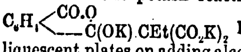
$C_6H_4\left<\begin{array}{l}CO.O\\\text{——}C{:}C(CO_2Et)_2\end{array}\right.$.

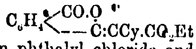
[75°]. S. (ether) 7·1 at 9°; 58·8 at 35°. One of the products of the action of phthalyl chloride on sodium malonic ether (Wislicenus, *A.* 242, 23). Triclinic prisms (from ether), v. sol. alcohol.

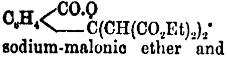
Reactions.—1. Decomposed by long boiling with *water* into phthalic acid and malonic ether. 2. Hot *potash* forms malonic and phthalic acids. A solution of caustic potash at 0° forms

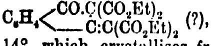


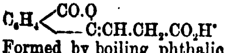
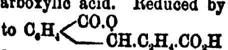
$C_6H_4\left<\begin{array}{l}CO.O\\\text{——}C(OH).CK(CO_2Et)_2\end{array}\right.$

whence acids liberate oily 'phthalyloxymalonic' ether, which quickly decomposes into phthalic anhydride and malonic ether.—3. NaOEt forms the compound  $C_6H_4\left<\begin{array}{l}CO.O\\ C(OEt).CNa(CO_2Et)_2\end{array}\right.$, crystallising in prisms, v. e. sol. water, yielding the cupric salt $Cu(C_{17}H_{19}O_7)_2$ 2aq and, on adding an acid, oily $C_{17}H_{20}O_7$. The dry salt, $NaC_{17}H_{19}O_7$ is converted by EtI at 100° into oily $C_{17}H_{19}EtO_7$, upon which alcoholic potash reacts forming the salt  $C_6H_4\left<\begin{array}{l}CO.O\\ C(OK).CEt(CO_2K)_2\end{array}\right.$ ppd. as very deliquescent plates on adding alcohol to its aqueous solution, yielding amorphous $Ag_3C_{13}H_9O_7$, and splitting up on acidification into ethyl-malonic acid and phthalic acid.—4. *Zinc-dust* and HOAc yield *o*-carboxy-benzyl-malonic ether (*v.* vol. i. p. 705).—5. Alcoholic NH_3 forms the diamides of malonic and phthalic acids.—6. *Sodium-malonic ether* forms yellow $C_{22}H_{24}Na_2O_{10}$, decomposed by boiling water into phthalyl-dimalonic ether, malonic ether, and phthalic acid.

Seminitrile  $C_6H_4\left<\begin{array}{l}CO.O\\ C:CCy.CO_2Et\end{array}\right.$ [c. 175°]. Formed from phthalyl chloride and sodium cyano-acetic ether in dry Et_2O (Muller, *C. R.* 112, 1140). White substance, sol. benzene.

Phthalyl-di-malonic ether $C_{22}H_{26}O_{10}$, *i.e.*  $C_6H_4\left<\begin{array}{l}CO.O\\ C(CH(CO_2Et)_2)_2\end{array}\right.$. [49°]. Formed from sodium-malonic ether and phthalyl chloride (Wislicenus, *A.* 242, 23, 80). Prisms (from alcohol), insol. water.

Reactions.—1. *Potash* forms a yellow solution containing $C_{22}H_{24}K_2O_{10}$, which separates as orange needles (containing 2aq) when Et_2O is added to a solution of the ether in alcoholic potash. Boiling aqueous potash forms phthalyl-diacetic acid $C_{12}H_{10}O_6$ [158°].—2. Alcoholic NaOH forms, in like manner, lemon-yellow $C_{22}H_{24}Na_2O_{10}$ 2aq, decomposed by hot water into malonic and phthalyl-dimalonic ethers and sodium phthalate. EtI at 100° converts the Na derivative into $C_{22}H_{24}Et_2O_{10}$, which yields ethyl-malonic ether on boiling with water.—3. The di-sodium derivative $C_{22}H_{24}Na_2O_{10}$ is converted by treatment with Ac_2O, phthalic anhydride, or phthalyl chloride into 'phthaloxy-dimalonic ether' $C_{22}H_{24}O_9$ or  $C_6H_4\left<\begin{array}{l}CO.C(CO_2Et)_2\\ C:C(CO_2Et)_2\end{array}\right.$ (?), S. (alcohol) ·57 at 14°, which crystallises from ether in needles melting at 117° when slowly heated and at 106° when quickly heated. 'Phthaloxy-dimalonic ether' is also one of the products of the action of phthalyl chloride on sodium malonic ether (Wislicenus, *A.* 242, 28, 61). It forms a yellow solution with aqueous K_2CO_3 and KOH. Alcoholic potash forms $C_{22}H_{23}KO_{10}$, which is the mono-potassium derivative of phthalyl-dimalonic ether. Zinc-dust and HOAc reduce 'phaloxy-dimalonic ether' to oily $C_{22}H_{28}O_9$.

PHTHALYL-PROPIONIC ACID $C_{11}H_8O_4$ *i.e.*  $C_6H_4\left<\begin{array}{l}CO.O\\ C:CH.CH_2.CO_2H\end{array}\right.$ [245°-248°]. Formed by boiling phthalic anhydride (5 pts.) with propionic anhydride (10 pts.) and sodium propionate (1 pt.) for 45 minutes (Gabriel a. Michael, *B.* 11, 1013, 1679). Slender needles. Converted by boiling KOHAq into phenyl ethyl ketone *o*-carboxylic acid. Reduced by sodium-amalgam to  $C_6H_4\left<\begin{array}{l}CO.O\\ CH.C_2H_4.CO_2H\end{array}\right.$ [140°] which yields BaA'_2 and AgA′ and is converted by boiling baryta-water into oxy-carboxy-phenyl-butyric acid $CO_2H.C_6H_4.CH(OH).C_2H_4.CO_2H$. H_2SO_4 at 100° forms $C_{20}H_{14}O_5$ [237°].

Salt.—AgA′: white powder.

Amide $C_{11}H_7O_3NH_2$. [195°]. Leaflets.

PHYCITE *v.* Erythrite.

PHYLLIC ACID $C_{72}H_{64}O_{16}$ (?). [170°]. S.G. 1·014. Extracted by alcohol from the leaves of the cherry-laurel, apple, almond, and elder (Bougarel, *Bl.* [2] 28, 148). Crystalline granules, decomposing at 180°. The K salt crystallises in needles, sl. sol. water, sol. alcohol.

PHYLLOCYANIN *v.* Chlorophyll.

PHYSALIN $C_{14}H_{16}O_5$. Occurs in the leaves of the winter cherry (*Physalis Alkekengi*), from which it may be extracted by chloroform (Desaignes a. Chautard, *J. Ph.* [3] 21, 24). Yellowish amorphous powder, with bitter taste, v. sl. sol. cold water and ether, v. sol. alcohol. Softens at 180°, and decomposes at a higher temperature. Sl. sol. acids, m. sol. NH_3Aq. Salt.—$Pb_3(C_{14}H_{15}O_5)_2O_2$: white pp., got by adding $Pb(OAc)_2$ and NH_3Aq to the alcoholic solution.

PHYSETOLEIC ACID $C_{16}H_{30}O_2$. [30°]. Occurs in sperm oil, and is perhaps identical with hypogæic acid (Hofstädter, *A.* 91, 177). Stellate groups of needles. Not affected by nitrous acid. —BaA'_2: crystals, sol. hot alcohol.

PHYSICAL METHODS USED IN CHEMISTRY. The object of this article is to present a general account of the chief physical methods of inquiry which are made use of in attacking chemical questions. In each section of the article it has been sought to lay down the principles of the method discussed, and to present, in a general way, the more important results that have been obtained. No section claims to give a complete account of the subject with which it deals. The following articles, which are not specially referred to in their alphabetical positions in the present article, should be consulted: Aggregation, States of, vol. i. p. 87; Atomic and molecular weights, vol. i. p. 336; Chemical and physical properties of bodies, connections between, vol. i. p. 730; Densities, relative, vol. ii. p. 370; Dissociation, vol. ii. p. 385; Molecular constitution of bodies, vol. iii. p. 410.

Table of contents of this article.

I. *Capillarity, Methods based on*, pp. 171–2.
II. *Crystallographic methods*, p. 172 (references only).
III. *Dialysis and diffusion, Methods based on*, pp. 172–4.
IV. *Dynamical methods*, p. 172 (references only).
V. *Electrical methods*, pp. 175–221.
VI. *Freezing-points of solutions, Methods based on*, p. 221 (references only).
VII. *Optical methods*, pp. 221–61.
VIII. *Osmotic pressure, Methods based on*, p. 261 (references only).
IX. *Photographic methods*, p. 261 (reference only).
X. *Specific heats of solids, Methods based on*, p. 261 (reference only).
XI. *Thermal methods*, pp. 261–8.
XII. *Vapour-pressures of solutions, methods based on*, p. 268 (references only).

XIII. *Viscosity of liquids*, pp. 268–71.

XIV. *Volume changes, methods based on*, p. 271 (reference only).

I. CAPILLARITY, METHODS BASED ON. The term 'capillarity' is given to that property of bodies which is the cause of the rise of liquids in narrow tubes, the spherical shape of raindrops and soap-bubbles, the spreading of oil on the surface of water, and many other phenomena.

The generally accepted theory by which these phenomena are connected and explained is due mainly to Laplace, and rests on the assumption that the parts of a body are held together by attractive forces which are insensible except at very small distances. We have evidence of the existence of these forces in the cohesion of bodies, in the latent heat of evaporation, which is merely the energy that has to be supplied to separate the parts from each other, and in the fact that at high pressures, when the parts of which a gas is composed are so near together that they never get altogether away from each other's influence, the compressibility is found to be greater than is required by Boyle's law. Though Laplace made no reference to molecules it is now usually supposed that the attractions in question are the forces acting between the molecules.

Imagine a molecule of a liquid surrounded by a sphere, whose radius is the distance at which the force ceases to be sensible. If the molecule is so far from the surface of the liquid that this sphere is entirely immersed, it will be on an average equally attracted all round, and no work will have to be expended to move it, but if it be so moved that part of the sphere is outside the surface, there will be a resultant force tending to draw it back again, so that to bring a molecule into the surface requires an expenditure of work. Now if we distort a given volume of liquid so as to increase its surface we bring more molecules into the surface, and we increase the potential energy of the liquid by an amount proportional to the increase of surface, or the total potential energy arising from this source is proportional to the extent of surface. Hence, since in the position of equilibrium of any system the potential energy is a minimum, the liquid will of itself assume such a shape that the surface is as small as possible consistently with other conditions, such as the action of gravity.

It is plain that what has been said is not restricted to liquids, but applies equally to solids and to the surface separating two different media. In the latter case a molecule at the surface of separation is acted on by both media, but unless the attractions are equal there will be a resultant force acting on it, and it will have potential energy by virtue of its position.

Capillary phenomena are often regarded as due to the external film of the substance being in a state of tension. It is not easy to imagine a tension at the surface of a solid, but the conception leads mathematically to the same results as the assumption of the existence of surface energy, and is practically only another way of stating the same thing, for we have seen that on the hypothesis of molecular attractions we arrive at the result that the surface tends to become a minimum, and this is equally well described by saying that it behaves as though it were in a state of tension. Further, the measure of the tension—that is, the total force acting across a line of unit length—is numerically equal to the potential energy per unit area, which is easily proved as follows. Imagine a rectangular piece of the surface a cm. long and b cm. wide—increase it to a rectangle a' cm. long and b cm. wide. Then we have produced $(a'-a)b$ sq. cm. of new surface, and if E is the potential energy per sq. cm. we shall have done $E(a'-a)b$ units of work. On the other hand, if T is the surface tension, the force acting on the side b will be Tb, and we have moved it through $a'-a$ cm., and hence have done $Tb(a'-a)$ units of work. These two measures of the work must be equal, and hence $E=T$; and since the rectangle can be taken anywhere on the surface and with its sides in any direction, it follows that the surface tension is the same at every point and in any direction.

It is to be observed that this tension differs from that of a stretched piece of indiarubber, for instance, in the fact that it does not depend on the amount of stretching. No matter how much a soap film is extended, the tension remains the same until the film becomes so thin that there are only a few molecules in the thickness.

The surface tension, then, is a consequence of the molecular attractions which tend to draw the molecules as close together as possible. In order to balance this tendency and to allow the substance to be in equilibrium, Laplace imagined the existence of an internal hydrostatic pressure, which, from the value of the latent heat, is calculated by Stefan to be about 1300 atmospheres in the case of water. The potential energy due to this pressure is proportional to the volume, which is constant in most capillary phenomena, and hence has no effect on the equilibrium position.

The forms of crystals are probably conditioned to some extent by capillary forces. Most of the properties of crystals being different in different directions, the potential energy of a surface may be expected to depend on its direction, and those faces will be formed which have least energy. Further, as a large crystal has less surface in proportion to its volume than a small one, the familiar phenomenon of the large crystals absorbing the small ones is explained by the loss of potential energy resulting from the operation (*v.* Liveing, *Camb. Phil. Trans.* 14, 370).

If two immiscible fluids are in contact with a solid, the surface separating them meets that of the solid at a constant angle, called the angle of contact. The most important case is where one of the fluids is air and the solid is glass. Many experiments have been made to determine this angle, the conclusion being that in most cases it is probably zero, but on this point see Magie (*W.* 25, 429), Quincke (*W.* 27, 219), and Worthington (*P. M.* [5] 20, 65).

The constant which is most commonly used is the surface tension as defined above, but Quincke and some others use another called the specific cohesion, denoted by a^2, which is twice the surface tension divided by the density of the liquid, or the height to which the liquid would rise in a tube of unit radius.

The following are the principal methods that have been used in determining these constants: 1. By determining the rise of liquids in capillary tubes (Quincke, *P.* 139, 8; Frankenheim, *J. pr.* 23, 401).—2. By weighing or measuring the drops from a rod or pipette (Quincke, *P.* 135, 621; Duclaux, *A. Ch.* [5] 13, 76; Linebarger, *Am. S.* 44, 83).—3. By measurement of large drops or bubbles (Quincke, *P. M.* [4] 41, 245; Eötvös, *W.* 27, 448; Worthington, *P. M.* [5] 20, 51).—4. By determining the force required to detach a disc or ring from the surface of a liquid (Weinberg, *Z. P. C.* 10, 34).

Mendeléeff states as one of the characteristics of a perfect liquid that its surface tension should be a linear function of its temperature, and Selby (*P. M.* [5] 31, 430) has given thermodynamical reasons for this relation. The subject has been investigated experimentally by Frankenheim, Weinberg, and others, and it is found that the equation $\gamma = a - bt$ holds approximately, where γ is the surface tension, t the temperature, and a and b are constants; hence by determination of γ at two temperatures we can calculate roughly the temperature $\frac{a}{b}$ at which the surface tension is zero—that is, the critical temperature. Eötvös extends this result by showing that the rate of change with temperature of $\gamma v^{\frac{2}{3}}$, where v is the molecular volume of the liquid (and hence $\gamma v^{\frac{2}{3}}$ is proportional to the energy of the amount of surface which contains a given number of molecules), has a constant value which is the same for all liquids.

The only measurements of the surface tensions of pure liquids which have been carried out extensively are those of Schiff (*A.* 223, 47; and *G.* 14, 368). Schiff determined the surface tensions of a large number of organic substances at their boiling-points, and divided the observed values by the molecular weights, denoting the quotient by N. This quantity was found to be in general unchanged by the substitution of one carbon atom for two hydrogen atoms, of one oxygen for three hydrogens, and similarly for other elements, so that each atom had its hydrogen equivalent, and compounds with the same total of hydrogen equivalents gave the same value for N. Taking N for ordinate, and x, the total hydrogen equivalent, for abscissa, Schiff plotted a curve from which he obtained the relation

$$\log N = 2{\cdot}8155 - {\cdot}00728x - \log x.$$

This equation enables us to calculate the surface tension of a liquid compound from its formula.

There are many exceptions to the law that each atom has a fixed hydrogen equivalent. For instance, C must be put equal to 3H in the free fatty acids instead of 2H as in most compounds; Cl generally has the value 7H, but when several chlorine atoms are attached to different carbons in a compound it has the value 6H; Br is usually equivalent to 13H, but sometimes to 11H, and so on.

A few preliminary measurements of the capillary constants of the surface separating water and organic liquids which do not mix with it, have been made by Linebarger (*Am. S.* 44, 83), by allowing the liquid to drop through the water, upwards or downwards, according to its specific gravity, and counting the drops from a given volume. The results already published show that the introduction of two methyl groups in the meta- position into a benzene ring does not affect the surface tension. while if they are in the para- position the surface tension is greatly diminished.

The surface tension of an aqueous solution of a salt is greater than that of water, and increases proportionately to the amount of salt present. Quincke (*P.* 160, 337, 560) found that for solutions of chlorides of equivalent concentrations—that is, containing the same amount of chlorine per c.c.—the constant of proportionality is the same; but Volckmann (*W.* 17, 353), on repeating the work, concluded that the agreement is not within the errors of experiment. Traube (*J. pr.* [2] 31, 192) showed that the capillary constant of a 10 p.c. solution of water in alcohol is not raised, like that of water, but is lowered, by the presence of a dissolved salt.

Determinations of the surface tensions of solutions of organic substances in water have not hitherto led to any important general laws. Such substances lower the surface tension but not proportionally to the concentration, as appears from the work of Duclaux (*A. Ch.* [5] 13, 76), and of Traube (*B.* 17, 2294; *J. pr.* [2] 31, 177; 34, 292). The former gives the law that if aqueous solutions of two alcohols, or of two acids, have the same surface tension, the percentage compositions of the two solutions will have a constant ratio. Traube's work confirms this result, but leads to nothing farther of interest beyond the fact that solutions of isomerides have not generally the same surface tensions. J. W. C.

II. CRYSTALLOGRAPHIC METHODS; *v.* CRYSTALLISATION, vol. i. p. 278; and ISOMORPHISM, vol. iii. p. 88.

III. DIALYSIS AND DIFFUSION, METHODS BASED ON. When a solid is dissolved in a solvent a movement of the particles occurs from the places where the solution is more concentrated to the places where it is less concentrated, and continues until the concentration is uniform throughout. Similarly when gases which do not react chemically are mixed, movements of the particles take place until the gases are equally distributed throughout the space. The mixing of gases or liquids, by reason of the movements of their particles, is called *diffusion.* When the diffusion of a liquid is accompanied by a total or partial separation into unlike bodies, the process is generally called *dialysis*; this process is usually effected by allowing the diffusion to take place through an animal or vegetable membrane. The chemical applications of diffusion are chiefly connected with the diffusion of substances in solution, and generally in solution in water.

Graham (*T.* 1850. 1, 805; 1851. 483) was the first to measure the rates of diffusion of different compounds, in aqueous solution, without a separating membrane. He nearly filled glass jars with the various solutions, carefully poured water on the top of the solutions, placed the jars in glass dishes, and filled these with water until the water extended in the dishes about 3 c. above the tops of the jars. The dishes were set aside for some time; when the process was to be stopped, glass plates were slid over the mouths of the jars, which were then removed, and the quantities of substance in the liquids outside the jars, called the *diffusates* by Graham, were determined.

Graham found that the quantities which diffused varied much according to the compositions of the diffusing substances. The quantity of a specified substance which diffused in a determinate time was found to be nearly proportional to the concentration of the original solution. Graham also found that diffusion was able to effect a tolerably complete separation of two salts whose rates of diffusion differed considerably. He looked on his results as showing that nearly equal quantities of chemically similar salts diffused in equal times.

A few years after Graham's fundamental experiments, Fick, reasoning from Fourier's theory of the conduction of heat, came to the tentative conclusion that *the quantity of a salt which diffuses through a stated area is proportional to the difference between the concentrations of two areas infinitely near one another.* Assuming the truth of this statement, a definition was obtained for the *diffusion-constant* of a salt as *the quantity of a salt which diffuses through unit area in unit time, when unit difference of concentration prevails throughout unit distance.* A long series of researches by Beilstein (*A.* 99, 165), Simmler a. Wild (*P.* 100, 217), Stefan (*W. A. B.* 79, 161), and especially by Weber (*W.* 7, 469, 536) and Graham (*T.* 1861. 183), has fully confirmed Fick's law, and has given measurements of the diffusion-constants of many substances. Attention should be drawn, in this connection, especially to Graham's method of allowing salts to diffuse in water gelatinised by starch, gum, &c. (*T.* 1861. 183; *v.* also Voigtländer, *Z. P. C.* 3, 316). In 1880, Long (*W.* 9, 613) made a number of determinations of rates of diffusion; he divided the numbers obtained by the molecular weights of the salts used, and thus obtained figures which represented the number of molecules of each salt which diffused under the same conditions. The results showed somewhat regular arrangements of the molecular diffusion-values. For instance, Long found that the haloid compounds of K had nearly the same value, that the sulphates of Mg, Zn, Mn, Co, Ni, and Cu had approximately equal values, and so on.

Marignac (*A. Ch.* [5] 2, 546 [1874]) followed up Graham's observations on the simultaneous diffusion of pairs of salts, and arrived at the important result that the order of the rates of diffusion of the salts of any acid is independent of the nature of the acid, and that the order of the rates of diffusion of the salts of a metal is independent of the nature of the metal. Marignac was thus able to construct a table showing the order of the diffusion-coefficients of acid radicles, on the one hand, and of metals, on the other hand. The table is as follows:—

Cl, Br, I	H
NO_3	K, NH_4
ClO_3, ClO_4, MnO_4	Ag
F	Na
CrO_4	Ca, Sr, Ba, Pb, Hg
SO_4	Mn, Mg, Zn
CO_3	Cu
	Al

Crystalloids and colloids. Graham observed that the rates of diffusion of different substances differ much. He found certain substances which diffused in water with very great slowness; these substances included gums, tannin, albumen, caramel, &c. Inasmuch as the substances which diffused comparatively rapidly generally assumed crystalline forms when they solidified, while substances which diffused very slowly solidified in amorphous forms, Graham called the former *crystalloids* and the latter *colloids.* The solution in water of crystalloids is usually accompanied by thermal changes; the solutions boil and freeze at temperatures different from the boiling- and freezing-points of water, and the properties of the solutions differ considerably from those of the solvent. On the other hand, the solution in water of a colloidal substance is not attended with any marked changes.

The solution of a colloidal substance allows the diffusion through it of a crystalloid, in solution, but scarcely permits the diffusion of another colloid. If, then, a solution containing a crystalloid and a colloid is separated from water by a colloidal membrane, such as animal or vegetable parchment, the crystalloid will diffuse through this membrane into the water outside, but the colloid will be retained in the interior liquid; in this way colloids can be separated from crystalloids by diffusion; this process was called *dialysis* by Graham.

By means of dialysis, Graham prepared many compounds in a colloidal, or jelly-like form (*T.* 1861. 183). Most inorganic colloidal compounds were found to exist in two forms; one soluble in much water, and the other gelatinous and insoluble in water. For instance, an aqueous solution of silicic acid, containing 14 p.c. of this acid, was obtained by adding a solution of sodium silicate to excess of dilute HClAq, and dialysing (by pouring into a flat saucer formed of parchment paper which was floated on pure water) for some days, until the liquid inside the dialyser ceased to give a reaction with $AgNO_3Aq$; the liquid in the dialyser was then concentrated by boiling in a flask. The solution of silicic acid gelatinises after a few days, or at once by addition of a trace of an alkaline or earthy carbonate, or by a few bubbles of CO_2, or by certain soluble colloids, such as gelatin or soluble alumina. The gelatinised colloidal silicic acid is insoluble in water.

Graham prepared soluble and gelatinised colloidal forms of Al_2O_3, Fe_2O_3, Cu_2FeCy_6, Cr_2O_3, stannic acid, &c. Other soluble inorganic colloidal compounds have been obtained in recent years.

Graham looked on colloids as very different in their constitution from crystalloids. He regarded colloids as prone to undergo changes which take place very slowly; he thought it possible that the molecule, or molecular aggregate, of a colloid is formed 'by the grouping together of a number of smaller crystalloid molecules.' Colloids, according to Graham, are capable of loosely combining with various proportions of water; this process of 'gelatinous hydration' was regarded by Graham as being 'as truly chemical as that of crystalline hydration.'

Graham's views on the nature of colloids have been confirmed, on the whole, by more recent work. J. M. van Bemmelen has especially studied the hydration of colloids. He gives the name *hydrogels* to those gelatinous hydrates which contain varying quantities of water not agreeing with any definite formula; he describes the reactions of hydrogels with gases and liquids to form what he calls *absorption-compounds*, and discusses the part played by such compounds in the soil (*L. V.* 35, 69; Abstract in *C. J.* 54, 985). For van B.'s work on various individual colloids *v. R. T. C.* 7, 37, 69, 75, 87, 106, 114; Abstracts in *C. J.* 54, 1157-1162.

Picton (*C. J.* 61, 137) and Picton a. Linder (*C. J.* 61, 114, 148) have recently prepared a number of soluble colloidal forms of metallic sulphides, such as CuS, HgS, As_2S_3. The colloidal solutions were obtained (1) by pouring solutions of the metallic salts into H_2SAq, into which H_2S was continuously passed, and dialysing, after removal of excess of H_2S by a current of H; (2) by passing H_2S into water with metallic hydrates in suspension; (3) by suspending freshly ppd. metallic sulphides in water and passing in H_2S. All the solutions contained combined H_2S, and were therefore solutions of hydrosulphides. The solution of As_2S_3 contained about 5 g. As_2S_3 per litre, and that of HgS about 10 g. per litre. These colloidal solutions were shown to contain solid particles. In some cases the particles were visible through a powerful microscope; in other cases the particles were proved to be present by passing a ray of bright light through the liquids, and showing the scattering of polarised light which thus occurred. Solutions of 'colloidal molybdic acid,' and colloidal silicic acid containing free HCl, seemed to be free from solid particles. Solution of colloidal antimony sulphide showed no particles under the microscope, but the presence of particles was revealed by the passage of a beam of light; after keeping for about ten days, particles had formed sufficiently large to be seen by the help of the microscope; and after some weeks the Sb was all ppd. as Sb_2S_3. In this case the passage could be followed from a liquid containing very minute particles, whose presence was detected only by the fact that they scattered light, to a liquid containing particles sufficiently large to be seen under the microscope. On the other hand, a solution of $CrCl_3$ in water containing a little chromous acetate was able to scatter light, and therefore contained solid particles; but after a few days the particles were no longer present. In this case the passage could be traced from a liquid containing very minute particles to a liquid free from such particles.

The colloidal solutions did not diffuse, with one exception—namely, arsenious sulphide. The diffusible solution was obtained by running As_2O_3Aq into H_2SAq, into which H_2S was continuously passed, and removing excess of H_2S by a current of H. This solution showed no particles under the microscope, but as it scattered polarised light particles were present in it. The liquid was put into a small wide-mouthed bottle, which was placed in a beaker and covered with water; a distinct amount of As_2S_3 had diffused in one day, and after eleven days about 12½ p.c. of the As_2S_3 was found in the diffusate. This colloidal solution therefore presented the interesting phenomenon of a liquid containing solid particles capable of scattering polarised light from a beam passed through, and yet able to diffuse in exactly the same way as true solutions undergo diffusion.

Picton a. Linder consider that their experiments establish 'a good *prima facie* case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution.' They look on the very small particles in some of these colloidal solutions as large molecular aggregates, and they think that these aggregates become very small in the solutions which can diffuse, and that the forces by which the aggregates are held in solution 'become more definitely those of chemical attraction.' (In connection with colloidal solutions *v.* Paterno, *Z. P. C.* 4, 457; and Barus a. Schneider, *Z. P. C.* 8, 278.)

Diffusion of gases. The fact was observed by Dalton (*P. M.* 24, 8) that if a heavier gas is placed in a bottle which is connected with another bottle containing a lighter gas, and placed beneath the first bottle, after some days the gases will be equally mixed in both bottles. The same fact was observed, and some measurements were made, by Berthollet (*Mém. S. d'A.* 2, 463). Graham (*Q. J. S.* 1829. 74; *P. M.* 1833. 175, 269, 351) made a great many measurements of the rates of diffusion of different gases. For most of these he employed a *diffusiometer*, which consisted of a glass tube about 20 cm. long and about 1¼ cm. diameter, having a plug of plaster of Paris in one end extending inwards about ½ cm., and graduated from this end downwards. The tube was filled with the gas under examination and placed in water; when the level of the water in the tube had become constant, the total volume of gas now in the tube was measured, and the amounts of air and original gas contained in the tube were determined. With gases lighter than air there was a decrease in the contents of the tube, as the lighter gas passed out through the porous plate more quickly than air passed in; with gases heavier than air there was an increase in the gaseous contents of the tube, as air passed in more quickly than the heavier gas passed out.

The conclusion which Graham arrived at was that 'the diffusion or spontaneous intermixture of two gases in contact is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas.'

Modifications in Graham's apparatus have been made, and many determinations of the rates of diffusion of gases have been conducted; the results have fully confirmed Graham's law, which may be stated in the form $c:c' = \sqrt{d'} : \sqrt{d}$, where c and c' are the diffusion-rates of two gases whose relative densities are d and d'.

It is evident that Graham's law of diffusion gives a means for finding the molecular weights of gases; inasmuch as the law enables measurements to be made of the relative densities of gases, and the density of a gas, referred to hydrogen, multiplied by 2 is (approximately) the molecular weight of that gas. For a description of an instrument for this application of the law of diffusion *v.* Bunsen's *Gasomet. Methoden*, p. 160.

M. M. P. M.

IV. DYNAMICAL METHODS. Several methods used in attacking chemical problems may be put together under this general title: *v.* Chemical change, vol. i. p. 731; Affinity, vol. i. p. 67; Aggregation, States of, vol. i. p. 87; Dissociation, vol. ii. p. 385; Equilibrium, Chemical, vol. ii. p. 434; Molecular constitution of bodies, Theories of, vol. iii. p. 410.

V. ELECTRICAL METHODS.

Historical.—The history of the science of electricity divides itself into two well-defined periods, the boundary between which lies at the close of the last century, and is marked by Volta's discoveries concerning the production of electricity when different substances are brought into contact. The investigations in the older period, when only the phenomena of frictional electricity, characterised by small quantity and high tension, were known, showed no connection with chemical problems. It is true, Deimann and Paets van Trostvijk had decomposed water by means of the electrical machine; this effect was, however, assigned as due more to the high temperature of the electric spark than to a specific property of electricity.

It is only with Galvani's discovery of the electricity which appears when different substances are brought into contact, and with the scientific investigation of this discovery by Volta, that the period of *electro-chemistry* begins. This branch of science is thus of nearly exactly the same age as the current century. It was by means of the *pile* as constructed by Volta that chemical changes were recognised to be essential phenomena concurrent with the passage of an electric current through certain substances. Directly this apparatus became known, Nicholson and Carlisle (1800) used it for the decomposition of water, and since then the fact that there is a close connection between chemical and electrical phenomena has always been present to the mind of investigators. The mysterious and unexpected mode of action of this apparatus soon revived the hope that by means of it the problem of *vital activity* might be fathomed. Consequently, the electric current was made to pass through various animal fluids, such as blood, protein, &c., with the object of following the changes produced by this influence, and thus obtaining information concerning the processes taking place in the organism. It was found that, along with other effects, a basic reaction was always observed at one pole, and an acid reaction at the other. On further investigation it was found that the acid and the base still appeared, even when water was taken instead of the animal fluids, and thus the electric current seemed to be a means for producing acids and bases from pure water. This is the point at which the classical researches of Humphry Davy began. In order to decide whether acids and bases were really produced from pure water by means of electricity, he repeated the experiments. He soon recognised that the vessels in which the water was contained exerted a determinant influence on the results; he proved that very small quantities of the substance of the vessels were always dissolved by the water, and that vessels of glass, clay, basalt, &c., were subject to this influence. The electric current had the power of decomposing the very small quantities of saline matter present into acids and bases, and of accumulating these at the poles, where they could be detected easily. Only vessels of gold proved to possess the necessary resistance, and when these were used not the least quantity of either acid or base was obtained from pure water.

After Davy had thus become acquainted with the great power of decomposing compounds possessed by the electric current, he proceeded at once to submit the most diverse substances to its influence. By means of the large batteries of the Royal Institution, which had been constructed according to his plans, he succeeded in obtaining great effects; he decomposed the alkalis, and isolated the metals potassium and sodium.

At the present day it is difficult to imagine the impression which this discovery made on his contemporaries. It was not scientific circles only that were full of it; the public at large and the daily press occupied themselves most diligently with this fact. Everyone who could procure some dozens of copper and zinc plates tried to repeat the experiment, and gave an account of it. Napoleon, who then had just nearly reached the zenith of his power, proceeded at once to have larger batteries constructed in order to smooth the way for similar discoveries by the French scientists. He also offered great prizes for scientific works dealing with voltaic electricity.

Davy's discovery was of great importance for the development of the science of chemistry, because it enabled the alkalis to be classed with other basic metallic oxides. Chemical classification was thus simplified considerably. The investigations of Davy were, however, without influence on the knowledge of chemical affinity, sound as were the views held by this man of genius concerning the relation between chemical and electrical processes.

It was at this same time that the two Swedish naturalists Berzelius and Hisinger carried out work which then, it is true, did not attract anything like the same attention as had justly been aroused by Davy's investigations, but which had an even more lasting influence on the later development of scientific chemistry. Davy's experiments dealt chiefly with the fact that the electric current split compounds into their constituents, and aimed at the isolation of these constituents. Berzelius and Hisinger went a step farther; they tried to grasp the laws underlying this decomposition, and from these they developed a theory concerning chemical compounds. The generalisations under which Berzelius and Hisinger comprised their results were as follows:

(*a*) Chemical compounds are decomposed by the electric current, and their components collect at the poles.

(*b*) The combustible substances, the alkalis, and earths go to the negative pole; oxygen, the acids, and oxidised substances go to the positive pole.

The fact that Berzelius had experimented chiefly on the salts of the alkalis determined the theoretical conception of electrolysis. Since acids and bases appeared at the poles when alkali salts were electrolysed, acids and bases were considered to be the components of salts. Berzelius assumed further that a similar binary division prevailed throughout the whole domain of chemical compounds. He conceived every atom as endowed with a definite quantity of positive or negative electricity, and this led him to distinguish between positive and negative elements, and to arrange the elements in a series, beginning with the most positive down to the most negative. It was thus that for Berzelius the combination of elements with each other was simply an act of electrical attraction; according to him the thermal and optical effects which are produced along with chemical combination are due to the same cause as the corresponding phenomena which accompany the electric spark. It is true that at this point Berzelius, with the caution peculiar to him, himself brings forward the objection that when the opposite electricities have neutralised each other a further cause of their keeping together is no longer present. It seems, however, that he did not consider this difficulty of sufficient importance to give up his theory for it.

When a positive and a negative atom interact, their electricities, according to Berzelius, are in general not completely neutralised, as the quantities of electricity present differ according to the nature of the atoms. The compound formed thus retains a surplus of positive or of negative electricity, and acts therefore similarly to an element, but less intensely. It is in this way that compounds can again combine with each other to form compounds of a higher order, and so on, and thus is brought about a binary constitution of all compounds.

This electro-chemical theory of Berzelius, which he developed more fully at a later time, has exerted a very marked influence on the progress of chemistry, since it has impressed on this science the form which was the only one recognised from 1810 to 1840. It was characteristic of this phase that after this first investigation Berzelius did not again undertake any experimental work on the action of electricity on chemical compounds. The places wherein the Berzelian theory was weak from the physical point of view were not considered at all, as the theory was used only for the purposes of chemical classification; no attempt was made to explain by means of it the problems of chemical affinity.

After an almost uncontested reign of twenty years' duration the theory of Berzelius proved itself insufficient to follow the progress of the science. Since it was deduced from the phenomena of the decomposition of compounds by electricity, it was not surprising that it could not represent the chemical relations of organic compounds, which, as a rule, are not decomposed by electricity. Investigations on this subject proved more and more conclusively that in chemical compounds individual atoms could be substituted by other atoms or groups of atoms, quite independently of the 'electro-chemical' nature of the elements; in the most conspicuous and best-known examples it was a question of the substitution of 'positive' hydrogen by 'negative' chlorine. Such a process Berzelius considered to be quite impossible in the light of his theory.

But it was not this proposition of the electro-chemical theory alone, but the whole foundation of Berzelius's system, which was made doubtful and proved to be untenable by the newer development of organic chemistry. The theory of the *binary* constitution of chemical compounds was no longer capable of being brought into accord with facts, which rather led to the *unitary* conception of substances. Closely connected with this development is the establishment of the conception of the chemical molecule, a conception which assigned a sharply-defined existence to the combinations of the elementary atoms, and which led to the view that these structures would split up in the most diverse ways, according to the nature of the influences to which they were subjected, although no such division appeared pre-existing in the molecule.

At the same time (after 1840) at which purely chemical facts had proved Berzelius's system insufficient for the domain of organic chemistry, the insufficiency of its physical foundations was also made apparent. This happened in consequence of Faraday's fundamental work.

A lively discussion concerning the cause of the production of electricity in the galvanic pile had been carried on ever since the days of Volta. While Volta and his successors sought for the cause of the electric tension at the extremities of the pile in the contact of the metals, a number of other workers held to the opinion, as first expressed by Fabbroni, that the cause of galvanic electricity was to be found in the chemical processes which take place in the pile. It is not possible to enter here into the history of the contest which has lasted up to the present day. Faraday attempted to solve the problem, and in so doing he discovered the electrolytic law (1834) which goes by his name.

This law affirms, firstly, that when electricity passes through a body which is decomposed by it—that is, through an *electrolyte*—the quantity of substance decomposed is proportional to the quantity of electricity that has passed through. Secondly, the law affirms that when the same quantity of electricity passes through different electrolytes, the quantities of the different substances which are thereby decomposed are to each other in the ratio of their chemical equivalents.

These two generalisations primarily supported the chemical theory of galvanic electricity, as according to them a galvanic current is never possible without a corresponding chemical process. At the same time, however, they were in unresolvable contradiction to the foundations of the theory of Berzelius as conceived by him; since, if one and the same quantity of electricity is always necessary in order to decompose chemically equivalent quantities of any substances, it cannot be true that different quantities of electricity cause their combination, in which act they neutralise each other. Berzelius was keenly alive to this contradiction, but as he did not wish to doubt his own theory he preferred to doubt the laws of Faraday, and he continually argued against them.

It was through the work of Daniell (*T.* 1839. i. 97, and 1840. i. 209), which followed up the researches of Faraday, that the electro-chemical theory was fought on the very ground from which it had sprung. The results of the electrolysis of neutral salts, such as potassium sulphate or sodium chloride, when the two electrodes of the electrolytic cell were separated by a porous diaphragm, showed that detonating gas (or hydrogen) was formed in the same quantity as in a voltameter with dilute sulphuric acid inserted in the circuit, and besides this an equivalent quantity of the salt was decomposed into acid and base. This phenomenon cannot be brought into accordance with the law of Faraday otherwise than by assuming that electrolysis does not split up the salts into base and acid, but rather into the metals and into the elements (such as Cl) or radicles (such as SO_4) combined with these. Thus, when potassium sulphate is electrolysed, hydrogen and oxygen are only secondary products, just as the free acid and the base are only secondary products; the salt K_2SO_4 splits up rather into free potassium K_2, which acts on the water, forming potash ($K_2+2H_2O = H_2+2KOH$), and into the radicle SO_4, which with water gives sulphuric acid and oxygen ($SO_4+H_2O=H_2SO_4+O$). Correspondingly, when copper sulphate is electrolysed we obtain, not copper oxide and sulphuric acid, but on the one side metallic copper, and on the other side SO_4 which gives sulphuric acid and oxygen. Thus Daniell arrived at the conclusion that the conception of salts as consisting of base and acid would have to be given up, and that they rather consist of a metal and a simple radicle (Cl, S, &c.), or a compound radicle (SO_4, NO_3, &c.), and he further pointed out that Davy had already expressed similar ideas.

The same result to which the application of Faraday's law led in this case had meanwhile been arrived at by chemical methods. After Graham (*T.* 1833. ii. 253) had reduced the differences exhibited by the salts of phosphoric acid to differences in the amounts of water held by the acid, and had thus founded the theory of the polybasic acids, Liebig (1838), in his celebrated paper (*A.* 26, 113), enunciated the theorem that all acids must be looked on as hydrogen compounds, and that the formation of salts consists in the replacement of this hydrogen by metals or metallic radicles. By means of this conception the unnatural division between the salts of oxy-acids on the one hand, and the halogen compounds of metals on the other, was again put aside. The necessity for such a division had been felt by Berzelius to be a great trouble, and to do away with it he had for long clung tenaciously to the assumption that the halogens were oxygen compounds.

The first attempt to utilise the facts of galvanism for chemistry had failed. In 1850 Berzelius's electrochemical theory had but few supporters left. Still the consciousness survived that the mistake had lain in the form in which the relation between chemical and electrical properties had been represented; and it continued to be recognised that this relation actually did exist, and that it was of the greatest importance. A sign of this recognition is found in the fact that although Berzelius's theory had been rejected, the elements which form bases were still called *positive* and those which form acids were called *negative*. In fact, the electrochemical contrast of the two constituents of salts is a fact which becomes obvious with each electrolysis, and which, therefore, cannot be doubted. It was only necessary to modify the view of Berzelius and to say that it is not the acids and bases (or more correctly their anhydrides) which are the constituents of salts, but rather it is the metal and the acid radicle. This modification of the electrochemical theory has, however, scarcely left any traces in the development of the chemistry of that time. The reason of this is that compounds of the nature of salts receded quite out of the foreground of interest. Organic chemistry, which at that time developed brilliantly, dealt with substances very few of which could be decomposed by the electric current, which were not electrolytes, and for which, therefore, the electrochemical contrast did not exist. The unitary conception was consequently involuntarily extended to the salts, and the important distinction between electrolytes and non-electrolytes was not at all taken into account by chemists. It is true that Faraday attempted to account for these two classes of bodies by supposing that in the one case the number of positive and negative atoms was the same, but in the other case these numbers were different; but this rule proved to be incorrect, and for a long time these relations were neglected because they could not be grasped scientifically. After the refutation of the erroneous views of Berzelius, people thought themselves justified in altogether ignoring the electrochemical relations.

This was the condition of electrochemistry till quite recently. The only attention it received was from the hands of some physicists, and it is only natural that purely chemical problems did not fare particularly well under these circumstances, the more so as even up to the present day it often happens that from this side the electrolysis of dilute sulphuric acid is represented as the electrolysis of water 'which has been made conductive by an addition of sulphuric acid. Although the direct furtherance thus given to chemistry was insignificant, yet the indirect effects were important. If it is possible to speak to-day of the development of a new electrochemical theory, it is almost exclusively to these physicists that we owe the means for so doing.

The first investigator to be mentioned at this point is Hittorf. He connected his work with the experiments of Daniell, and took up the consideration of a phenomenon which had remained incomprehensible to the latter. When Daniell experimented with sulphuric acid in his apparatus, he found that besides the electrolysis of the acid a change in the concentration had occurred; at the negative pole the acid solution had become more dilute, at the positive pole it had become more concentrated. It occurred to Hittorf that this phenomenon must be due to the different velocities with which the two constituents or ions of sulphuric acid—that is, 2H and SO_4—travel through the liquid. If, for instance, the hydrogen remained at rest and the group SO_4 alone moved, it would follow that after the electrolysis of one molecular weight of sulphuric acid, there must be an increase, by that amount, in the concentration at the positive pole towards which SO_4 had travelled. If, on the other hand, the hydrogen alone travelled, the concentration would remain unchanged. Now, it had been found by Daniell that the increase in concentration at the positive pole was equal to less than a quarter of the quantity of acid electrolysed; the necessary conclusion was, therefore, that both ions travelled, but that SO_4 moved much more slowly than $2H$. Hittorf proved by a great number of careful experiments (*P.* 89, 177; 98, 1; 103, 1; 106, 337) that this conclusion always agreed with observed facts. He then used the knowledge thus gained to answer chemical questions, for the solution of which no other means existed at the time. But in spite of their great importance, Hittorf's results have been all but completely ignored by chemists.

These experiments afforded verification of the conclusion that the more immediate components of salts—or what is the same, the ions of salts—really are the metal and the acid radicle. At the same time electrolysis furnished Hittorf with the means of solving certain old problems. Thus, for instance, opinion was divided as to whether potassium platinichloride and similar salts should be considered as double salts—for example, as $2KCl$ and $PtCl_4$—or as salts of chloroplatinic acid H_2PtCl_6. Hittorf submitted sodium platinichloride to electrolysis. If it consisted of $2NaCl + PtCl_4$, it followed that sodium and platinum were the positive ions and chlorine the negative; if, on the other hand, it was Na_2PtCl_6, the ions would be $2Na$ and $PtCl_6$. In the first case, therefore, the platinum must travel to the negative pole, in the other case to the positive. Experiment decided for the latter view; the platinum did not go to the negative pole, as the metals generally do, but travelled with the chlorine to the positive pole, thus proving itself to be a constituent of the acid radicle. In a like manner Hittorf decided quite a number of similar questions.

During these investigations, Hittorf drew attention to another point, which at a later time proved to be of the utmost importance. The fact that electrolysis can be started by the weakest currents is in contradiction to the usual chemical views, according to which the constituents of salts, such as KCl, Na_2SO_4, &c., are held together by very strong affinities. At the same time, Hittorf emphasised the fact that those substances which conduct electrolytically are the most ready to interchange their constituents. This fact also is against the assumption of a specially firm binding together of the constituents of salts. Occasion will be found later to refer to this remark.

There are other parts of the science of electricity, besides the phenomena of electrolysis, in which the chemical nature of substances has to be considered. These are the electrical conductivities of electrolytes, the electromotive force of galvanic cells, and galvanic polarisation. These fields have been cultivated till quite lately only by physicists to whom purely chemical questions were foreign.

The electrical conductivity of an electrolyte is a quantity the determination of which was formerly attended with great difficulties. These difficulties occur because the ions which separate where the electric current enters or leaves the liquid 'polarise' the electrodes, and thus produce new and unknown electromotive forces. Details of the various attempts which have been made to overcome this difficulty will be given later. It was, however, only in 1880 that, after long and varied preliminary investigations, F. Kohlrausch (*W.* 11, 658) indicated a really practical and accurate method. As soon as the values of the electrical conductivities of electrolytes could be determined easily, by Kohlrausch's method, important relations soon came to be recognised between the conductivities and the chemical properties of electrolytes. The most important of these relations, the discovery of which was made by Arrhenius (*Bigh. Swensk. Ak.* 8, Nos. 13 and 14, 1884), lies on the path opened up by Hittorf. The fact that substances capable of conducting the current and of being electrolysed are also specially capable of entering into chemical reactions, which was emphasised by Hittorf, can now be made definite by saying that both powers are nearly proportional for different electrolytes.

From this discovery there has grown a new electrochemical theory, which, in its entirety, will be expounded later on.

The other problem concerning the connection between the electromotive force of galvanic cells and the chemical processes within them was solved by Helmholtz (*Die Erhaltung der Kraft*, 1847), and later on also by Sir William Thomson (*P. M.* December, 1858), and this was done primarily on the basis of a hypothetical assumption. According to Faraday's law, when equivalent quantities of different substances are used in the galvanic cell, equal quantities of electricity are always put into motion. This being so, the intensity of the motion, or the electromotive force of the galvanic cells, must be proportional to the quantity of heat produced by the chemical processes within the cell. The supposition is made here that all heat is used for electrical work—a supposition which Thomson found verified by an experiment of Joule. Meanwhile it has been proved, however, that the heat produced in chemical changes is not generally completely transformed into electrical work, and Helmholtz (*B. B.* 1882) himself has worked out the formula representing the general relation between these two quantities.

To these problems are joined those concerning the nature and the value of galvanic polarisation. In this province investigation has, however, made so little way as yet that it suffices to point out that most important problems here await their solution.

The foundations of the science of electricity. General considerations.—If a bar of perfectly pure or amalgamated zinc is placed in dilute sulphuric acid, no chemical action takes place, nor is there any such action if a bar of platinum be introduced into the acid. But as soon as the two metals are made to touch each other an action occurs; the zinc is transformed into zinc sulphate by expelling the hydrogen from the sulphuric acid, which hydrogen, however, is evolved at the surface of the platinum bar.

Direct contact of the two metals is not necessary. If, for instance, the zinc is touched with the end of a copper wire and the platinum is touched with the other end, the same effect is produced. On the other hand, there is no effect if the connection is made through glass, wood, or such like substances.

The copper wire which connects the two metals has acquired special properties which remain as long as the chemical action of the sulphuric acid on the zinc lasts. If the wire is held parallel to a movable magnetic needle at a short distance above it, the needle will be deflected; further, the wire becomes heated; and finally, if the wire is cut in one place, and the two ends are placed close to each other on a paper moistened with solution of potassium iodide and starch, it can be perceived that a chemical decomposition of the potassium iodide has occurred, since a blue spot of iodide of starch appears under one end of the wire.

Work, or, speaking generally, *energy*, is gained by the chemical action between the zinc and the sulphuric acid; the energy usually appears in the form of heat. The arrangement described shows that it is possible to conduct this energy away from the place where it is set free—that is, from the point of contact between zinc and sulphuric acid—and to make it effective at any point of the connecting wire we please. And further, we can obtain this energy at will in the form of thermal energy, chemical energy, or mechanical energy.

The sole difference that can be perceived between the metals in their usual state and when dipped into the acid is that they have become *electric*; the platinum shows itself charged with positive, and the zinc with negative, electricity. By means of a suitable electrometer this electric charge can be measured. It appears to be dependent on the nature of the metals, as well as on that of the acid.

Hence we conclude that the chemical action between the zinc and the acid does not, as usual, give out its energy in the form of heat, but in that of electrical energy. As to whether the transformation from chemical to electrical energy is complete or partial, and, if the latter, by what this partial amount is determined, these are questions with which we can occupy ourselves only at a later stage.

As is generally the case with all forms of energy, electrical energy allows itself to be resolved into two factors, one of which is a *capacity*, and the other is an *intensity*. For these factors the general law holds, that a system can be in a state of rest only if the intensity of the energy is the same throughout the whole. An exception to this occurs only if different kinds of energy are present simultaneously in one system; then there can exist a difference of *one* intensity, if a compensation is produced by a corresponding difference of the *other* intensity.

The two factors of electrical energy are called *quantity of electricity* and *electromotive force* or *potential*; the first is the capacity, the second the intensity. In accordance with the above-mentioned law, we shall therefore say that in a system in which electrical forces alone act there is equilibrium if the electromotive force or the potential is the same throughout. This is the well-known law for conductors of electricity.

With substances which do not allow of any motion of the electricity—that is, with non-conductors—the potential can, it is true, be different in different places. But then, owing to the striving for equalisation on the part of the potential, small displacements are produced in the body, and the reacting forces of elasticity which accompany these form the compensation for the inequality of the electric intensity or potential.

When contact between two different substances occurs, a mutual action at the surface of contact is generally set up, and a displacement of energy is thus brought about. The changes in the surface-energy which thus occur seem to be generally compensated by corresponding differences in the electric intensity, *i.e.* the surfaces of different substances in contact attain different potentials. If the substances are conductors of electricity, each of them must be at a uniform potential at every point within it; hence a difference of potential exists at the surfaces of contact only.

Electrical measurements. In order to examine systematically the nature of electrical phenomena we are at the very beginning obliged to find a measure for them. We generally start from a definition of quantity of electricity, since the historical development of the science has led to the notion that this is one of the most important factors in the phenomena. And yet we have no proof that such things as the hypothetical electric fluids actually exist. What we do know of electrical phenomena are the mechanical, thermal, and chemical effects, *i.e.* the manifestations of the *electrical energy*, and it is this which is the real thing underlying the electrical phenomena. Quantity of electricity is a magnitude of the same order as perhaps a volume, and one which can be increased or decreased at will. But electrical energy cannot be destroyed, nor can it be produced; it can only be changed into, or obtained from, other forms of energy.

Electrical energy is then to be measured by the same units as other forms of energy, mechanical energy especially. The unit used for kinetic energy, which is represented by the formula $\frac{m}{2}v^2$ (where m stands for the mass, v for the velocity), is double that energy which the mass of one gram possesses when moving with the velocity of one centimetre in one second. This being so, the unit accepted for electrical energy is that quantity of energy which is obtained by the transformation of the above-defined quantity of kinetic energy into electrical energy. And further, since, as has been already mentioned, electrical energy has to be looked upon as the product of two factors, the quantity of electricity Q and the potential E, the unit by which the product QE must be measured is thus also fixed.

The units of the two factors Q and E are still arbitrary, in so far as we can choose one of them at will, that for the other being then fixed. In fact, different units have been chosen for different purposes, and accordingly different systems of electrical magnitudes have been obtained. Faraday's law, that equal quantities of electricity travel with equivalent quantities of separate ions, supplies the chemist with a natural unit for *quantity of electricity*. Hence that quantity of electricity which is combined with one gram of hydrogen as ion will serve as unit of quantity of electricity. Then the unit of potential would have to be the potential at which the above-defined quantity of electricity must be in order to produce unit of work.

This system of units has not become general;

it has been displaced by a system which is derived in a somewhat complicated manner from the action of current electricity on magnets. This system also has not been retained unchanged, but another one has been deduced from it, in which instead of the unit of length of 1 cm. a 10^9-fold value has been introduced, while instead of the unit of mass of 1 g. a value 10^{-11} times as small is accepted; the second has been retained as the unit of time. Hereby the unit of electrical energy has been changed also; it no longer coincides with the mechanical unit, but is 10^7 times greater.

In this system the unit of potential is called a *volt*; in order to get a conception of its magnitude it is to be remembered that the difference of potential at the ends of a Daniell cell is about 1·1 volt.

The unit of quantity of electricity has been called a *coulomb*. When a coulomb is forced through a volt a quantity of work equal to 10^7 mechanical units is done.

In order to fix the relations of these units to other units of energy, we must first remember that the work necessary to move 1 g. through 1 cm. against gravity is equal to 980 mechanical units, approximately. The above-defined unit of electrical energy would therefore be equal to $\frac{10^7}{980}$, or approximately to 10200 gravitation-units. Further, the unit of thermal energy is the quantity of heat which raises the temperature of 1 g. of water by 1°C., and which, according to the measurements of Joule, is equal to 42350 gravitation-units, *i.e.* 42350 g. would on falling through 1 cm. give up 1 calorie of heat, or would heat 1 g. of water by 1°C. Hence this magnitude is equal to $4·15 \times 10^7$ mechanical units. Since the unit of electrical energy amounts to 10^7 mechanical units, it follows that 1 calorie is equal to 4·15 electric energy units, or 1 volt × coulomb is equal to 0·241 calories. A number obtained more recently by Dieterici by direct measurements is probably more accurate. According to him, the energy of 1 volt × coulomb is equal to 0·2356 cal.; the unit of quantity of heat here used is $\frac{1}{100}$ of the quantity of heat given out by 1 g. of water in cooling from 100° to 0°. This factor is important for the relations between the heat produced in chemical changes and the corresponding electrical phenomena. Finally, we know from measurements by F. Kohlrausch and Lord Rayleigh that 1 g. of hydrogen as ion carries with it 96540 coulombs. The same quantity of electricity is carried by each equivalent of any other ion, for instance, by 107 g. of silver, $\frac{1}{2} \times 63·4$ g. of copper, $\frac{1}{3} \times 27$ g. of aluminium, &c.

Electric currents. If the potential of electricity is different at different places of a conductor, a movement of the electricity is produced in the same way as motion is produced in a mass capable of moving freely when it is at a higher level than its surroundings. If the difference of potential is maintained, the movement is maintained also.

The compensation of a difference in electric potential necessitates a decrease in the electric energy, which in this process changes into another form. The form most easily produced is thermal energy, but, as has been mentioned above, it is possible also to obtain mechanical or chemical work.

The measure of the quantity of energy changed into another form is given by the product of the quantity of electricity moved into the decrease of the potential. If the differences of potential are distributed over measurable distances the process is called an *electric current* The term has been taken from the analogy which in fact does exist between currents of water and currents of electricity. The level of the water corresponds to the potential of the electricity, and the quantity of water corresponds to the quantity of electricity. In both cases the transformable energy, or the available work, is equal to the product of the quantity (of electricity or of water) into the difference of level or of potential, and a current sets in when a difference of level exists. It must only be borne in mind that the phenomena which are brought about by the *kinetic energy* of the moving masses in water currents have no analogy in the domain of electricity. The electricity behaves as if it possessed only an inappreciably small velocity or mass. Therefore, when the electricity has sustained a definite decrease in potential, it has lost the whole corresponding quantity of energy, while the water can retain a part of it in the form of velocity-energy.

Electric currents are measured by their *intensity*. By this is understood the quantity of electricity which flows in the unit of time through a cross-section of the current-path; hence the intensity I has to be put as $\frac{Q}{t}$, where t stands for the time. Since electricity moves only when using energy, a loss of electrical energy corresponds to every current, the lost energy generally reappearing as heat. When heat is the only form into which electric energy is transformed, the following equation must hold; $W = EQ$, and $\frac{W}{t} = EI$, where E stands for the loss of potential between the two ends of the path of the current considered.

Experience has further shown that different conductors when introduced into a circuit cause different losses of potential along their lengths. This property has been ascribed to a *resistance* of the conductor to the motion of the electricity, in a way similar to that wherein tubes of different bore offer different resistances to the motion of water within them. In accordance with this, the resistance R is defined as the ratio between the difference of potential E and the quantity of electricity forced by means of it, in unit time, through the conductor, or, what is the same, the intensity I. Here we have $R = \frac{E}{I}$ or $I = \frac{E}{R}$. This is the celebrated law of Ohm, that the intensity or the strength of the current is equal to the ratio between electromotive force and resistance.

Combining this law with the preceding one, it follows that $\frac{W}{t} = I^2R$. This expression is the law arrived at experimentally by Joule, according to which, for currents of equal strength, the heat evolved in unit of time is proportional to the resistance, and for equal resistances it is proportional to the square of the current strength.

It is easy to deduce from the units already given the values for the units of the two new terms introduced when defining electric currents, namely, the strength of the current S and the resistance R. The unit of intensity I is that strength of current at which, in every second, one coulomb flows through the cross-section of the conductor; the unit of intensity is called an *ampère*. The unit of resistance is that resistance by means of which a current of unit intensity (1 ampère) produces in unit of time the unit of heat. As we have seen above, this last is equal to 10^7 mechanical units, or to 0·2356 calories. An attempt has been made to represent this resistance with the utmost possible accuracy, and it has been found that it equals the resistance of a column of mercury of 1 sq. mm. section and 106·3 cm. in length, at the temperature of melting ice. This unit of resistance has the name *ohm*. Slightly different to this is the *legal ohm*, which has been fixed arbitrarily as equal to the resistance of a column of mercury 106 cm. long and 1 sq. mm. section, the exact determination of the true ohm being a very difficult operation. The commercial resistances are graduated according to the legal ohm, and in scientific works in which the absolute value of the ohm comes into consideration, this difference of 3 per thousand must be taken into account. In most cases this is not necessary, just as in most cases it is immaterial whether or not a set of weights is made according to exact grams, as long as it is only made exact in its proportions.

The Law of Faraday. Those substances which allow a movement of electricity through them, *i.e. conductors* of electricity, are divided into two classes. In the cases considered so far, the assumption has been made that the only form of energy into which the electric energy of the current is transformed is heat. Conductors which undergo no change other than that they get heated when the current passes through them are called *conductors of the first class* or *metallic conductors*. To this class belong the metals, their alloys, carbon, and certain compounds.

Now, there are many substances which permit a movement of electricity through them, but in so doing themselves suffer chemical change. To these belong aqueous solutions of acids, bases, and salts, as also salts in the molten state, and a few other compounds. Such substances are called *conductors of the second class* or *electrolytes*.

The movement of electricity in electrolytes takes place in such a manner that the components of the electrolyte move independently of each other. Hydrogen, the metals, and the metallic radicles move with the positive electricity, or, according to the usual designation, from places of higher to places of lower potential. The halogens, the acid radicles, and hydroxyl, on the other hand, travel with the negative electricity, or from places of lower to places of higher potential.

According to Faraday's nomenclature the components of electrolytes—that is, on the one hand the metals, hydrogen, &c., on the other hand the halogens, the acid radicles, &c.—are called *ions*. The first named, which travel down with the current, are called *cations*, those which travel up *anions*.

In a circuit consisting exclusively of an electrolyte, a motion of electricity can take place without the corresponding chemical action being apparent. But if a conductor of the first class directly touches an electrolyte, whenever there is a movement of electricity there is also a production of the ions at the surface of contact, and the chemical effects become apparent. As proposed by Faraday, the surfaces of metallic conductors, where they touch the electrolytes, are called *electrodes*. The surface at which the anions appear is called the *anode*, and that whereat the cations appear is called the *cathode*.

Faraday also formulated the general law to which all movement of electricity in electrolytes is subject. *In every electrolyte the quantity of ion separated out is proportional to the quantity of electricity which has passed through, and the same quantity of electricity passing through different electrolytes separates quantities of the different ions that are in the ratio of the chemical equivalents of those ions.* In these propositions it has been assumed for simplicity's sake that the ions are actually separated out at the electrodes, but this is not essential for the truth of Faraday's law. The following wording completely expresses the actual meaning of Faraday's law: *Electricity can move in electrolytes only simultaneously with the ions, and so that chemically equivalent quantities of the different ions carry with them equal quantities of positive or of negative electricity.*

We arrive at a perfectly appropriate conception of the nature of electrolytic conduction if we assume that each equivalent of the different ions possesses an equally large capacity for electricity, or, to use the words of Helmholtz, 'the electricity in electrolytes behaves as if it were divided into equal atoms.'

In applying Faraday's law, it is important that we should keep in mind the difference between the equivalent and the atom; the equivalent weight is equal to the atomic weight divided by the valency. Thus the same quantity of electricity travels with 107 g. of silver, ½ × 65·5 g. of zinc, and ⅓ × 27 g. of aluminium; also with 35·5 g. of chlorine there travels only half as much electricity as with 96 g. of SO_4. As an amplification of the illustration used above, we must assign to each atom as many equal capacities for electricity as the number of valencies it possesses. Perhaps this is the path by which in the future we may arrive at an elucidation of the nature of chemical valency.

The truth of Faraday's law was tested by its discoverer himself in many ways (*Exp. Res.* vii. ser.). He convinced himself that the same quantity of dilute sulphuric acid was always decomposed by the same current, whether the electrodes, or the E.M.F., were large or small. Nor did the strength of the acid exert any influence. Finally, he introduced into the same circuit dilute sulphuric acid and tin chloride, lead chloride, or lead borate, or he led the same current through different beakers with dilute sulphuric acid, using electrodes of different metals; in all cases he found his law verified. Later on, other investigators have tested whether part of the electricity is not perhaps conducted through electrolytes in the same way as through metals, but no trace of this has been discovered; in every case the electricity passed through has been strictly proportional to the quantity of ion separated out. And the law of equivalency has also proved itself so correct that it has been used lately as a means for determining equivalent weights, and hence atomic weights.

The cases in which the same element exhibits different valencies according to circumstances are of special interest. Many such cases have been examined by Regnauld (*A. Ch.* [4] 11), who formed cells by taking platinum and different metals, along with the corresponding electrolytes, and then determined the quantities of metal dissolved when equal quantities of electricity had been allowed to pass. Thus it was found that mercury in dilute nitric acid has the equivalent 200, since it is changed into $HgNO_3$, a compound of mono-valent mercury; in a solution of potassium cyanide it has the equivalent 100, because it becomes $Hg(CN)_2$, in which the mercury is di-valent. Similarly, copper in hydrochloric acid forms $CuCl$ and has the equivalent 63·4; in nitric acid it forms $Cu(NO_3)_2$, and has the equivalent 31·7. Tin scarcely ever passes into solution except as a di-valent element; it is only in alkaline polysulphides and in a solution of caustic potash containing nitre that it acts as a tetra-valent element. Tellurium also can be made to act as a di-valent and a tetra-valent element. It is known that the elements mentioned show quite different reactions in their solutions, according as they are present as mercurous or mercuric, as stannous or stannic compounds, &c. Hence in these cases the nature of the chemical reactions depends on the quantity of electricity with which the ions are combined.

This is the place to refer back to a misunderstanding concerning the law of Faraday into which Berzelius first fell, and which has recurred many times since. As has been mentioned, Berzelius saw in this law a contradiction to his theory, and tried to refute it by the following argument: if equal quantities of electricity were required for the decomposition of equivalent quantities of the most diverse compounds, it would follow that these could be decomposed by equal forces; this, however, is not possible, since the different substances are evidently held together by quite different forces of affinity. From the illustration given above it can be seen that, contrary to the assumption of Berzelius (which, however, was very excusable, considering the state of electrical science at that time), Faraday's law does not in any way deal with *forces*, but rather with quantities of electricity. Comparing electrical decomposition to the raising of water out of wells by means of buckets, Faraday's law asserts that in spite of the differences in the depths of the wells, the size of the buckets is always the same. We would fall into an error similar to that of Berzelius if we concluded from the equal size of the buckets that the work necessary for raising the water out of all the wells of different depths was the same. The illustration also shows directly wherein the differences in chemical work, corresponding to the different depths of the wells, assert themselves, namely not in the quantities of electricity required, but in the differences of potential.

Electrolytes and ions. It follows from the nature of an electrolyte that it must be a compound substance, since otherwise its parts or ions could not transport the electricity in both directions. Yet all compounds do not possess the power of conducting electricity. In particular, we do not know of any substance liquid at the ordinary temperature which is an electrolyte; amongst pure substances it is only the salts melted at a higher temperature which conduct at all appreciably.

On the other hand, all substances having the character of salts, acids, and bases possess electric conductivity when in aqueous solution. In these cases the water exerts a specific influence, since solutions of the same substances in alcohol conduct much less if at all; and solutions in ether, carbon disulphide, and similar solvents are scarcely conductive.

There are two factors, therefore, which are necessary for the production of electric conductivity, *i.e.* the nature of the substance and the condition in which it is.

In electrolysis the molecule of the conducting compound appears to be split into two parts. There can be no doubt as to what these parts are with substances such as chloride of silver or potassium iodide; since they consist of two elements only, the metal must be one ion and the halogen the other. The question gets more doubtful with ternary compounds, such as nitric acid, sodium acetate $NaCO_2CH_3$, or ammonium chloride NH_4Cl. Since, however, no important distinction manifests itself in the behaviour of these substances and those mentioned above, it is simplest and most obvious to assume that their ions correspond to those of the substances first named. Hence the ions of nitric acid are H and NO_3, those of sodium acetate Na and CO_2CH_3, and those of ammonium chloride NH_4 and Cl.

It is possible to examine this assumption on the basis of Faraday's law. In the electrolysis of potassium sulphate as much oxygen and hydrogen are obtained as from the electrolysis of dilute sulphuric acid by means of the same current, but in addition to this there is found at the anode an equivalent quantity of free sulphuric acid, at the cathode a corresponding quantity of free caustic potash. If we assume with Berzelius that the current has decomposed the potassium sulphate into potassium oxide and sulphur trioxide, K_2O and SO_3, which combine with the water to form $2KOH$ and H_2SO_4, we should have to assume further that the same current had in the same electrolyte simultaneously decomposed an equivalent quantity of water. But this is in contradiction to the law of Faraday. If we assume, however, that the ions are K_2 and SO_4, it is comprehensible that the potassium separated out should act on the water of solution, evolving hydrogen, according to the equation $2K + 2H_2O = 2KOH + H_2$; in like manner the ion SO_4 acts on the water and forms sulphuric acid and free oxygen, according to the equation $H_2O + SO_4 = H_2SO_4 + O$. With those metals which do not decompose water, such as zinc, copper, and silver, we actually obtain the metal only at the cathode; and similarly, solutions of chlorides, bromides, and iodides do not generally give free oxygen, but free halogen.

It is necessary, therefore, to distinguish carefully between the primary and the secondary effects of electrolysis. The primary effects consist in the separation of the ions at the electrodes. But since the ions do not continue to exist as such after having given up their electricity, they undergo further changes according to circumstances. The simplest case is that of the metallic ions, when these cannot act on the water; they simply become solid or liquid metals. So also the separated atoms of the halogens pass on, combining into gaseous chlorine, Cl_2, or into the molecules of the dissolved bromine or iodine.

The metals which decompose water can still be obtained in the metallic state when water is excluded or reduced to as small a quantity as is possible. A classical example of this is furnished by the electrolysis of slightly moistened potash, by means of which H. Davy discovered potassium. The electrolysis of molten salts, that of the chlorides especially, furnishes a means for preventing the secondary reaction of the metals; such electrolyses, which had first been used by Bunsen for scientific investigations, have obtained at the present time great technical importance in the production of magnesium and aluminium.

Complex cations of the type of ammonium, NH_4, are very unstable, and until recently it was doubtful whether the so-called ammonium amalgam, which is obtained on using a mercury cathode in the electrolysis of ammonium chloride, really contained the compound radicle NH_4. By measurements of another kind (viz. of the electromotive force) the existence of ammonium in the amalgam has now been placed beyond a doubt.

The compound anions as such are all of them very unstable. Many of them, such as the anions of the nitrates, phosphates, sulphates, &c., simply act on the water by taking up from it the hydrogen required to produce acids, and liberate the oxygen. The latter, which appears in the nascent state, is capable of bringing about powerful oxidising effects. If, for instance, lead or manganese salts are electrolysed, the oxygen acts on the dissolved metal and separates it at the anode as peroxide. In other cases the anion splits up into more stable compounds. Thus in the electrolysis of formates we obtain carbon dioxide and hydrogen from the ion $HCOO$, according to the equation $2HCOO = H_2 + 2CO_2$. The acetates give carbon dioxide and ethane $2CH_3CO_2 = C_2H_6 + 2CO_2$, and similarly the salts of the higher fatty acids give the corresponding paraffins.

In some cases the secondary action can take place in another direction; in this manner the formates can produce—instead of hydrogen and carbónic acid—water, carbon dioxide, and carbon monoxide, as is shown in the following equation, $2HCO_2 = H_2O + CO + CO_2$. In most cases such secondary processes take place along with the primary actions, and the proportion between the two depends on external circumstances, temperature, concentration, current-density, &c.

In a few cases it is somewhat difficult to recognise the primary or secondary character of a product of electrolysis. On electrolysing potassium silver cyanide or sodium platinichloride, silver or platinum separates at the cathode, so that it seems as if the silver cyanide or the platinichloride were decomposed primarily. This, however, would be an erroneous view, since the ions of the salts are K and $Ag(CN)_2$, and Na_2 and $PtCl_6$ respectively, and the heavy metals are only secondarily reduced from the solutions by the alkali metals. We can convince ourselves of this by using small electrodes and strong currents, when the salt near the cathode is soon used up, and potassium (or sodium), or, more correctly, hydrogen which has been formed secondarily, separates. More distinct proof of the nature of the ions is, however, obtained by studying the migration of the ions, to be discussed later.

So far the assumption has been made that the ions exert no action on the metal of the electrode; this, however, is not always correct. Only a few metals when used as anodes offer resistance to the chemical attack of the anions. If the metal can combine with the anion it forms the corresponding salt, which either dissolves in the water of solution, or, if insoluble, remains attached to the electrode and often interrupts the current. But also when used as cathodes the metals often combine with the cation; thus mercury forms amalgams, and the hydrogen separated at the cathode is occluded in greater or smaller quantities, especially by palladium and platinum, and also by iron. In other cases the cathode simply becomes coated with a layer of the corresponding metal, which separates more or less uniformly according to its nature and that of the electrolyte. These processes are used for coating substances which are conductors, or if non-conductors, whose surfaces at least have been made conductive; such processes have also been employed for galvanoplastic coating with gold, silver, copper, &c.

The constitution of electrolytes. It has already been remarked that all compounds are not electrolytes, and that some substances which do not conduct electrolytically by themselves obtain this power when dissolved in certain solvents, especially in water. From this it follows that electrolytes have a special constitution with which their special property is connected. The question as to what this constitution is has scarcely been raised yet, much less has it been answered. This is because most of the compounds known in the days of the electrochemica system of Berzelius were electrolytes, and late on, when many organic compounds, which ar mostly non-electrolytes, were discovered, th electrochemical theory had been given up, and the interest in it had disappeared. The first investigator who proposed the question clearly —and who, as far as he could, answered it—wa Hittorf. He it was who established the proposition 'electrolytes are salts.' Under the nam of 'salt' Hittorf comprised all those compound which are capable of exchanging their constituents within the shortest time. Hence alon with the salts proper must be classed acids an bases.

By enunciating this law, Hittorf was the first to draw attention to a most important relation which has become the starting-point for the due comprehension of the constitution of electrolytes. The power to conduct electricity and the power to exert chemical reactions are so closely parallel that both must be considered as the outcome of the same cause. This cause, however, has to be looked for in the constitution of the electrolytes themselves.

Electrolytic conduction is brought about by the positive and negative electricities moving through the conductor bound to their ponderable carriers, the ions; it is necessary, therefore, to assume a considerable mobility of the ions.

And, further, electrolytic conduction occurs in consequence of any difference in potential, however small. It is necessary, therefore, as was already pointed out by Clausius (*P.* 101, 338), that in every electrolyte there should be present a certain number of ions capable of moving freely, *i.e.* in every electrolyte a portion of the salt-like compound which produces the conduction *must be partly split up into ions.* Clausius left undecided how great this portion is, as he possessed no means to determine it. To the chemists who, in consequence of a peculiar shifting of judgment, considered electrolytes generally as specially stable compounds, he made the concession that this portion might be very small. In the imagery of the kinetic hypothesis he conceived that, owing to the collision of the molecules of the electrolyte with each other and with those of the solvent, one or other occasionally splits into its constituents, and so gives the necessary free ions.

It is now possible to urge similar considerations from the chemical side. While gaseous substances at the ordinary temperature react but seldom, acids, bases, and salts dissolved in water do so instantaneously. A mixture of oxygen and hydrogen does not form water until it has been heated to between 400° and 500°; a mixture of hydrochloric acid and potash, however, when in aqueous solution, passes so quickly into potassium chloride that it has been found impossible as yet to determine the time required for the change, and yet in the first case 68,000 cal. of heat are produced, while in the second the heat produced, or the energy liberated, is only 13,700 cal.—that is, five times less. In general, non-electrolytic solutions also react with each other extremely slowly. An example of this is afforded by the means which must be taken to hasten the reactions of non-electrolytes, and especially of organic compounds; this has to be done by heating the reacting mixtures, often under increased pressure. For the formation of acetic ether from a mixture of alcohol and acetic acid—that is, for a process intimately connected with that of the formation of salts—at least ten years are needed, at the temperature of the room, before it has approximately attained the end which under these conditions it can reach. From the chemical point of view, therefore, it is necessary to suppose that compounds which react instantaneously—that is, electrolytes—possess a special mobility of their parts or ions; and that it is the constituents of 'salts'—the term being used in the widest sense—which are the ultimate causes of electrolyses as well as of chemical reactions. These constituents of salts are, on the one hand, the metals, the metallic radicles, and hydrogen; on the other hand, the halogens, the acid radicles, and hydroxyl. It is possible, therefore, to apply to substances which react rapidly—that is, to salts, as this term was used by Hittorf—the same kinetic considerations as were made use of by Clausius to show the presence of ions in electrolytes.

We are now confronted on both sides by the question of how great is the proportion of free ions, or of decomposed molecules, in solution of electrolytes. The fact that a maximum reacting power exists for a given class of substances is in contradiction to the assumption that this proportion is inappreciably small. It has already been explained (compare the article AFFINITY) how the substances which have been most carefully examined from this point of view—the acids—exert their chemical reactions according to a definite co-efficient which is characteristic of each acid. This co-efficient—which can be determined, for instance, by means of the velocity of inversion of cane sugar—cannot be increased at will, and does not exceed a definite maximum value, which maximum is possessed by hydrochloric acid, nitric acid, benzenesulphonic acid, &c. All the conditions—such, for instance, as the introduction of oxygen, sulphur, or halogen into the molecule—which increase the velocity of reaction of weak acids are without any measurable effect on the strongest acids. From this it follows that the circumstance which is the cause of the velocity of reaction—that is, the unimpeded mobility of the ions—has in these substances already reached its highest degree, or is at least very near to it, since, in opposition to Clausius and to the views current till now, we must assume that in aqueous solutions of these strong acids it is not, perhaps, a few hundredths or thousandths of the molecules present which are split into their ions, *but rather that by far the greater part of the electrolyte is split into ions.*

A similar conclusion can be drawn from the degree in which electrolytes conduct the current. The more detailed consideration of this subject will be taken up presently. Here it will only be mentioned that the results of these investigations agree completely with those on the velocities of reactions.

A third entirely independent verification of the unexpected conclusion that aqueous solutions of the strong acids are nearly completely dissociated can be gained from a study of the properties of these solutions.

Only so much of van't Hoff's theory of solutions (*Z. P. C.* 1, 481) as is necessary for understanding the constitution of electrolytes will be explained here.

The fundamental idea of van't Hoff's theory is as follows. The physical properties of gases, and especially the relations between pressure, volume, and temperature, are practically independent of the special nature of the substance, while such an independence does not exist with liquid and solid substances. The cause of this phenomenon may be sought in the fact that the smallest parts or molecules of gases are always at such a distance apart that they are not capable of exerting an action on each other. In liquid and solid substances, however, the molecules are in close proximity, and exert, therefore, their specific reciprocal actions. But there is another condition in which the molecules of a substance are relatively distant from each other, namely, when the substance is present in a solvent in the state of a dilute solution.

We should expect, therefore, that in this state matter would be subject to laws analogous to those which hold for gases.

The first property characteristic of gases is their power of extending uniformly through any given space. Solutions exhibit the same peculiarity. When the pure solvent is placed over the solution of any substance, the substance begins directly to enter into the solvent (the pure solvent playing the part of a vacuum), and the movement does not cease until, as with gases, the substance is uniformly distributed through the whole space. The only apparent difference is that in the case of gases this process is completed in a very short time, while with solutions months, and even years, are needed in order to bring it, practically speaking, to an end. This movement can be impeded by introducing between the solution and the pure solvent a partition which allows the passage of the latter but not of the former. Such a 'semi-permeable' partition can be produced by saturating a porous clay cell, for instance, with a solution of copper sulphate, washing the cell, and filling it with a solution of potassium ferrocyanide. A pp. of amorphous copper ferrocyanide is thus formed in the pores of the clay, and this pp. allows the passage of water through it, but does not allow various other substances to pass. In order to arrive at a conception of the cause of such a property we can imagine that the pp. of copper ferrocyanide acts as a filter which allows the passage of the smaller water molecules, while it retains the larger molecules of the dissolved substance.

W. Pfeffer, who has studied such cells very thoroughly, found that if the cells are closed a very considerable amount of pressure is produced in their interior. A 1 p.c. solution of sugar produces a pressure of more than 50 cm. of mercury; a solution of nitre of equal strength gives pressures of between three and four atmospheres. Pfeffer also found that the pressures increased, at constant temperature, to maximum values, which remained constant as long as the partition remained intact. These pressures proved to be proportional to the concentrations, and further, they increased with a rise of temperature.

According to van't Hoff, this pressure, the 'osmotic pressure,' is to be looked on as analogous to the gaseous pressure. It is possible to form a similar conception of its cause as is formed of the cause of gaseous pressure; the molecules of liquids, like the molecules of gases, possess a quantity of kinetic energy which is proportional to the temperature. The solvent—for instance, the water—can pass through the semi-permeable wall, and since it is present on both sides its pressure is the same on both. The substance dissolved, however, bombards the wall from one side only, and thus a pressure is set up. This view—which, however, is only hypothetical, and which can be accepted or rejected without the theory itself being called in question—has been objected to on the ground that if it were true a weak-walled vessel must needs be broken by a solution placed in it. But this assertion overlooks the important point that the osmotic pressure can exert itself only *within* the solution. If we imagine for simplicity's sake a drop of a solution floating in space, it is true that a pressure due to the substance dissolved will be exerted on the internal surface of the drop, which pressure may easily amount to 100 atmospheres. But to this pressure there is opposed the normal capillary pressure of the liquid, the magnitude of which we do not yet know very exactly, but of which we can assert that it has to be measured by thousands of atmospheres (in the case of water it is approximately 20,000 atmospheres). Hence this pressure is under all circumstances quite sufficient to maintain equilibrium with the osmotic pressure, and the only effect of the latter is to slightly increase the volume of the solution.

It has been shown by van't Hoff that the laws of osmotic pressure exactly coincide with those of gases. Boyle's law enunciates that pressure and volume are inversely proportional. Pfeffer's law says that pressure and concentration (or density) are proportional; this agrees with Boyle's law. Further, the law of Gay-Lussac tells us that at constant volume (or at constant density) the pressure of a gas increases with the temperature, and that for each degree it does so by $\frac{1}{273}$ of the value at 0°. A similar thing has been proved by van't Hoff from the numbers obtained by Pfeffer. And finally for gases we have the law of Avogadro, that, temperature and volume being the same, equimolecular quantities of different gases exert the same pressure. Taking the molecular weights in grams, and taking for the common volume 1 litre, then at 0° this pressure is equal to 22·37 atmospheres. Now, it has been observed by Pfeffer that the osmotic pressure of a one per cent. solution of cane sugar, which therefore contains 10 g. in one litre, is 0·649 atmospheres at 0°. The molecular weight of sugar $C_{12}H_{22}O_{11}$ is 342; a solution containing this quantity in grams in one litre would exert a pressure $\frac{342}{10}$ times as great—that is, a pressure of 22·2 atmospheres. This number agrees within the limits of experimental error with that which holds good for gases; and hence Avogadro's law holds also for solutions, or, more correctly, so far, for solutions of cane sugar.

The question whether the law holds for other dissolved substances must be answered in the affirmative. It is true that only very few measurements of osmotic pressures have been made, but these phenomena are so closely connected with others to be considered shortly, that it has been possible to place the general validity of the law beyond doubt.

Let us imagine a solution poured into a vessel of the form of an inverted funnel, the opening of which is closed by a semi-permeable wall in contact with which is a quantity of the pure solvent. Then the solution will rise in the tube, because of the greater internal pressure, and equilibrium will be established only when the pressure of the liquid column in the tube has become equal to the osmotic pressure. Let this arrangement be covered by a bell-jar, from which the air has been completely expelled; the solution will then be surrounded by the vapour of the solvent only. But the pressure of the vapour is slightly smaller in the upper part of the bell-jar, at the level of the solution, than below at the level of the pure solvent, and it is smaller by an amount which is equal to the pressure of the weight of the vapour present between the two levels. Moreover, it is by this amount that the vapour-pressure of the solution must fall short of that of the solvent, because, if this were not the case, liquid would either continually evaporate, or condense, at the surface of the solution;

in consequence of the osmotic pressure, the changes in level produced would always equalise themselves again, and we should have a *perpetuum mobile*, which is impossible.

It follows, therefore, that in general the vapour-pressure of a liquid must decrease when a substance is dissolved in it, and that this takes place according to laws which run parallel with those of osmotic pressure.

This theoretical conclusion is in accordance with observation. It has been found by Wüllner (*P.* 103, 529) that, at a constant temperature, the decrease of the vapour-pressure of an aqueous solution is proportional to the concentration of the solution. Babo on his part had established that the ratio between the vapour-pressures of the pure solvent and the solution is independent of the temperature. Both results have been confirmed, on the whole, by later investigations. Raoult especially has occupied himself with this question; he has shown that this behaviour is general, and he has also found that equimolecular weights of different substances dissolved in the same solvent produce equal diminutions of the vapour-pressure, and finally that on using equimolecular quantities of different solvents the relative diminution in the vapour-pressures is the same. If f stands for the vapour-pressure of the solvent, f' for that of the solution, and if further N stands for the number of molecules of the solvent (in gram-units), n for the number of molecules of the substance dissolved, the general expression holds

$$\frac{f-f'}{f}=\frac{n}{\mathrm{N}+n}.$$

While Raoult discovered this law empirically, van't Hoff has deduced it theoretically from the laws of osmotic pressure (*Z. P. C.* 1, 494).

This formula can be used for determining the molecular weight of a substance in solution. Let p grams of a substance with unknown molecular weight m be contained in 100 g. of the solvent, the molecular weight of which is M; then $\frac{p}{100}\mathrm{M}$ = grams of substance dissolved in one molecular weight of the solvent; let this $=s$; then putting $n=\frac{s}{m}$, and $\mathrm{N}=1$, and solving the equation for m, it follows that $m=\frac{sf'}{f-f'}$.

Finally, a third set of phenomena is known, governed by similar laws. It has long been known that salt water freezes at a lower temperature than pure water. As far back as 1788 Blagden (*T.* 1788) established the fact that the lowering of the freezing-point of a solution of salt in water is proportional to the amount of salt dissolved. Later on, Rudorff (*P.* 114, 63) rediscovered this fact, which had been forgotten, and de Coppet found that equimolecular solutions of salts having analogous constitutions exhibited equal lowerings of the freezing-points (*A. Ch.* [4] 23, 366). Raoult discovered that the same law held for the most diverse solvents. This law states that equimolecular quantities of whatever substances we take, added to a constant quantity of the solvent, lower the freezing-point by the same amount (*C. R.* 1882). Raoult thought for a time that the lowering of freezing-point was the same for equimolecular quantities of different solvents, but this proved to be erroneous. Van't Hoff has deduced this important relation from the laws of osmotic pressure, and his formula agrees well with experiment (*Z. P. C.* 1, 481).

We can convince ourselves of the necessity of these relations by an argument similar to that used in order to prove the connection between osmotic pressure and change of vapour-pressure. As the mechanical theory of heat tells us, below 0° the vapour-pressure of ice decreases more rapidly than that of over-cooled water. A temperature must therefore exist whereat a salt-solution, which has a vapour-pressure less than that of water, exhibits the same vapour-pressure as ice. This is the only temperature at which the solution can exist side by side with ice, as otherwise a *perpetuum mobile* would be possible. Since, therefore, this temperature, which is the freezing-point of the solution, is in inseparable connection with its vapour-pressure, the laws holding for the one must also hold for the other, and from this the laws already stated follow directly. Formulating these laws, we get $\Delta=r\frac{p}{ml}$ where Δ is the lowering of the freezing-point, l the weight of the solvent, p that of the substance dissolved, and m the molecular weight of the substance, while r is a constant dependent on the nature of the liquid. From the formula it follows: $m=\frac{rp}{\Delta l}$. Having, therefore, once for all determined the constant for a solvent, it is possible to find the molecular weight of a substance by determining the lowering of the freezing-point of its solution in that solvent. Van't Hoff has shown that the constant can be deduced thermo-dynamically from the heat of fusion of the substance.

If we now apply these methods for determining the molecular weights of dissolved substances to solutions of electrolytes, we find that the molecular weights appear smaller, and hence the number of molecules in solution are greater, than correspond with the formulæ. In many cases the amount of this deviation is very considerable, and its existence at first proved a great obstacle in the way of van't Hoff's theory of solutions. To Arrhenius (*Z. P. C.* 1) we owe the means of accounting for the deviation. The views propounded by this investigator have shed such a flood of light over difficult questions in chemistry and physics that we must consider the work of Arrhenius to be one of the most important advances ever made in this and in allied domains.

Arrhenius' idea consists in ascribing the deviations of the observed from the calculated molecular weights, to a dissociation of the electrolytes into their ions. From the magnitude of this deviation a conclusion can be drawn as to the number of molecules which are dissociated; the problem which was left unsolved by Clausius thus receives its solution.

Reserving the numerical proofs of the truth of this view till later on, it is proposed to deal first with some possible objections and difficulties of a general nature.

The application of the hypothesis leads to the conclusion that in moderately dilute solutions of strong acids and bases, and also of normal salts, as much as 80 to 90 per cent. of the substance in solution is dissociated into its ions. Hence a solution of potassium chloride contains little else than ions of chlorine and potassium. How is it that the chlorine does not escape into the air as a greenish yellow gas, and the potassium does not act on the water?

The answer lies in the consideration that the chlorine which we know as a greenish yellow gas is the electrically neutral molecule Cl_2, and does not consist of the separate atoms of Cl which are charged with a large amount of negative electricity.[1] The potassium again is not present as the compact metal, but in the form of strongly positively charged ions. Considering the great differences exhibited by allotropic forms of the same element (oxygen and ozone, red and yellow phosphorus, &c.), we cannot wonder that in these cases also considerable differences appear.

And it is further possible to produce solutions in which such ions—as, for instance, potassium—are present in excess, and therefore certainly in the free state. For this purpose, let us imagine two vessels filled with potassium chloride solution and placed on an insulating stand, and then connected conductively by means of a syphon filled with the solution. Let us now bring near to the one vessel a body charged with negative electricity. The vessel becomes charged positively by induction, and an equivalent quantity of negative electricity moves through the syphon into the second vessel. If we now remove the syphon, and then the body charged, the first vessel remains charged positively, the second vessel negatively. So far the experiment contains nothing that is new; it is the elementary experiment used for proving the inductive effect of electricity. If, however, we pay attention to the fact that, according to the law of Faraday, electricity can move in electrolytes only simultaneously with the ions, the conclusion is inevitable that an excess of potassium ions must be present in the vessel charged positively, and the same excess of chlorine ions must be present in the vessel charged negatively. These excesses of ions are maintained as long as the electric charge of the vessels exists. On discharging the vessels the ions give up their electricity, and the substances appear at the point of discharge endowed with their usual properties.

Owing to the magnitude of the quantities of electricity contained in the ions, the question may be raised whether the experiment which has just been indicated really can be carried out. Ostwald and Nernst have shown (*Z. P. C.* 3) that this is actually possible. By means of a mercury electrode contained in a capillary tube, such small quantities of hydrogen can be observed that the experiment becomes quite feasible. Since under ordinary conditions one gram of hydrogen occupies a space of about 12,000 c.c., a small bubble of 0·1 mm. diameter, which one can still see with the naked eye, has a weight of only 10^{-10} g., and one of 0·01 mm. diameter, which can be seen under a microscope, has a weight of only 10^{-13} g. This is as small a quantity of matter as can be recognised in any way, and the electricity combined with it can be detected in an apparatus of very moderate dimensions.

Thus the experiment described above is not only conceivable, but feasible; and thus it is proved that free ions, such as those of potassium, can be present in aqueous solutions without acting on the water.

The assumption that some of the molecules of electrolytes are split into ions in solutions explains many properties of these solutions. In the following paragraph we will assume for simplicity's sake that the splitting up is complete—an assumption which is nearly correct in the cases of salts, strong acids, and bases; the modifications which must be introduced into these considerations by taking into account the portions not split up, will be considered afterwards.

Let us consider, first, the chemical reactions of electrolytes. As is well known, certain reactions are used in analytical chemistry for indicating definite substances. These reactions must take place quickly, as otherwise they would be of no practical use; hence they must be reactions between ions. If asked what it is that the ordinary analytical reactions allow us to recognise, we are inclined to answer, the different chemical elements. But this is not at all appropriate. A solution of a salt of silver is called a reagent for chlorine, and in fact by its help chlorine can be detected in metallic chlorides. But the chlorine in potassium chlorate or in monochloracetic acid cannot be detected by means of silver solution. In the same way chlorides indicate silver; but the silver in potassium silver cyanide cannot be recognised by means of chlorides. The different oxyacids of sulphur also give quite different reactions, though they all contain the same elements; similarly, the reactions of iron, copper, mercury, tin, &c., are quite different, according to the degree of oxidation of the metal.

These examples prove that it is not the elements which are indicated by analytical reactions. A more careful consideration shows that since it is the ions which react, the ions are indicated by the analytical tests.

This simple proposition removes all the difficulties which confronted us. If a solution of silver is a reagent for chlorine ions, naturally it cannot indicate the chlorine in potassium chlorate, whose ions are K and ClO_3; nor in monochloracetic acid, whose ions are H and CH_2ClCO_2. And, conversely, silver is indicated by chlorides only where it appears as the ion; but the ions of potassium silver cyanide are K and $Ag(CN)_2$. The behaviour of chloroplatinic acid H_2PtCl_6 towards silver solutions is specially remarkable, a behaviour about which an incredible confusion has reigned in chemistry, because it has always been believed that its chlorine must be precipitated by silver solution as silver chloride. The matter was first cleared up by Jörgensen (*J. pr.* [2] 16), who found that no silver chloride is formed at all, but rather the silver salt of chloroplatinic acid Ag_2PtCl_6; sodium platinichloride is completely precipitated by two equivalents of silver solution only, instead of by six, which correspond to the proportion of chlorine.

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[1] From the number, already given, of 96,540 coulombs, which are combined with 1 g. of hydrogen and which are also present in one litre of normal potassium chloride solution—as positive electricity on the potassium, or negative electricity on the chlorine—it is possible to calculate that this quantity of electricity would suffice to charge a sphere of an approximate diameter of 10^{16} cm.—which, therefore, would be larger than the whole solar system—to a potential of one volt.

Thus the so-called anomalies of analytical reactions are fully explained. It is further explained why, for instance, all the different sulphates give the same reaction with barium chloride. The nature of the metal is of no account, because the reacting ion SO_4 is not combined with the metal at all, but exists by itself.

It is a remarkable fact that similarly constituted ions give, under certain conditions, different reactions. According to this view, the iron in a solution of $FeCl_2$, and also in a solution of $FeCl_3$, is contained as an ion; yet the two act differently. In like manner, solutions of $K_4Fe(CN)_6$, as well as those of $K_3Fe(CN)_6$, contain the same negative ion $Fe(CN)_6$, and these two substances give quite different reactions. The explanation lies in recognising that these similarly composed ions are endowed with different quantities of electricity according to their valency. Thus iron appears divalent and trivalent, mercury and copper monovalent and divalent, the atomic group $Fe(CN)_6$ tetravalent and trivalent, in that they contain corresponding numbers of positive or negative electric units or 'atoms.'

If the theory developed so far is correct, then all properties of salt solutions must be of an *additive* nature with regard to the two ions—*i.e.* their properties must be made up of two parts, one of which depends only on the positive ion, and the other only on the negative ion. This fact was recognised before it found an explanation in terms of the hypothesis of the independent existence of ions in solutions. Arrhenius drew attention to this fact (*Z. P. C.* 1) when he was establishing his theory. Some examples will make the point clearer.

In 1874 Valson enunciated a law concerning the specific gravities of salt solutions (*C. R.* 73), which he called the *law of the moduli*. By means of it the specific gravity of a 'normal' solution—that is, of a solution containing one equivalent of the salt in grams in one litre—of any salt can be found by adding to the specific gravity of a solution of ammonium chloride (chosen as the standard) two values, one of which depends on the metal only, and the other on the acid radicle only. According to Valson, these moduli are (NH_4ClAq of specific gravity 1015 being taken as the standard);—$K = 30$, $Na = 25$, $\frac{1}{2}Ca = 26$, $\frac{1}{2}Mg = 20$, $\frac{1}{2}Sr = 55$, $\frac{1}{2}Ba = 73$, $\frac{1}{2}Mn = 37$, $\frac{1}{2}Fe = 37$, $\frac{1}{2}Zn = 41$, $\frac{1}{2}Cu = 42$, $\frac{1}{2}Cr = 61$, $\frac{1}{2}Pb = 103$, $Ag = 105$; $Br = 34$, $I = 64$, $\frac{1}{2}SO_4 = 20$, $NO_3 = 15$, $\frac{1}{2}CO_3 = 14$, $HCO_2 = 16$. To these are added the value zero for NH_4 and Cl. These values allow us to calculate the specific gravities of solutions of 14 × 7 = 98 salts, and the calculations agree very well with experiment. Later on (1883), the law was confirmed by C. Bender (*W.* 20, 560), and by Nicol (*P. M.* [5] 18, 179), and was also extended by the first named.

A similar law was established by Gladstone (*Pr.* 16, 439) for the refraction-equivalents of salts. Gladstone expressed his generalisation in the form that the difference between the refraction-equivalents of the salts of two metals with the same acid is always the same, and is independent of the composition of the acid. The following table shows how the values agree in the cases of salts of potassium and sodium with acids of different compositions:—

	Potassium	Sodium	Difference
Chloride	18·44	15·11	3·3
Bromide	25·34	21·70	3·6
Iodide	35·33	31·59	3·7
Nitrate	21·80	18·66	3·1
Hydrate	12·82	9·21	3·6
Alcoholate	27·68	24·28	3·4
Formate	19·93	16·03	3·9
Acetate	27·65	24·03	3·6
Tartrate	57·60	50·39	3·6
Carbonate	34·93	28·55	2 × 3·2
Bichromate	79·9	72·9	2 × 3·5
Hypophosphite	26·94	20·93	2 × 3·0

A similar law exists for the salts of strong acids, but with the weak acids the differences are much greater. We are now in a position to account for this discrepancy, which was left unexplained by Gladstone. Since the weak acids are only very partially split into their ions, it cannot be expected that hydrogen as an ion should have the same refraction-equivalent as it has in the undecomposed compound.

Gladstone also enunciated the general law that the colour of the solutions of salts whose acid or whose metal form coloured compounds is independent of that of the other constituent (*P. M.* [4] 14, 418). If we consider how dependent colour is on constitution in other cases, this fact must be considered as a specially weighty proof of the mutual independence of the ions.

The knowledge of the fact that the characteristic colours of salts are dependent on the nature of the coloured ion only, and are independent of that of the other ion, has existed for a very long time, almost, as one might say, unconsciously. In green liquids we should always expect nickel, in red ones cobalt, in pale blue ones copper, &c. Some exceptions to this can easily be explained. One such exception is that most copper salts show the blue colour of the copper ions, while concentrated solutions of copper chloride appear green. The cause of this is that in concentrated solutions a considerable number of *undecomposed* molecules $CuCl_2$ are present, which molecules are coloured a deep yellow, as can be seen in dry copper chloride, which looks almost reddish brown. This yellow colour mixes with the blue colour of the copper ions, and produces the green colouration. From the fact that as the temperature is raised the green colour becomes more intense, it must be concluded that with rise of temperature more molecules $CuCl_2$ form at the cost of the ions (*v.* Ostwald, *Z. P. C.* 9, 579).

Another additive property has been found by Marignac (*A. Ch.* [5] 8, 410) in the specific heats of salt solutions. This property is, however, partly hidden by small deviations which, though capable of explanation, require the knowledge of some quantities the measurement of which has not yet been undertaken.

And, further, Ostwald (*J. pr.* [2] 18, 353) has proved such relations to hold in a fairly extensive manner for the volume-changes accompanying neutralisation. On saturating solutions of potash, soda, and ammonia by the same acid the total volume changes in a very different manner. These volume-changes are, however, governed by the law that on saturating two bases by the same acid the difference of the volume-changes is independent of the nature of the acid; and in like manner the difference in the volume-change on saturating two different acids by the same base is uninfluenced by the nature of the base. Hence the volume-change always depends on two constants, one of which is determined by the acid only, and the other by the base only; the specific nature of the salt formed has no influence. The following table shows these relations:—

	Potassium	Sodium	Ammonia
Nitric acid . .	20·0	19·8	− 6·4
Hydrochloric acid .	19·5	19·2	− 6·6
Hydrobromic acid .	19·6	19·3	− 6·6
Hydriodic acid .	19·8	19·6	− 6·4
Formic acid . .	12·4	12·1	−13·6
Acetic acid . .	9·5	9·3	−16·3
Monochloracetic acid	10·9	10·6	−15·1
Dichloracetic acid .	13·0	12·7	−13·0
Trichloracetic acid.	17·4	17·1	− 8·7
Isopropionic acid .	7·8	7·7	−17·8
Butyric acid . .	7·0	6·8	−18·6
Isobutyric acid .	6·3	6·1	−19·3
Glycollic acid. .	9·6	9·8	−16·5
Lactic acid . .	8·3	8·1	−17·7
Sulphuric acid .	11·9	11·5	−14·4
Oxalic acid . .	9·9	9·7	−16·1
Succinic acid. .	8·2	7·9	−17·6
Malic acid . .	8·6	8·5	−17·4
Tartaric acid. .	9·4	9·2	−17·0

The differences between the corresponding members of two horizontal or of two vertical columns in this table are seen to be constant within the limits of error. The all but complete equality of the values for the four first-named acids, which are almost completely split up into their ions, is remarkable.

The most striking case of the additive properties of salt solutions is, however, given by their thermal relations. Hess long ago established the law of the thermo-neutrality of salts; this law declares that there is no thermal effect on mixing the solutions of two salts provided that everything remains in solution. This fact is difficult to understand as long as we assume the existence in an undecomposed state of normal salts in solutions, since the mutual changes of the salts would have to proceed without any energy-change, and this is a behaviour without analogy. If we assume, however, that the solutions of the salts contain chiefly the ions of the salts, the fact becomes explicable, because on mixing the solutions, the ions remain unchanged, they do not influence each other, and hence there is nothing to cause thermal effects.

More remarkable still is the explanation which the theory gives concerning the heats of neutralisation of acids and bases. At first sight it seems as if no action could take place between such compounds, if we consider the strong acids and bases to be almost wholly separated into ions. Because if the solution of the acid, of the base, and of the salt contains ions only, no change ought to occur when the acid and the base are mixed. If, however, we consider the reaction more carefully, we arrive at different results. For instance, let there be given soda and hydrochloric acid; the reaction will be

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{Na} + \overset{-}{Cl} + H_2O$$

The ions sodium and chlorine remain unchanged; but since water conducts very badly, only a very slight separation of H_2O into the ions OH and H can occur, hence when the ions OH and H meet they must combine to form H_2O.

Hence the process of neutralisation in aqueous solutions is not a combination of the constituents of the salt, but only a combination of the constituents of water.

It is true that this remarkable result is somewhat contradictory of the usual views on the subject, but it is in complete agreement with the facts. If the process of neutralisation between acids and bases decomposed into their ions really consists only in a formation of water from hydrogen and hydroxyl, then *its concomitant phenomena must be independent of the nature of the acids and the bases.*

The most important of these concomitant phenomena is the heat of neutralisation. This value has been determined by different observers, with special exactness by Thomsen (*Th.* 1). A number of measurements are collected in the following table, calculated for one equivalent; the unit used is the rational calorie, K = 100 gram-units of heat:—

	NaOH	KOH	LiOH	½BaO_2H_2	½CaO_2H_2
HCl. .	137	137	137	139	139
HBr .	137	137	—	—	—
HI . .	137	136	—	—	—
HNO_3 .	137	138	—	140	139
$HClO_3$.	138	138	—	140	—
$HBrO_3$.	138	138	—	—	—
HIO_3 .	138	138	—	—	—
$HClO_4$.	141	143	—	—	—
½$H_2S_2O_6$.	135	—	—	139	—
½H_2PtCl_6 .	136	—	—	—	—

And, similarly, tetramethylammonium hydroxide, platinodiamine hydroxide, and triethylsulphine hydroxide give with hydrochloric acid 138, 137, and 137 K respectively.

From this table, which could easily be enlarged, it follows that the heat of neutralisation of the strong acids and bases is a constant, and is approximately equal to 13,700 cal. This number must be looked on as very nearly equal to the heat of formation of water from the ions $\overset{+}{H}$ and $\overset{-}{OH}$. (A more exact calculation gives 13,500 cal.) The small deviations which are still present originate in the fact that the splitting up of the acids and bases referred to, though very considerable, is yet not quite complete; it is in this undecomposed remnant that the individual nature of the two substances still asserts itself a little.

The conditions become quite changed when we consider the weak acids and bases. Here the constancy of the heat of neutralisation ceases completely, and values are observed which fluctuate between 163K and 10K. In these cases the quantities of heat which are concerned in the splitting up of the acid and the base into their ions must be taken into account, besides the heat of formation of water from its ions, and the heat of neutralisation may be represented by an expression of the form $N = 13{,}500 + A + B$, where $A + B$ is the quantity of heat necessary for decomposing the acid and the base into ions. As experiment has shown that the salts when in dilute solution are uniformly and nearly completely decomposed, their heats of decomposition need not be taken into account meanwhile. This formula also expresses a law which, discovered some time back by Favre and Silbermann (*A. Ch.* [3] 37, 486), has been confirmed by the younger school of thermo-chemists. This law is, that the difference between the heats of neutralisation of any two bases is always the same whatever acid is taken, and that likewise the difference between the heats of neutralisation of any two acids is independent of the base. This is only another expression for the proposition that the acid and the base each contributes towards the heat of neutralisation a definite portion, which is independent of the nature of the substance with which the acid or the base reacts.

Very similar facts may be noticed concerning the other phenomena which accompany neutralisation. A table has already been given (p. 189) showing that the same relations hold good for the changes of volume that accompany neutralisation; the strong acids and bases give, on neutralisation, very nearly the same change of volume, *i.e.* 20 c.c. per litre of normal solutions of acid and base. The same holds good for the changes in the refractive indices.

The electrical conductivity of electrolytes.—Ohm's law $I = \frac{E}{R}$ gives a definition of R, the resistance of a conductor. It has been shown that the resistance is dependent on the nature of the conductor, and on its dimensions, in that it varies directly as the length and inversely as the cross-section. It has been agreed to call the resistance of a conductor of cross-section 1 sq. millim. and length 100 centim. its *specific* resistance; this depends on the nature of the material of which the conductor consists, and on its temperature.

If we define a quantity $C = \frac{1}{R}$, and call it the *conductivity*, Ohm's formula becomes $I = EC$. We may best regard C as the power of the conductor to allow the electricity to pass through, or the power to transport the electricity. In the illustration of a current of water in a tube, C would be comparable to the cross-section of the tube. The conductivity is the reciprocal of the resistance. In calculating the strength of currents it is more convenient to work with resistances; if these are connected end to end, the total resistance is the sum of the individual resistances; but if the resistances are connected side by side, the conductivities must be summed up. For electro-chemical purposes the idea of conductivity has always proved more useful than that of resistance.

Measurements of resistances or of conductivities are made according to different methods, all of which rest on the application of the formula above given. For instance, we can measure the current strength, I, using the same electromotive force E (from a constant cell, as, for instance, a Daniell), there being included in the circuit at one time the resistance R, which is to be determined, and at another time a resistance of known magnitude R_0. We then get the equations $I_1 = \frac{E}{R_1}$ and $I_0 = \frac{E}{R_0}$, and from these $R_1 = R_0\frac{I_1}{I_0}$. It is not necessary to discuss here the various methods of measuring resistances.

As mentioned before, the unit of resistance used is the *ohm*—*i.e.* the resistance of a mercury column of 1 sq. mm. section, and 106 or 106·3 cm. length at 0°. The unit of conductivity is given by the same quantity; since this represents the reciprocal value of the resistance, it has been proposed to designate it by Mho, which is the name Ohm reversed, and for which Mo might be put shortly.

While so far the different powers for conducting electricity possessed by the metals have remained more a question of practical than of theoretical importance, the study of the electrical conductivity of electrolytes has led to most important and suggestive views as to their nature. These have only been arrived at quite lately, chiefly because until recently there existed no convenient and good method for determining the conductivities of electrolytes in solution.

The difficulty to be surmounted consists in the fact that the current must be conducted through the electrolyte by means of electrodes, and that these get coated with the ions which separate—*i.e.* they become *polarised*. In consequence of this the electrodes become the seat of new electromotive forces, the magnitude of which is variable, and therefore not capable of being determined exactly. One method only has been brought forward as yet in which this difficulty is completely obviated; it is due to Guthrie and Boys (*P. M.* 1880. 328), and consists in allowing a system of strong magnets to rotate rapidly round the axis of a cylindrical vessel filled with the electrolyte and suspended by a long thin wire. By this means currents are produced in the electrolyte (as would be produced in every conductor), the electrodynamic effect of which tends to rotate the vessel in the same direction. The strength of these currents is proportional to the conductivity of the liquid, and the vessel is rotated until the torsion of the suspending wire becomes sufficient to maintain equilibrium against this rotatory effect. We are therefore justified in putting the deviation as proportional to the conductivity, the velocity of the magnets remaining the same. As the currents produced in the electrolyte occur exclusively within it, no polarisation is possible. The method has not been applied, because the apparatus required is expensive and difficult to handle.

Becquerel and Horsford tried to bring up polarisation to its highest value by using strong currents. In this method the current is led through the electrolyte, then through an adjustable resistance, and finally through an instrument for measuring currents (galvanometer, &c.), and its strength is determined. The distance between the electrodes is next decreased by an accurately measured amount, and resistances are inserted until the strength of the current has regained its value; then the resistance inserted is equal to that possessed by the portion of the liquid taken out. The method suffers from the disadvantage that it is difficult to keep the electromotive force of polarisation constant as presupposed; and, further, the liquid is changed at the electrodes by the use of the stronger currents required, so that what we measure is the resistance of the changed, and not that of the original, liquid.

By using electrodes of zinc, which in solutions of zinc salts give no polarisation, Beetz (*P.* 117, 1) was able to determine the conductivities of such solutions by the methods used for metals. Paalzoff showed (*P.* 136, 489) that the method can be applied to other solutions also if we bring the two zinc electrodes into two separate vessels, and establish conduction through a syphon filled with the liquid to be investigated. The process is based on the fact that no polarisation is produced when a current is passed through the surface of contact of different liquids.

But this method is again far surpassed in convenience by one given by F. Kohlrausch (*W.* 11, 653), in which polarisation is made harmless by using alternating currents. Such currents, in which equal quantities of electricity flow alternately in opposite directions, are produced most easily by means of an ordinary induction apparatus. It is true that by such currents the electrodes are also polarised, but the polarisations occur rapidly in opposite directions, so that the polarisation produced by the first current-impact increases the strength of the second current-impact which has the opposite direction, and the polarisation resulting from the latter adds itself on to the third current-impact, and so on. Kohlrausch has shown that by using platinum electrodes of ten sq. cm. surface coated with platinum black, the effect of polarisation may be reduced to less than 0·1 p.c. of the resistance. Kohlrausch uses for his method Wheatstone's bridge in Kirchhoff's arrangement. For details reference is made to Kohlrausch's memoir.[1]

The definition of specific conductivity as given above, and as employed in physics, is not of practical use in considering electrical conductivity from the point of view of the chemist. Since, according to the law of Faraday, the ions alone conduct, and since each ion carries the same quantity of electricity, it is evident that the conductivities of different solutions must be referred to the same number of ions in order to obtain comparable numbers. That we may form a conception of *equivalent conductivity* following from this, let us imagine two electrodes of indefinite extension placed at a distance of 1 cm. apart, and let there be brought between them so much of a solution as contains the equivalent weight in grams of the dissolved electrolyte; the conductivity of such a system is the *equivalent conductivity* of the electrolyte. In order to find the relation between the specific and the equivalent conductivity, we bear in mind that the length of the solution of the electrolyte is 106 times less than 106 cm., which was the length of the conductor assumed in the definition of specific conductivity. When the solution is normal—*i.e.* contains one g. equivalent per litre—the cross-section is 1,000 sq. cm.; when the same weight is dissolved in v litres it is 1,000v sq. cm.; this is 100,000v times greater than the cross-section for the specific conductivity, which is ·01 sq. cm. Hence from the specific conductivity l we obtain the equivalent conductivity λ by the equation $\lambda = 1{\cdot}06 \times 10^7 lv$. It should be remembered that the specific conductivity of an electrolyte is not usually referred to ohms, but to the unit of Siemens, formerly commonly employed, which is equal to the resistance of a column of mercury 100 cm. in length; hence instead of 106 we must put only 100, and the equivalent conductivity becomes $\lambda = 10^7 lv$.

In addition to the equivalent conductivity we can calculate the *molecular conductivity*, which is as many times greater than the equivalent conductivity as the molecular weight contains the equivalent weight. So the molecular conductivity of sulphuric acid is twice as great as the equivalent conductivity, that of aluminium chloride three times as great.

For the general facts which have been established regarding equivalent conductivities we are specially indebted to Kohlrausch, and to several investigators who succeeded him. The most simple relations are exhibited by dilute solutions in which v is greater than 1 lit., and these will be considered first.

1. The equivalent conductivities of normal salts are of the same order of magnitude, but are not the same (Kohlrausch).

2. The conductivities of all salts increase slowly with increase of dilution, and generally reach a maximum value, which is not surpassed after dilutions of 20,000 to 50,000 litres per gram-equivalent (Kohlrausch).

3. The increase of conductivity is least for salts which consist of two monovalent ions; it is about twice as great for salts which contain one divalent and one monovalent ion; and about four times as great for salts whose ions are both divalent (Ostwald).

4. The equivalent conductivities of equally concentrated solutions of the most different salts can be represented as the sum of two constants, one of which is determined solely by the positive ion, the other solely by the negative ion (Kohlrausch). This law agrees the better with experience the more dilute the solutions are.

In order to give an illustration of these laws, I append the equivalent conductivities of several normal salts as measured by Kohlrausch. The values are for 18°.

Dilution	KCl	NaCl	LiCl	$\frac{1}{2}BaCl_2$	$\frac{1}{2}K_2SO_4$	$\frac{1}{2}MgSO_4$
1l	91·9	69·5	59·1	65·8	67·2	27·0
10l	104·7	86·5	77·5	86·1	89·7	47·4
100l	114·7	96·2	87·5	100·6	109·8	71·5
1,000l	119·3	100·8	92·1	109·2	120·7	93·5
10,000l	120·9	102·9	94·3	112·6	124·9	103·4
50,000l	121·7	102·8	95·5	114·4	126·6	105·2
100,000l	121·6	102·4	96·5	114·2	127·5	105·6

If we attempt to form a picture of the processes occurring in electrolytic conduction, we must first bear in mind that, according to the statements of Kirchhoff (*P.* 78, 506), free electricity must be present along the surface of each current-path; and the fall of this potential causes the motion of the electricity inside the conductor. Hittorf pointed out that the theories of electrolysis hitherto held could not satisfy this requirement. Assuming the presence of free ions, it is evident at once that the surface charge is formed by these. Owing to the fall of potential which exists, the positive electricity is now driven to the one side, the negative to the other. Both are bound to the ions; which are, therefore, moved in the same way by forces that are of equal magnitudes on both sides.

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[1] A detailed description of the method for carrying out such measurements is to be found in *Z. P. C.* 2, 561.

The velocities acquired by the ions under the influence of these equal and opposite forces will not generally be the same, since it cannot be assumed that the resistances to motion encountered by the ions in the solution will be the same. But in dilute solutions, anyhow, the nature of the second ion, travelling in the opposite direction, will have no influence on the velocity of any definite ion—such as, for instance, Cl. Hence the conductivities of salts, when referred to equal quantities of ions, can be represented as the sum of the migration-velocities of the positive and negative ions. Calling these migration-velocities u and v, we get

$$\lambda = u + v.$$

But this is exactly the relation discovered by Kohlrausch (p. 191), to whom also the argument just given is due.

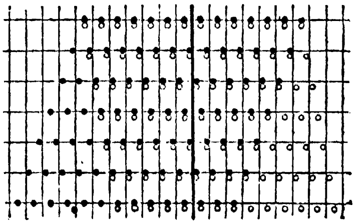
Viewed thus, the phenomena of electrical conductivity are brought into connection with another group of facts, the comprehension of which had presented great difficulties to the older naturalists. These are the phenomena of the '*migration of the ions.*' It has been mentioned that Daniell observed the corresponding manifestations, but they were not explained till Hittorf did so.

From the table already given it follows that the different ions must possess very different migration-velocities. On comparing, for instance, KCl and LiCl, we find differences of 27 to 30 units. Since the chlorine must possess the same velocity in both cases, and hence participate to the same amount in the conductivity, the difference is due solely to the ions K and Li. In the same manner we can convince ourselves that different negative ions migrate with different velocities.

On electrolysing a substance whose ions travel with different velocities, different quantities of the ions will collect at the electrodes, and, in addition to decomposition, the liquid will undergo an unequal change of concentration at the electrodes. In order to get as good a representation as is possible for these relations, let the ions be represented in the figure in the next column by black and white circles. The different horizontal rows represent different phases of the electrolysis, these being such that between them there is a distance equal to the mean distance of the ions. It is assumed that the black ions migrate twice as quickly to the left as the white ones do to the right. At first there are seven ions on each side of the central line. At the end of the process six ions have been liberated at each end, and, in addition, five out of the seven pairs have remained behind at the left side, and two have disappeared; while of the equal quantity at the right side three have remained behind and four have disappeared. Hence the proportion of salt has decreased at the right side twice as much as at the left—that is, *in the same ratio as that in which the two ions migrate.*

Therefore, in order to determine the ratio of the migration-velocities of the two ions of a salt it is only necessary to determine the proportion of undecomposed salt at each electrode before and after electrolysis; the ratio of the decrease of this proportion at each side is equal to the ratio of the migration-velocities, or is the 'migration-measure.'

This representation holds good on the supposition that the ions which separate at the electrodes do not again go into the solution. If, however, we electrolyse a solution of copper sulphate between copper electrodes, the copper, it is true, will leave the solution at the cathode, but the ion SO_4 will not separate out at the anode, but will combine with the copper of the anode to form copper sulphate, which will go into solution. The solution will, therefore, become, not more dilute, but more concentrated. It is, however, easy to take this circumstance into account. It is only necessary to determine the total quantity of electricity passed through the solution (for instance, by means of a silver voltameter); from this we can calculate how much copper has gone into solution, and we need then only deduct this quantity from the total quantity of copper at the anode, as determined by analysis. It is simpler still to weigh the cathode before and after the experiment: the increase of weight is equal to the weight of copper which has dissolved at the anode.



Hittorf examined (*P.* 89 to 106) a great many salts and acids with respect to their 'migration-measures,' and established the fact that the current-strength has no influence on the ratio of the migration-velocities, the temperature has an inappreciably small influence, but the concentration exerts a changeable effect—in some cases it is inappreciably small, while in others it is fairly important.

Hittorf found, for instance, that the concentration of KClAq at the electrodes scarcely changes at all; hence chlorine and potassium must migrate with very nearly equal velocities. If we consider the solution $v = 1{,}000l$ in the table given on p. 191, it follows that of the 119·3 units of conductivity of potassium chloride, 59·65 belong to the chlorine and the same number to the potassium. Knowing these numbers, we can calculate the velocities of migration of all the other ions in the table. NaCl has 100·8; on subtracting from this 59·7 for the chlorine, the velocity of the sodium ion becomes 41·1. Similarly, Li = 32·4, $\frac{1}{2}$Ba = 49·5. As K = 59·7, and as $\frac{1}{2}K_2SO_4 = 120{\cdot}7$, it follows that $\frac{1}{2}SO_4 = 61{\cdot}0$; hence $\frac{1}{2}$Mg = 32·5.

From these numbers we can again calculate the migration-measures, or the changes of concentration at the electrodes, of other salts.

Thus $\frac{u}{v}$ is for NaCl $= \frac{41 \cdot 1}{59 \cdot 7} = 0 \cdot 69$; for LiCl $\frac{32 \cdot 4}{59 \cdot 7} = 0 \cdot 54$; for $BaCl_2$ $\frac{49 \cdot 5}{59 \cdot 7} = 0 \cdot 83$, &c. It is evident that when one migration-measure is known, the migration-measures of all corresponding salts can be calculated from the measured conductivities. And since, on the other hand, the conductivities of salts represent the sums of the velocities of their ions, we can realise the very great simplification which these considerations, due to F. Kohlrausch, have produced in the relations of electrical conductivity which formerly appeared so complicated. If, for instance, we know the conductivities of ten salts with the negative ion A and the positive ions B_1 to B_{10}, and of other ten salts with the ion B_1 and the ions A_1 to A_{10}, and in addition to these the migration-measure of one salt, we can calculate from these 21 measurements the conductivities and the migration-measures of 100 salts – that is, we can deduce 200 data.

An extensive examination of these relations, undertaken by Kohlrausch (*W.* 6, 164), and later by Ostwald (*Z. P. C.* 1, 74), as well as by Loeb and Nernst (*ib.* 2, 948), has proved that they hold good with very sufficient accuracy for very dilute solutions. But deviations from these relations become apparent in concentrated solutions, and these deviations are greater the more concentrated the solutions. And, further, different salts behave differently, inasmuch as salts consisting of two monovalent ions show the smallest deviations, salts with one monovalent and one divalent ion show greater deviations, and salts with two divalent ions show the greatest deviations. Now these are the classes of salts which exhibit differences in the changes of conductivity accompanying dilution (p. 191), and we are, therefore, led to the conclusion that the same cause underlies both phenomena.

The free acids and bases only partially conform to Kohlrausch's law. The following data, taken from Kohlrausch's determinations, exemplify this statement. Temp. = 18° :—

preserving very dilute solutions of alkalis perfectly pure.

From these measurements it follows primarily that hydrogen and hydroxyl possess much greater migration velocities than the other ions – namely, 284 and about 150, respectively. It follows, therefore, that if the law of Kohlrausch were generally valid, the conductivities of all acids would be > 284, and the conductivities of all bases would be > 150. On looking at the numbers in the table, we find that phosphoric acid and acetic acid, as well as ammonia, are at a quite hopeless distance from these values. Sulphuric acid, also, does not obey the law. For $\frac{1}{2}SO_4$ the value 61·0 was found above; on deducting this number from $\frac{1}{2}H_2SO_4 = 331 \cdot 6$, there remains $H = 270 \cdot 6$, and the difference of this value from the one found before, 284, exceeds the limits of experimental error.

On carefully studying the table we now see that the acids and bases which form exceptions to the law exhibit the same peculiarity as the exceptional salts; they change their conductivities very markedly upon dilution. While the substances which follow the law have nearly reached the maximum of the equivalent conductivity at 1000*l*, the numbers show that this is far from being the case in the exceptional substances. We are thus led to inquire as to the cause which brings about the change in conductivity that accompanies dilution.

The arguments used so far have tacitly assumed that all the molecules of the electrolyte participate in the electrical conductivity, and that the electrolyte is therefore completely split into ions. This assumption is evidently arbitrary; and when we remember that aqueous solutions of ammonia and acetic acid exhibit nearly normal lowerings of the freezing-points, and that, therefore, dissociation occurs only to a small extent, if at all, we see that the assumption is completely erroneous in these cases. The former equation $\lambda = u + v$, established without reference to the degree of decomposition, must be changed into $\lambda = x(u + v)$ where x represents the degree of decomposition—*i.e.* the ratio between the molecules decomposed and the total number of molecules orginally present. In doing this we make the most obvious, and probably only possible, assumption, that, *cæteris paribus*, the conductivity is proportional to the number of conducting particles or ions.

Dilution	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	$\frac{1}{3}H_3PO_4$	$CH_3.CO_2H$	KOH	NaOH	NH_4OH
1*l*	278·0	277·0	188·9	29·0	1·2	171·8	149·0	0·84
10*l*	324·4	322·5	208·4	43·0	4·3	198·6	170·0	3·1
100*l*	341·6	339·5	285·5	79·0	13·2	212·4	187·0	9·3
1000*l*	345·6	342·7	331·6	96·8	38·0	214·0	188·0	26·0

Among the substances quoted, HCl, HNO_3, KOH, and NaOH follow the law of Kohlrausch. Thus, if 59·7, which is the migration-velocity of K, is deducted from 118, which represents the conductivity of KNO_3 as determined by Kohlrausch, the difference, 58·3, is the velocity of NO_3. On deducting this number from the conductivity of nitric acid at 1000*l* – that is, from 342·7—it follows that the velocity of hydrogen is 284·4. From HCl = 345·6 it follows that H = 285·9, since Cl = 59·7; these numbers agree to within less than one per cent. In the same way the difference between KOH and NaOH is equal to 26·0, thus approximating to equality with that between KCl and NaCl, which is 19·2. The larger difference proceeds from the difficulty of

We may find a method for determining x in the deviations of electrolytes from the simple laws of solutions with respect to vapour-pressure and freezing-point. We have another and much more accurate method, however, in the determination of the electrical conductivity itself. As was found by Kohlrausch, the equivalent (and also the molecular) conductivity increases with rising dilution, reaching a maximum value in the case of salts within limits which are still practically measurable. We can interpret this behaviour from the standpoint now gained in the sense that the number of molecules split into ions continually increases with increasing dilution, and that the maximum value of conductivity corresponds to a (practically speaking) complete splitting up. Then $x=1$, and the formula $\lambda = x(u+v)$ changes into the former, $\lambda = u+v$. Now, for most salts the maximum value is reached at a dilution of 1000*l*, and the decomposition is nearly complete; it follows from this, that the law of Kohlrausch $\lambda = u+v$ holds good for this maximum dilution. This can be asserted for the strong acids and bases, such as HCl, HNO_3, KOH, and NaOH. On the other hand, as can easily be seen from the course of the numbers, the increase has not nearly reached its limit for acetic acid and ammonia at a dilution $=1000l$; hence the value x is still very far removed from unity, and the law of Kohlrausch cannot hold in its simplest form.

On the assumption that the molecular conductivities of dilute solutions depend only on the number of ions present, the values of x can be easily calculated from a knowledge of the values of the conductivities at different dilutions, as well as of their maximum values; designating the molecular conductivity at the dilution of v litres by μ_v, and the maximum value by μ_∞, then, according to the assumption made, $x = \frac{\mu_v}{\mu_\infty}$.

Whether the above-mentioned assumption is strictly correct cannot be asserted *a priori*. It must be looked upon as probable, since the resistances to motion which the ions experience, and which determine the velocities u and v, depend on the nature of the solvent, which in these cases is water; and considering the small differences which exist between the properties of very dilute solutions and those of water, no appreciable difference in the resistances to motion can be supposed to exist in those differently diluted solutions. But the admissibility of the assumption can also be put to experimental proof in determining x on the one hand by the deviations from the laws of solution, and on the other hand by the equation just given.

If m_0 is the theoretical molecular weight, and m the molecular weight determined from the laws of solution (for instance, from the lowering of the freezing-point), then for electrolytes $m > m_0$; following van't Hoff, we put the ratio of the two $\frac{m_0}{m} = i$. If, on the other hand, x is the number of molecules split up, the total number of molecules being put equal to 1, and if n is the number of ions into which each molecule splits (for KCl $n=2$, for $BaCl_2$ $n=3$, &c.), the number of molecules in the solution will have increased in the ratio $1 : 1-x+nx$, that is, in the ratio $1 : 1+(n-1)x$, and we have, therefore, $i = 1+(n-1)x$.

Arrhenius, to whom we owe this calculation, has shown (*Z. P. C.* 1, 634) that in the greatest number of cases investigated there is an excellent accordance between the values of i as calculated from the electrical conductivities and those deduced from the freezing-points. Individual cases which at first seemed to be exceptions have, on later investigation, also proved to be subject to the law (*Z. P. C.* 2, 491), and the apparent deviations have been shown to be due to incorrect observations. It is only at greater concentrations, where the suppositions made in determining molecular weights from the freezing-points, and those made in determining x from the electric conductivities, become uncertain, and not applicable, that marked deviations are apparent.

In addition to this confirmation of Arrhenius' assumption that in electrolytes a more or less considerable portion of the molecules is split up, a further confirmation has been found by W. Ostwald, which is based on the following considerations (*Z. P. C.* 2, 36, and 270). The spontaneous decomposition which the electrolytic molecules undergo in solutions is of the nature of dissociation; and since, according to van't Hoff, the substances in solution are subject to the gaseous laws, it must be possible to represent the process by the same formulæ as hold for the dissociation of gases. Considering the simplest case, that each molecule splits into two parts, there holds for gases (vol. ii. p. 406) the relation $\frac{p_2^2}{p_1} = \text{constant}$, where p_1 is the partial pressure of the undecomposed portion, and p_2 that of the decomposed portion.

In order to apply this equation to electrolytes, we notice that the pressures are proportional to the numbers of the molecules, and inversely proportional to the volumes occupied by these. If x is the part dissociated, and v the volume, then $p_1 = a\frac{1-x}{v}$ and $p_2 = a\frac{x}{v}$; a represents a factor dependent on the units chosen. Further, according to the former equation, we have $x = \frac{\mu_v}{\mu_\infty}$; introducing these values into the dissociation equation, we get $\frac{1-x}{x^2}v = k$, where k is a constant, and from this $\frac{\mu_v^2}{(\mu_\infty - \mu_v)\mu_\infty} = kv$.

This equation represents a relation between the conductivity and the volume, or the dilution, which must be followed by all binary electrolytes, if the assumptions made are correct.

The equation cannot well be tested in the case of salts, as these very nearly reach complete decomposition; the value $\mu_\infty - \mu_v$ thereby becomes very small, and the experimental errors exert a preponderating influence. Those electrolytes which are only partially dissociated, such as acetic acid &c., lend themselves much better to applying the test. Here also it seems as if a difficulty met us, the quantity μ_∞ not lending itself to direct measurement because, with the very great dilutions necessary, the inevitable impurities of the purest water make accurate measurements impossible. But the law of Kohlrausch provides us with a means for making the measurements. It appears that the *salts* of weak acids are dissociated to just the same extent as those of strong acids; it is possible, therefore, as was shown at pp. 192–3, to calculate the migration-velocity of the negative ion. On adding to this the migration-velocity of hydrogen, which can also be determined (p. 193), the sum represents the conductivity of the completely dissociated acid—that is, μ_∞, the quantity sought (Ostwald, *Z. P. C.* 2, 840).

In this manner, then, we obtain all the data for testing the above equation, and it proves itself to be in direct accordance with the facts. The examination is best carried out by calculating the constant k for a number of values of μ at different dilutions, and seeing whether it really is constant. In the following tables a few examples are given. The numbers hold for 25°, and are molecular conductivities referred to the mercury unit:—

Acetic acid, $\mu_\infty = 364$.

v	μ	$100\frac{\mu}{\mu_\infty}$	k
8	4·34	1·193	0·000180
16	6·10	1·673	179
32	8·65	2·380	182
64	12·09	3·33	179
128	16·99	4·68	179
256	23·82	6·56	180
512	32·20	9·14	180
1024	46·00	12·66	177
			0·000180

The values of k, calculated from eight different measurements, agree within the limits of experimental error.

The osmotic pressure of acetic acid at $v = 8$ corresponds to about three atmospheres, that at $v = 1024$ to about $\frac{1}{45}$ atmosphere, or to 1·7 mm. mercury pressure. The dissociation law has, therefore, proved correct within these wide limits; no examination of the law so far-reaching as this has ever been possible in the case of gases.

Further examples are:—

Cyanacetic acid, $\mu_\infty = 362$.

v	μ	$100\frac{\mu}{\mu_\infty}$	k
16	788·0	21·7	0·00376
32	105·3	29·1	373
64	139·1	38·4	374
128	176·4	48·7	361
256	219·1	60·5	362
512	260·9	72·0	361
1024	297·3	82·1	368
			0·00370

Here also the individual values of the constant vary irregularly about the mean value, so that the discrepancies have to be ascribed to experimental errors.

In the accompanying tables, which have been taken at random from a great number, the dissociation law proves itself everywhere to be accurate. It has, in fact, been verified in every case in the course of an investigation which, for reasons to be discussed later, has been carried out with more than 400 acids, and it can be looked upon as generally valid.

Oxyisobutyric acid, $\mu_\infty = 355$.

v	μ	$100\frac{\mu}{\mu_\infty}$	k
32	20·05	5·65	0·000106
64	28·05	7·91	106
128	38·86	10·95	105
256	53·91	15·20	106
512	73·49	20·70	106
1024	99·52	28·05	106
			0·000106

Oxysalicylic acid, $\mu_\infty = 356$.

v	μ	$100\frac{\mu}{\mu_\infty}$	k
64	84·1	23·6	0·00114
128	112·5	31·6	114
256	147·0	41·3	113
512	187·0	52·6	114
1024	230·0	64·7	116
2048	270·4	76·0	117
			0·00115

Orthochlorobenzoic acid, $\mu_\infty = 356$.

v	μ	$100\frac{\mu}{\mu_\infty}$	k
64	89·2	25·1	0·00131
128	119·4	33·5	131
256	156·1	43·8	133
512	197·0	55·3	133
1024	238·7	67·1	134
			0·00132

We must not omit to remark, however, that, as observed above in the cases of the very strong acids, and the neutral salts, which are very nearly completely dissociated, the calculation of the constants becomes very uncertain, and that greater deviations exist between the observations and the formula than can be ascribed to experimental errors. Which of the assumptions already made will have to be modified in order to explain these small discrepancies cannot as yet be determined; but anyhow the discrepancies are so inconsiderable, and there are so many cases of agreement, that the deviations must be looked upon as of a secondary nature, and undoubtedly they will receive their explanation later on. It is well not to pass over in silence, nor to attempt to hide, such deviations from a law which is otherwise generally valid, since in most cases theoretical progress is connected with the investigation of the causes of deviations from general laws. Examples of this are found in the deviations of gases from the simple laws, and the theory connected with this by van der Waals, and in the deviations of some substances from the law of Avogadro and the elucidation thereof by the theory of dissociation.

Chemical applications.—The laws of electrical conductivity, as developed in the preceding pages, give us the means for solving many chemical problems. This they do, because they ive a deeper insight into the constitution of issolved substances than is afforded by the isual chemical methods. A series of such appliations is already contained in the preceding ages; others are considered in the following aragraphs.

The first of these applications is connected vith the question as to the nature and composiion of the current-conducting particles or ions f salts. The conception of Berzelius that these re the 'anhydrous' acid and base has, in the ight of Faraday's law, been recognised as erroeous. Afterwards, in analogy with the comounds of organic chemistry, the salts were looked ipon as having a unitary composition, and this iew is still generally held. But this conception annot be regarded as quite correct, since it does not take into account the fundamental difference which undoubtedly exists between salt-like compounds and indifferent compounds, a difference which manifests itself chiefly in the capacities for reaction of the two groups. The conception of Berzelius rested on the correct recognition that salts are dual compounds; he had only misconceived their constituents.

The new electro-chemical theory of Arrhenius avoids both errors, and retains what is correct in each conception. The solid salts, and, according to concentration, a greater or smaller portion of the salts dissolved in water, 'salt' being understood to include acids and bases, have, it is true, a unitary composition; but that portion of them which is capable of reacting chemically, and which therefore is of preponderating interest to the chemist, is split binarily.

'Salts,' in the general meaning, are therefore substances which very readily undergo such a binary splitting, and herein lies their binary character, correctly recognised by Berzelius.

It is a most remarkable fact that in the splitting up of 'salts' their constituents appear in oppositely charged electrical conditions. This indicates that probably both phenomena stand in the closest connection. It may be asked whether the salts split up so easily because their parts readily acquire opposite electric charges, or, conversely, whether the parts are easily charged electrically because they are readily separated. Not less remarkable is the fact that whenever a salt molecule is split up an equal quantity of electricity is produced (or separated), independently of the nature of the parts. It is beyond doubt that this fact is of decisive importance for the recognition of the nature of electricity, as well as of that of chemical affinity; when the one is elucidated, the other will be so also. But which of the two will first be thus advanced cannot as yet be foreseen.

A further remarkable fact is, that pure salts at ordinary temperatures do not conduct appreciably; the ordinary solid salts do so as little as pure sulphuric acid, acetic acid, &c. Even the halogen acids HF, HCl, HBr, and HI, when liquefied by pressure or cold, are all non-conductors. According to the dissociation theory of electrolytes this is quite conprehensible; the pure substances do not conduct because they are not dissociated, and they are not dissociated because their molecules have no space wherein to dissociate, or because they do not possess sufficient mobility.

Whether dissociation occurs or not when salts are dissolved depends in a marked way on the nature of the solvent. Hydrochloric acid, which when liquid is not dissociated, dissociates at once when dissolved in water. But on using as solvent benzene, xylene, hexane, or ether, no dissociation ensues; these solutions are non-conductors (Kablukoff, *Z. P. C.* 4, 430). On using alcohols as solvent, methyl alcohol is found to behave almost like water; the solutions of hydrochloric acid in it have a molecular conductivity about three times smaller than aqueous solutions. The conductivities of the solutions become less and less as we use ethyl alcohol, isobutyl alcohol, and isoamyl alcohol.

It is still quite unknown what the condition is which determines the property of different solvents to cause dissociation to a different degree, and it is not known whether, as is somewhat probable, these effects remain proportional in the cases of all salts. Here it seems, however, as if the capability of the solvent itself to separate into ions, even if to a small degree only, determined its power to cause the dissociation of substances dissolved in it.

Although the questions just mentioned still await solution, partly for lack of experimental researches in this domain, yet the new conception of the binary character of salts allows us to distinguish more sharply between the different classes of these compounds than was possible before. This is especially so in the case of the so-called *double salts*. This name is at present somewhat uncertain in its application. Potassium copper sulphate $K_2SO_4.CuSO_4$ is called a double salt, but sodium platinichloride is also formulated as such, $2NaCl.PtCl_4$; the first formula is correct, but the latter is wrong. This is so because potassium copper sulphate gives all the reactions of potassium sulphate as well as those of copper sulphate, but from sodium platinichloride silver solutions do not precipitate silver chloride as from sodium chloride, but silver platinichloride Ag_2PtCl_6 (Jörgenson, *J. pr.* [2] 16, 345). It is probable, therefore, that sodium platinichloride is a salt of chloroplatinic acid H_2PtCl_6. If this is correct, the ions of the sodium salt are 2Na and $PtCl_6$, and in electrolysis the platinum must not, like the other metals, go to the cathode, but as a constituent of the acid radicle to the anode. And, in fact, Hittorf has proved (*P.* 106, 520) that this is the case.

Similarly with other salts; for instance, that which is obtained from chromium oxide and potassium binoxalate, and which has the empirical formula $3K_2C_2O_4.Cr_2(C_2O_4)_3$. Since this salt gives no pp. with calcium salts it cannot be regarded as an oxalate. In fact, in electrolysis the chromium goes to the anode; the chromium is, therefore, a constituent of the acid radicle, and the salt must be looked upon as the potassium compound of a tribasic chromoxalic acid $(HC_2O_4)_3Cr$—that is, as $K_3C_6O_{12}Cr$ (Kistiakowsky, *Z. P. C.* 6, 107).

Such salts, therefore, are not double salts, but are salts of complex acids; it is possible to test, in the way already indicated, in every case whether a definite salt is a true double salt or the salt of a complex acid. On examination we find that, not a double salt, but a salt of a complex acid is present whenever the reactions of the salt in question are not those of its constituents. This decision is specially convenient when the solution of the salt is coloured. Because, since the properties of the positive ions, and therefore their colour also, are independent of the negative ions, it will always be possible to conclude that the positive ions are no longer present when their colouration disappears. In the easily decomposable salt $2KCN.Ni(CN)_2$ we must not see a double salt, but the potassium salt of cyano-nickelic acid $H_2Ni(CN)_4$, because its solution is yellow, and not green as solutions of the nickel salts are which contain nickel as an ion.

The line of demarcation between the two groups of salts, however, is not absolute, as many salts exist which in aqueous solutions are both double salts and also complex ones. This is the case with potassium ferri-oxalate, for instance. Since this salt is green, while all true ferric salts are yellow or brown, it may be concluded that it is a complex salt, the compound of a ferri-oxalic acid $H_3C_6O_{12}Fe$ analogous to the above-mentioned chromo-oxalic acid. The solution of this salt gives, however, a precipitate with calcium solutions, which proves it to be an ordinary oxalate, but on the other hand the iron goes to the anode. From this it is seen that the aqueous solution contains chiefly the ions $3K + C_6O_{12}Fe$, but that a portion of the salt has split in the manner of a double salt into potassium oxalate and ferric oxalate, which on their part form the corresponding ions.

The study of such cases has as yet scarcely been begun, because until now we possessed neither theoretical nor experimental means for answering the questions which arise. The electrical methods, in conjunction with the methods for the determination of molecular weights arising out of the theory of solutions, now afford easy access to these hitherto closed and uncultivated domains.

The dissociation-constants of organic acids. The only province of chemistry which has been studied somewhat thoroughly in the light of the new electro-chemical theory is that of the organic acids. We have seen above that the molecular conductivity of these can be represented by the formula $\frac{\mu^2_v}{(\mu_\infty - \mu_v)\mu_\infty} = kv$. This formula contains only the single constant k, which constant depends on the nature of the acid, the temperature, and the solvent, but is independent of the dilution. At a given temperature, and in the same solvent, the quantity k is therefore a measure of the electrical conductivity, and hence it is the capacity for reaction of the acid; for the substance considered, k therefore represents the long sought for *numerical value of the chemical affinity.*

It is remarkable that the two conflicting views concerning the nature of chemical affinity, as represented by Bergmann and Berthollet (*cf.* vol. i. 68) here coincide. Berthollet, who represented the affinity as dependent on the mass, was right, and so was Bergmann, who desired to represent it by a constant. By accurately formulating the idea of the influence of mass as given by Berthollet, we obtain in the equation for the chemical effects a co-efficient independent of the quantity—that is, one referred to the chemical unit of quantity, which is Bergmann's measure of chemical affinity.

It has already been shown (vol. i. 81) that the electrical conductivities bear a definite relation to the composition and constitution of the acids. But the law of dissociation of electrolytes had not been discovered at the time when the article referred to was written, and the observed relations could not be represented numerically. This has now become possible, by means of the values of the constant k, which have been measured for about 400 acids (Ostwald, *Z. P. C.* 3, 170; Bethmann, *ib.* 5, 385; Bader, *ib.* 6, 289).

Before expounding these relations, it will first be shown how the laws which have been found empirically for the electrical conductivities follow directly from the above dissociation-formula. In order to make the consideration easier, the formula will first be somewhat simplified by substituting for the molecular conductivity μ_v its value referred to the maximum $\frac{\mu_v}{\mu_\infty} = m$. The equation then assumes the simple form $\frac{m^2}{1-m} = kv$.

In the first place, we see that as the dilution v increases infinitely, the quantity $1-m$ must approach zero. Hence m must approach unity; hence the electrical conductivity increases with dilution up to a maximum, as has been shown by experience.

Further, it was found that when at any dilutions, v_1 and v_2, two different acids have the same (relative) conductivity, they also have the same at other dilutions v_1' and v_2', as long as the new dilutions are in the same ratio as the old ones—that is, when $v_1 : v_2 = v_1' : v_2'$. This follows from the formula in this way: on the supposition that the relative conductivities are the same, we have first of all $\frac{m^2}{1-m} = k_1v_1$; $\frac{m^2}{1-m} = k_2v_2$; therefore $k_1v_1 = k_2v_2$. And in the same way for the other dilutions, $k_1'v_1' = k_2'v_2'$, from which it follows directly that $v_1 : v_2 = v_1' : v_2'$.

In addition, F. Kohlrausch had already pointed out that in the cases of acids which conduct badly (which, therefore, are but little dissociated), the molecular conductivity increases nearly as the square root of the dilution. If in the equation $\frac{m^2}{1-m} = kv$, m is very small, $1-m$ differs little from unity, and can be looked upon as constant; then approximately, $m^2 = kv$, or $m = \sqrt{kv}$.

Finally, on taking the logarithms of the dilutions as abscissæ and the values of m as ordinates, we also get from the formula a curve resembling a tangent-function (vol. i. page 82); the interpolation-formula given in vol. i. must be replaced by the present rational formula.

As regards the meaning of the constant k, we recognise what this is on putting $m = 0{\cdot}5$, when we get $2k = \frac{1}{v}$. $2k$ is therefore the reciprocal value of the volume, or the concentration at which the electrolyte is just half dissociated. This number is extremely characteristic for different acids, since its value may vary according to the nature of the substance between the limits 1 and 1,000,000.

The measurement of the quantity *k* for different acids has led to the following general law:—*The constant* k *is approximately the product of a number of factors, each of which depends on the nature of the constituents of the acid and on their position relatively to the carboxyl group.*

In order to realise what this law implies, and in what manner it is applied, we will proceed to discuss in the following pages the most important groups of the organic acids. The relations, the main features only of which could formerly (vol. i. page 82) be investigated, can now be represented numerically with perfect exactitude. The numerical values for *k* have been multiplied by 100 in order to get rid of ciphers; they all hold for aqueous solutions at 25°.

The fatty acids. The following constants were measured:—

Formic acid $H.CO_2H$	0·00214
Acetic acid $CH_3.CO_2H$	0·00180
Propionic acid $C_2H_5.CO_2H$	0·00134
Butyric acid $C_3H_7.CO_2H$	0·00149
Isobutyric acid $(CH_3)_2CH.CO_2H$	0·00144
Isovaleric acid $(CH_3)_2C_2H_3.CO_2H$	0·00161
Caproic acid $C_5H_{11}.CO_2H$	0·00145

Formic acid has the highest constant; the replacement of its hydrogen by methyl reduces the constant to half its value. But on again replacing one hydrogen atom in acetic acid by methyl the constant only decreases to $\frac{1}{1\cdot4}$ of its value, and further similar substitutions no longer produce a weakening of the acid, but some of them even bring about a slight strengthening. These changes are, however, but small, so that the constants of acids of this series having more than three carbon atoms vary irregularly about the mean value 0·0014.

It is evident, then, that the substitution of hydrogen by methyl acts quite differently, according as it occurs next to the carboxyl or at a greater distance from it. This is a result which will afterwards be shown to hold good in all cases; on the whole, the effect of each substituent is the smaller the more distant it is from the carboxyl. The inference that the interposition of even two carbon atoms nearly counteracts the effect is correct for methyl, for which it is relatively small. Other constituents of greater energy extend their action further, but yet not over more than three or four atoms of the 'open chains'; in the case of 'closed chains' other relations hold good.

Halogen derivatives of the fatty acids. The entrance of chlorine in the place of hydrogen in the fatty acids exerts very considerable influence. The constants are—

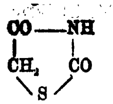
Acetic acid $CH_3.CO_2H$	0·0018
Monochloracetic acid $CH_2Cl.CO_2H$	0·155
Dichloracetic acid $CHCl_2.CO_2H$	5·1
Trichloracetic acid $CCl_3.CO_2H$	121

The constants are in the ratio of

1 : 86 : 2840 : 67200. The ratio of the values of the constants for the different acids, referred to the entrance of each separate chlorine atom, is 84, 33, and 24. It is only the ratios of the constants, and not their differences, which are important; the ratios, though not equal, are yet of the same order of magnitude, while the differences between 0·155, 5, and 121 are quite incomparable. Further, it follows that the relative change of the constants for the entrance of each chlorine atom is not of the same value; the first chlorine atom acts more intensely than the second, and the second more intensely than the third. We shall again meet with a similar relation when dealing with substitution in connection with the same carbon atom. From this it may be concluded that the first chlorine atom which enters into acetic acid exerts its influence under more favourable conditions, therefore probably from a less distance, than the second and third, and it becomes evident how well such measurements lend themselves to investigations and examinations of the relations in space of the atoms within the molecules. The action of other elements and radicles is very similar to that of chlorine.

Monobromacetic acid $CH_2Br.CO_2H$	0·138
Cyanacetic acid $CH_2.CN.CO_2H$	0·370
Thiocyanacetic acid $CH_2.SCN.CO_2H$	0·265
So-called 'carbamine thioglycollic acid' $CH_2(SCONH_2)CO_2H$	0·0246
Isothiocyanacetic acid $C_3H_3O_2S.N$	0·0000246
Thiacetic acid $CH_3.COSH$	0·0469

The constant of monobromacetic acid does not differ much from 0·155, that of monochloracetic acid, hence both halogens exert about the same influence. Cyanogen acts much more intensely. The ratio of cyanacetic acid to acetic acid has risen to 205 (from 86). Thiocyanacetic acid also is stronger than monochloracetic acid, but not so strong as cyanacetic acid, though sulphur is generally a negative substituent—that is, one which augments the acid properties. The idea of relations in space at once suggests itself; by the introduction of sulphur there has, in fact, taken place, on the one hand, an increase in the acid properties, but on the other hand, since the cyanogen is removed to a greater distance from the carboxyl, there has been a weakening, and the latter effect preponderates over the former. By taking up water, thiocyanacetic acid easily passes into the acid $CH_2.SCONH_2.CO_2H$, the group CN changing into $CO.NH_2$. This transformation is accompanied by a marked decrease in the conductivity, the constant falling to less than a tenth of its former value. The change can be conveniently studied in an aqueous solution of thiocyanacetic acid, by determining its electrical conductivity; the conductivity decreases continuously, and after even a few days the greater part of the thiocyanacetic acid is found to be changed. Finally, there is a compound isomeric with thiocyanacetic acid, which Volhard (*J. pr.* [2] 9, 6) obtained by the action of hydrochloric acid on sulphohydantoïn, and which is isothiocyanacetic acid. The constant for this compound is 10,000 times smaller than that for thiocyanacetic acid; it is also smaller than that of any other carbon acid, so that the inference must be drawn that the substance is not a carbon acid at all. This confirms the view expressed by Liebermann, and the reasons for which were given by Hantzsch (*B.* 20, 3129), that the compound is a dioxythiazole—



The feebly acid properties are ascribed to the hydrogen of the imide group. The thiacetic acid mentioned at the end of the last table contains sulphur in the place of oxygen in the hydroxyl of the carboxyl. In accordance with the negative nature of sulphur, this acid proves to be twenty-six times stronger than acetic acid, and this factor may be looked upon as the greatest to which sulphur can give rise when replacing oxygen, because in this case the sulphur atom acts from the most favourable position which is ever possible.

Oxyacetic acid and its derivatives.

Glycollic acid $CH_2.OH.CO_2H$ . . .	0·0152
Methoxy-acetic acid $CH_2.(OCH_3)CO_2H$.	0·0335
Ethoxy-acetic acid $CH_2(OC_2H_5)CO_2H$.	0·0234
Phenoxy-acetic acid $CH_2(OC_6H_5)CO_2H$.	0·0756
Glyoxylic acid $CH(OH)_2CO_2H$ . .	0·0474

The replacement of hydrogen by hydroxyl in acetic acid produces a rise in the constant of 9 times its former value; hydroxyl, therefore, acts much less intensely than the halogens. By introducing a second hydroxyl the constant again becomes greater, but only 3·1 times greater. Here we find quite the same effects as in the cases of mono- and di-chloracetic acid, the second substitution of the same substance acting less strongly than the first. In the numerical values, even, we cannot overlook a certain correspondence; in the case of chlorine the ratios are 1:86 and 1:33; in the case of hydroxyl they are 1:9, and 1:3·1. It may therefore be said that, using round numbers, in the derivatives of acetic acid chlorine acts ten times as intensely as hydroxyl. When the hydroxylic hydrogen of glycollic acid is replaced by radicles, the constant changes, and, strange to say, methyl acts in this case in a strengthening manner, the constant rising to a little more than twice its former value. The substitution of hydrogen in this methyl by methyl again has a weakening effect, as is the case with the fatty acids; ethoxy-acetic acid is 1·4 times weaker than methoxy-acetic acid. Finally, by the introduction of phenyl, the constant becomes appreciably greater; it is about five times as great as that of glycollic acid, and is 2·3 times greater than that of methoxy-acetic acid. The ratio is smaller than that between acetic acid and benzoic acid, which is 1:3·3, an indication that the exchange of methyl for phenyl has in the latter case taken place in greater proximity to the COOH group, a conclusion which follows also directly from the formulæ.

A number of other substances related to glycollic acid have given the following numerical values:—

Thioglycollic acid $CH_2(SH)CO_2H$ . .	0·0225
Thiodiglycollic acid $S(CH_2CO_2H)_2$.	0·048
Dithiodiglycollic acid $S_2(CH_2CO_2H)_2$.	0·065
Diglycollic acid $O(CH_2CO_2H)_2$ . .	0·11

As the constant of glycollic acid is ·0152, we see that the substitution of S for O in hydroxyl has caused the constant to increase 1·5 times; now, as substitution of S for O in COOH of acetic acid increased *k* from 1 to 26, we see here also the great influence of the position occupied by the replacing atom.

The three other acids quoted in the last table are dibasic, and the question at once arises how their constants must be calculated, since the dissociation-formula has been developed for binary electrolytes—that is, for monobasic acids only, and not for ternary ones, to which class the dibasic acids belong. It can, however, easily be shown that, as long as the dissociation is not great, the weaker dibasic acids are not electrolysed according to the formula $2H + R''$, but according to the formula $H + HR$. In other words, at first one hydrogen atom only is split off, and the dissociation takes place according to the binary scheme of the monobasic acids. This follows from the fact that the change in the molecular conductivity of such acids can be represented by the same formula $\frac{m^2}{1-m} = vk$, so that *k* remains constant. But the formula calculated on the assumption of a dissociation according to the scheme $H_2R'' = 2H + R$ does not represent the change in the conductivity of these acids as determined by experiment.

Malonic acid $CH_2(COOH)_2$ may serve as an example of dibasic acids. It gives:—

v	μ	m	$100k$
16	53·1	0·149	0·159
32	72·3	0·202	0·159
64	97·1	0·272	0·158
128	128·5	0·359	0·157
256	165·9	0·464	0·157
512	208·8	0·586	0·162
1024	253·2	0·708	0·168
2048	294·2	0·823	0·187

The constant does not change till the value $m = 0·586$ is reached—that is, till about half the acid has been dissociated according to the binary scheme; then it becomes greater—a sign that henceforward the formula loses its validity, and that the decomposition according to the ternary scheme $2H + R''$ begins to assume an appreciable value.

If, on the other hand, we attempt to calculate the conductivity according to the formula corresponding to ternary dissociation $\frac{m_2}{(1-m)v^2} = k$, the values of *k* decrease very rapidly and are far from being constant.

The values for the constants of dibasic acids given in the table preceding the last one have been calculated on this principle, and refer, therefore, to the first stage of binary dissociation $H_2R = HR + H$.

Comparing thioglycollic acid with thiodiglycollic acid and dithiodiglycollic acid, we find that the constants do increase distinctly, though only slightly; they are 0·0255, 0·048, and 0·065, and are in the ratio of 1:2·1:2·9. When, therefore, the residue of acetic acid, CH_2CO_2H, enters thioglycollic acid, this process has no appreciable influence on the constant. On the other hand, the constant of diglycollic acid is 7·2 times greater than that of glycollic acid. From the fact that the same substituent produces such different effects in glycollic acid and in thioglycollic acid, it may be presumed that in the first case the oxygen brings the negative substituent nearer to the carboxyl than the sulphur does in the second case, and this presumption may be further utilised for hypotheses concerning the configuration of the sulphur atom, and the arrangement of the affinity points on it. It has, however, not yet been established with certainty that the greater or less distance of the groups is the *only* cause of their different actions, and there are some circumstances which allow us to conclude that other conditions are effective also; therefore, until these have been cleared up, conclusions such as the above hold only hypothetically.

Derivatives of amido-acetic acid.

Phenylamido-acetic acid $CH_2(NHC_6H_5)CO_2H$	0·0039
Hippuric acid $CH_2(NH.CO.C_6H_5)CO_2H$	0·0222
Aceturic acid $CH_2(NH.CO.CH_3)CO_2H$	0·0230
Phthalylamido-acetic acid $CH_2(NC_2O_2C_6H_4)CO_2H$	0·100

Amido-acetic acid has not the character of an acid; the basic NH_2 group completely removes the acid properties of acetic acid. But if negative radicles are introduced into NH_2, well defined acids are again obtained. Phenyl has this effect; the constant of phenylglycocoll is 2·2 times as great as that of acetic acid. The constants of the acids obtained by introducing $CO.C_6H_5$ and $CO.CH_3$ for H in NH_2 are 12 to 13 times greater than that of acetic acid. The substitution of the divalent residue of phthalic acid for the two hydrogen atoms in the NH_2 group raises the constant of acetic acid 55 times.

Derivatives of propionic acid.

Propionic acid $CH_3.CH_2.CO_2H$	0·00134
Lactic acid $CH_3.CH(OH)CO_2H$	0·0138
β-Oxypropionic acid $CH_2(OH).CH_2.CO_2H$	0·00311
Glyceric acid $CH_2.OH.CH.OH.CO_2H$	0·0228
β-Iodopropionic acid $CH_2I.CH_2.CO_2H$	0·0090
Trichlorlactic acid $CCl_3.CH.OH.CO_2H$	0·465

The constant of α-oxypropionic or lactic acid is 10 times greater than that of propionic acid, but the constant of β-oxypropionic acid is only 2·3 times greater than that of propionic acid. The difference in the action of the same substituent, according to its nearer or more distant position relatively to COOH, asserts itself most clearly. The ratio between propionic acid and lactic acid is slightly greater than that between the analogous substances acetic acid and glycollic acid (1 : 9); it is, therefore, not quite immaterial whether the substitution does or does not take place in the group CH_3. The influence of the more distant position of the substituent can be recognised in β-iodopropionic acid and trichlorolactic acid. The first is only 6·5 times stronger than the parent substance. No measurement of α-iodopropionic acid has yet been made, but there is little doubt that iodine in the α- position must act very similarly to chlorine or bromine, and must, therefore, increase the constant by 70 or 80 times. The effect in the β- position is 10 to 12 times less than this. In the same way the substitution of 3Cl for 3H in $CH_3.COOH$ increases *k* about 67,000 times; but the introduction of 3Cl into $CH_3.CHOH.COOH$ in the β- position increases *k* only about 33·7 times. The ratio of these effects is about 1:2000; calculated for each Cl atom the ratio is $\sqrt[3]{2000} = 12{\cdot}6$; this ratio comes very near that estimated for α- and β-iodopropionic acids.

Derivatives of higher fatty acids.

Oxyisobutyric acid $(CH_3)_2CH.OH.CO_2H$	0·0106
Mononitrocaproic acid $C_5H_{10}(NO_2).CO_2H$	0·0123
Dinitrocaproic acid $C_5H_9(NO_2)_2CO_2H$	0·069
Lævulinic acid $CH_3.CO.CH_2.CH_2.CO_2H$	0·00255

Since the constant of isobutyric acid is 0·00144, the hydroxyl in the α- position here causes the factor 7·4, which is somewhat smaller than 9, the corresponding ratio between acetic acid and glycollic acid.

The ratio between caproic acid and its mononitro- derivative is 1 : 8·5. Since, as will soon be shown, the nitro- group has a more strongly negative action than chlorine, NO_2 must, in the present case, be in the β- position. The same holds for the dinitro- compound; it is 5·6 times stronger than the mononitro- compound; it is again evident that the second negative group has less effect than the first.

Lævulinic acid, or β-acetyl-propionic acid, allows us to recognise the smaller influence to be expected of the acetyl in the β- position; the constant is only 1·9 times larger than that of propionic acid.

Benzoic acid and its derivatives. The largest and most varied group of allied substances that has been investigated so far, is that of benzoic acid and its derivatives, and consequently it has been possible to trace here many and striking regularities.

Benzoic acid $C_6H_5CO_2H$	0·0060
Salicylic acid $C_6H_4(OH)CO_2H$	0·102
m-Oxybenzoic acid $C_6H_4(OH)CO_2H$	0·0087
p-Oxybenzoic acid $C_6H_4(OH)CO_2H$	0·00286
Oxysalicylic acid [1:2:3] $C_6H_3(OH)_2CO_2H$	0·114
Oxysalicylic acid [1:2:5] $C_6H_3(OH_2)_2CO_2H$	0·108
β-Resorcylic acid [1:2:4] $C_6H_3(OH)_2CO_2H$	0·052
α-Resorcylic acid [1:2:6] $C_6H_3(OH)_2CO_2H$	5·0
Protocatechuic acid [1:3:4] $C_6H_3(OH)_2CO_2H$	0·0033
m-Dioxybenzoic acid $C_6H_3(OH)_2CO_2H$	0·0091
Gallic acid [1:3:4:5] $C_6H_2(OH)_3CO_2H$	0·0040
Pyrogallic acid [1:2:3:4] $C_6H_2(OH)_3CO_2H$	0·055
Phloroglucin carboxylic acid [1:2:4:6] $C_6H_2(OH)_3CO_2H$	2·1

The numbers indicate the positions of the OH groups relatively to COOH supposed to be in position 1.

This table contains the constants of all hydroxyl-benzoic acids known up to the present time. These show such close connections with each other that, knowing the constants of benzoic acid and of the three monoxybenzoic acids, those of all the others can be calculated approximately. It is true the calculation is not quite exact, but it is sufficiently so to enable us to deduce the constitutions of the corresponding substances directly from a knowledge of the constants.

Between the constants of benzoic acid and its ortho-oxy- derivative the ratio is 1:17. This value is larger than the ratio when OH is introduced in the α- position into a fatty acid, in which cases the ratio did not exceed 10; in the β- position, which corresponds to the constitution of salicylic acid, the ratio was not larger than 2·3. From this it appears that the ortho- position involves a much closer relation in the benzene nucleus than even the α- position in the open chain, a fact which later on will be confirmed in many ways, and which seems to be of great importance in dealing with the question concerning the constitution of benzene.

The constant is increased but slightly by OH in the meta- position. But in the para- position the hydroxyl even produces a diminution of the constant to rather less than half the value. We deal in this case, therefore, not only as usual with a greater or smaller value of the influence exerted by a substituent according to its position, but with a reversal of the *direction* in which the influence is exerted. This fact, which has already become evident in the case of methyl, recurs with other feebly negative substituents in the para- position of the benzene nucleus. This promises to become very important in the construction of a theory to explain these phenomena.

We have then the following factors for the influence of the hydroxyl:—

Ortho- 1:2 or 1:6 = 17
Meta- 1:3 „ 1:5 = 1·4
Para- 1:4 = 0·5

By their help we are able to calculate the constants of the di- and tri-oxybenzoic acids by multiplying the constant of benzoic acid by the corresponding factor for every hydroxyl introduced. It must be remembered that such a calculation can only give approximate results; for we have seen that substituents already present somewhat influence the magnitude of the factor of a newly entering substituent, and that, generally, by decreasing it. It is, therefore, only the order of magnitude of the constants, and not their exact value, that we shall be able to find in the manner indicated.

Four dioxybenzoic acids can be derived from salicylic acid; the constants of these four acids are calculated thus:—

1:2:3 gives $\cdot 0060 \times 17 \times 1\cdot 4 = 0\cdot 143$
1:2:4 „ $\cdot 0060 \times 17 \times 0\cdot 5 = 0\cdot 051$
1:2:5 „ $\cdot 0060 \times 17 \times 1\cdot 4 = 0\cdot 143$
1:2:6 „ $\cdot 0060 \times 17 \times 17 = 1\cdot 73$

The numbers observed are 0·114, 0·052, 0·108, and 5·0. In the case of the first and the third acid which both contain a hydroxyl in the *m*- position, a diminution of the combined effect therefore makes itself felt as usual. In the second acid 1:2:4, calculation and experiment completely agree; while the fourth acid 1:2:6, which contains two ortho- hydroxyls, shows a value about three times greater than is furnished by the estimation. We shall see later that this behaviour is common; two substituents in the ortho- position do not, as is otherwise usual, weaken one another, but reinforce each other's effect.

For the two dioxybenzoic acids still remaining we must expect the following constants:

1:3:4 gives $\cdot 006 \times 1\cdot 4 \times 0\cdot 5 = 0\cdot 0042$
1:3:5 „ $\cdot 006 \times 1\cdot 4 \times 1\cdot 4 = 0\cdot 012$

Measurement gives ·0033 and ·009, both constants being therefore as usual somewhat smaller, a consequence of the combined effect, yet being quite of the expected order of magnitude.

The six possible trioxybenzoic acids allow us to estimate the following constants:

1:2:3:4 gives $\cdot 0060 \times 17 \times 1\cdot 4 \times 0\cdot 5 = 0\cdot 07$
1:2:4:6 „ $\cdot 0060 \times 17 \times 0\cdot 5 \times 17 = 0\cdot 9$
1:3:4:5 „ $\cdot 0060 \times 1\cdot 4 \times 0\cdot 5 \times 1\cdot 4 = 0\cdot 006$
1:2:3:5 „ $\cdot 0060 \times 17 \times 1\cdot 4 \times 1\cdot 4 = 0\cdot 2$
1:2:4:5 „ $\cdot 0060 \times 17 \times 0\cdot 5 \times 1\cdot 4 = 0\cdot 07$
1:2:3:6 „ $\cdot 0060 \times 17 \times 1\cdot 4 \times 17 = 2\cdot 4$

Of the six possible trioxybenzoic acids three are known and measured. The comparison between the observed and estimated constants gives 0·055 instead of 0·07; 0·004 instead of 0·006, where as usual the observed value is smaller than the estimated value; and in the case of the acid with two hydroxyls in the ortho- position we have 2·1 observed instead of 0·9 estimated, which therefore, as before, is about twice as great. In the same way we may expect in the cases of the three trioxybenzoic acids still unknown, that the real constants of the acids 1:2:3:5 and 1:2:4:5 will be somewhat smaller than the estimated values, and therefore about 0·15 and 0·05, while the third acid 1:2:3:6 with two ortho- hydroxyls will probably have a constant from 5 to 5·5. In spite of the uncertainty of the estimation, the differences are so considerable that when in future one of these acids is prepared the determination of the conductivity of an aqueous solution will suffice to decide its constitution.

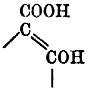
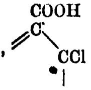
The constitutional relations of the oxybenzoic acids, as indicated by the dissociation-constants, are therefore in complete agreement with those deduced from chemical relations.

The methods just expounded may be directly utilised for elucidating constitutional relations. On heating orcin $C_6H_3(OH)_2CH_3$ with $KHCO_3$ there is formed 'paraorsellic acid,' whose constitution must correspond either to that of α- or β-resorcylic acid. On measurement, the constant appeared to be 4·1; the acid has, therefore, a constitution analogous to that of α-resorcylic acid, corresponding to the arrangement $CO_2H:OH:OH:CH_3 = 1:2:6:4$.

Further substitution products of benzoic acid gave the following numbers:—

o-Chlorobenzoic acid $C_6H_4Cl.CO_2H$	0·132
m-Chlorobenzoic acid $C_6H_4Cl.CO_2H$	0·0155
p-Chlorobenzoic acid $C_6H_4Cl.CO_2H$	0·0093
o-Bromobenzoic acid $C_6H_4Br.CO_2H$	0·145
m-Bromobenzoic acid $C_6H_4Br.CO_2H$	0·0137
Monobromgallic acid $C_6HBr(OH)_3CO_2H$	0·059
Dibromgallic acid $C_6Br_2(OH)_3CO_2H$	1·21
m-Fluobenzoic acid $C_6H_4F.CO_2H$	0·0136
m-Cyanobenzoic acid $C_6H_4CN.CO_2H$	0·020
o-Nitrobenzoic acid $C_6H_4NO_2.CO_2H$	0·616
m-Nitrobenzoic acid $C_6H_4NO_2CO_2H$	0·0345
p-Nitrobenzoic acid $C_6H_4NO_2CO_2H$	0·040
Bromonitrobenzoic acid [1:2:5] $C_6H_3BrNO_2CO_2H$	1·4
o-Amidobenzoic acid $C_6H_4NH_2CO_2H$	0·0010
p-Amidobenzoic acid $C_6H_4NH_2CO_2H$	0·0012
o-Acetamidobenzoic acid $C_6H_4(NHCOCH_3)CO_2H$	0·024
m-Acetamidobenzoic acid $C_6H_4(NHCOCH_3)CO_2H$	0·0085
p-Acetamidobenzoic acid $C_6H_4(NHCOCH_3)CO_2H$	0·0052
o-Acetoxybenzoic acid $C_6H_4(OCOCH_3)CO_2H$	0·033
p-Acetoxybenzoic acid $C_6H_4(OCOCH_3)CO_2H$	0·0042

m-Acetoxybenzoic acid $C_6H_4(OCOCH_3)CO_2H$ . .	0·0099
o-Methoxy-benzoic acid $C_6H_4(OCH_3)CO_2H$ . . .	0·0082
p-Methoxy-benzoic acid $C_6H_4(OCH_3)CO_2H$ . . .	0·0032

The same conclusion may be drawn from these numbers as to the influence of the halogens as had been deduced for hydroxyl—namely, that the ortho- position is that of greatest influence. The constant of benzoic acid rises to 22 times its value on the introduction of chlorine in the ortho- position, to 2·6 times its value when Cl is put in the meta- position, and to 1·5 times its value when Cl is put in the para- position. But along with this there is a remarkable difference between the behaviour of OH and that of Cl; hydroxyl acts much more strongly in the ortho-position of the benzene nucleus than in the α- position of the open chain, while chlorine, which in the α- position of the open chain increases the constant to more than 80 times its value, does so only 22 times when in the ortho-position in the benzene nucleus. For this discrepancy the explanation offers itself, on the one hand, that the system of carbon atoms which constitutes the benzene nucleus is not rigid, but alters its form according to the atoms present in it, and that if so, the difference in form must be especially great according as hydroxyl or chlorine enters near the carboxyl. On the other hand, the following possibility strikes us. According to the hypothesis of Kekulé, there are two sorts of ortho- positions, the one being represented by a double, the other by a single, linkage. Now it is quite possible that in benzene itself the change of the double or single linking to the right or the left takes place easily, but that when two adjoining carbon atoms have fixed different atoms or groups of atoms, only one sort of linkage, either a single one or a double one, is stable. Assuming that—in salicylic acid, for instance—double linkage exists between the carbon atoms, combined with carboxyl and hydroxyl respectively,  while in *o*-chlorobenzoic acid the single linkage only is stable,  , the difference emphasised above can be understood, since in the first case the ortho- relation is a much more intimate one than in the second.

The small changes which the constant of benzoic acid undergoes in *m*- and *p*-chlorobenzoic acid correspond to the greater distance of the chlorine from the carboxyl. According to the usual representation of benzene, the influence of the para- position proves to be the smallest. But this behaviour is by no means general.

Bromine behaves very similarly to chlorine. The effect for the ortho- position is somewhat larger than for chlorine—*i.e.* 24 instead of 22; that for the meta- position somewhat smaller—2·3 instead of 2·6.

When hydrogen in gallic acid is replaced by bromine in the ortho- position, the constant increases to 15 times its value, therefore less than in the case of benzoic acid. This corresponds to the general rule that several substituents simultaneously present diminish each other's action. Only when two substituents, which are the same, occupy the ortho- position is an increase in the simultaneous effect to be observed; in fact, a second bromine atom which occupies the ortho- position brings about a greater rise of the constant than does the first—21 instead of 15.

Hydrofluoric acid being much weaker than hydrochloric acid, it was to be expected that the fluobenzoic acids would be weaker than the chlorobenzoic acids. In case of the meta- compound this occurs, however, only to a small extent; the constants differ but little, and are nearly the same for the bromo- and fluo- compounds. It would be of interest to determine whether in the ortho- position also fluorine acts as strongly as chlorine, but *o*-fluobenzoic acid has not yet been examined; *m*-cyanobenzoic acid is markedly stronger than *m*-chlorobenzoic acid. This completely corresponds to the fact that cyanacetic acid is much stronger than chloracetic acid.

From measurements of the nitrobenzoic acids, the group NO_2 appears to be the most effective negative substituent. The ortho- compound exhibits a 103-fold increase of the constant, the meta- compound an increase equal to 5·8-fold, and the para- compound a 6·7-fold increase. With regard to the influence of position, the numbers agree with those found for the chloro- and bromo- compounds, in so far as the ortho- position is again that of greatest influence; but, on the other hand, the influence of the nitro- group makes itself more felt from the para- position than from the meta- position, in opposition to the relations found in the case of chlorine.

Bromonitrobenzoic acid contains the substituents in the order $CO_2H{:}NO_2{:}Br = 1{:}2{:}5$. The constant is made up of that of benzoic acid, and of the factor of the *o*-nitro- group 103, and that of the *m*-bromine 2·3, and is therefore calculated to be 1·38, which agrees well with 1·4, the value found by experiment. In this case, therefore, the mutual influence of the simultaneously present substituents is practically zero.

The constants of *o*- and *p*- amidobenzoic acid show that the amido- group considerably reduces the strength of the acid. But the values quoted can only be looked upon as approximations, since peculiarities appear in the determinations which are not yet elucidated.

But the numbers become regular when the basic properties of the amido- residue are compensated by the introduction of acetyl. Of the three acetamidobenzoic acids the ortho- compound is the strongest, it surpasses benzoic acid by four times its value. The meta- compound is only 1·4 times as strong as benzoic acid, and in the para- position the atomic group $NHCOCH_3$ acts similarly to hydroxyl—that is, it exerts a weakening effect—the constant is only 0·86 of that of benzoic acid. The acetyl-oxybenzoic acids behave quite similarly; their factors relatively to benzoic acid are 5·5, 1·6 and 0·76. On comparing with these and the former numbers the factors of the oxybenzoic acids—namely, 17, 1·4, and 0·5—it follows that the substituent which in the ortho- position acts most strongly also exerts the greatest weakening influence in the para- position.

But this relation again is not universal. Replacement of hydroxylic hydrogen by methyl in salicylic acid produces a quite extraordinary weakening of the acid; instead of 17 times, the constant is only 1·4 times, as great as that of benzoic acid. In the para- position, however, the same change produces scarcely any effect; the constants of *p*-oxybenzoic acid and of *p*-methoxy-benzoic acid or anisic acid are nearly the same, and the decreasing effect of the group OCH_3 is much greater in the para- than in the ortho- position.

It is further remarkable that acetosalicylic acid is weaker than salicylic acid, in spite of acetyl being a negative radicle. It may be that the cause of this curious behaviour is to be found in a change of linkage similar to that mentioned above.

Homologues of benzoic acid.

o-Toluic acid $C_6H_4(CH_3)CO_2H$	0·012
m-Toluic acid $C_6H_4(CH_3)CO_2H$	0·0051
p-Toluic acid $C_6H_4(CH_3)CO_2H$	0·0052
Phenylacetic acid $C_6H_5.CH_2.CO_2H$	0·0056
Phenylpropionic acid $CH_3.CH(C_6H_5)CO_2H$	0·0043
p-Phenylpropionic acid $CH_2(C_6H_5)CH_2.CO_2H$	0·0023
Cuminic acid $C_6H_4(C_3H_7)CO_2H$	0·0050

A comparison of the constant of benzoic acid with those of the toluic acids shows that a doubling of value has occurred by the introduction of methyl into the ortho- position, but that, as usual, the methyl group in the meta or para- position has a slightly weakening effect. The isomeric phenylacetic acid also has a very similar constant. This constant is 3·1 times greater than that of acetic acid—an indication that phenyl is a negative radicle—but it does not attain to the value of benzoic acid.

The constants for the two phenylpropionic acids show that, as in the case of α- and β- oxypropionic acids, the acid in which the phenyl is at a greater distance from the carboxyl is the weaker. The other relations to be expected are also found; between propionic acid and α-phenylpropionic acid there is the same ratio of the constants, 3·1, as between acetic and phenylacetic acid.

Cuminic acid differs from *p*-toluic acid only in that it contains isopropyl instead of methyl. To this small difference in constitution corresponds as small a difference in the constants.

Hydroxylised homologues of benzoic acid.

Mandelic acid $C_6H_5.CH(OH)CO_2H$	0·0417
Phenoxy-acetic acid $C_6H_5O.CH_2.CO_2H$	0·0756
o-Nitrophenylglycollic acid $C_6H_4(NO_2)O.CH_2.CO_2H$	0·158
p-Nitrophenylglycollic acid $C_6H_4(NO_2)O.CH_2.CO_2H$	0·153
Tropic acid $CH_2(OH).CH(C_6H_5)CO_2H$	0·0075
Phloretic acid $CH_3CH(C_6H_4.OH)CO_2H$	0·0020
Hydroparacoumaric acid $CH_2(C_6H_4.OH)CH_2.CO_2H$	0·0017

Mandelic acid is phenylated oxyacetic acid; the ratio of its constant to that of glycollic acid is 2·7, while that between acetic acid and phenylacetic acid is 3·1; both values approximate closely to each other.

On introducing into the phenyl of phenoxyacetic acid a nitro- group in the ortho- position, the constant rises to double its value. The introduction of NO_2 in the ortho- position into benzoic acid raises the constant to 103 times its former value. This enormous difference exemplifies most prominently the influence exerted by the varying distance of the substituent from the carboxyl. The same thing is made evident by the constant of *p*-nitrophenylglycollic acid, which is scarcely different from that of the ortho- compound; the change from the ortho- to para- position, which is generally so influential, is of scarcely any account at this distance from the carboxyl.

Tropic acid is α-phenyl-β-oxypropionic acid. It is 2·5 times stronger than oxypropionic acid. For the influence of phenyl in the α- position we have before found the factors 2·7 and 3·1.

Phloretic acid is phenylpropionic acid whose phenyl contains a hydroxyl in the para- position; its constant is half as great as that of phenylpropionic acid; hence the para- hydroxyl here exerts its characteristic weakening effect.

In the same way hydroparacoumaric is hydrocinnamic acid which contains a para-hydroxyl in the phenyl. This also has a decreasing action on the constant, but owing to the greater distance of the phenyl this effect is not so great as in the preceding case.

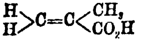
Unsaturated acids. The affinity co-efficients of these substances present a special interest owing to their isomeric relations, which cannot be represented by the ordinary chemical formulæ. Following up an idea of van't Hoff, an explanation of these phenomena has lately been given by Wislicenus (*Abh. König. Sächs. Ges. der Wiss.* 1887). In this explanation the cause of the chemical differences is supposed to lie in differences in the relative positions in space of the radicles linked to the carbon. Since the results so far obtained from a consideration of the affinity-constants invariably point to relations in space, it becomes possible to subject this hypothesis to an experimental examination.

Acrylic acid $CH_2:CH.CO_2H$	0·0056
Crotonic acid $CH(CH_3):CH.CO_2H$	0·00204
Isocrotonic acid $CH(CH_3):CH.CO_2H$	0·0036
Tiglic acid $CH(CH_3):C(CH_3)CO_2H$	0·00096
Angelic acid $CH(CH_3):C(CH_3)CO_2H$	0·0050
α-Chlorocrotonic acid $CH(CH_3):CCl.CO_2H$	0·0720
allo-α-Chlorocrotonic acid $CH(CH_3):CCl.CO_2H$	0·158
β-Chlorocrotonic acid $CCl.(CH_3):CH.CO_2H$	0·0144
allo-β-Chlorocrotonic acid $CCl.(CH_3):CH.CO_2H$	0·0095

A consideration of these numbers shows that the unsaturated acids have in general greater constants than the saturated ones. We must, therefore, ascribe to hydrogen a strongly basic character. And, further, as in the case of the saturated fatty acids, the constants on the whole decrease as the carbon increases. And, finally, we see that the isomeric acids for which, according to the views hitherto held, no difference of constitution could be formulated are in fact distinctly different.

Now Wislicenus represents the difference between crotonic acid and isocrotonic acid by the following formulæ :—

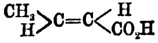
Crotonic acid



$\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{CH_3}\\ \mathrm{CO_2H}\end{matrix}$

and

Isocrotonic acid



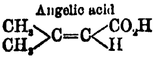
$\begin{matrix}\mathrm{CH_3}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{H}\\ \mathrm{CO_2H}\end{matrix}$

In crotonic acid the methyl group stands nearer to the carboxyl, in isocrotonic acid the hydrogen. Since, in accordance with present experience, a methyl group linked to carbon which is also directly linked to CO_2H decreases the constant, a smaller constant must be expected for crotonic acid than for isocrotonic, this difference being more pronounced owing to greater proximity in space. Experiment confirms this conclusion, and thus proves the appropriateness of Wislicenus' assumption.

It may be asked whether we are not here dealing with one of the cases of which some were mentioned before, in which, as an exceptional case, the methyl acts by increasing the strength. But this view is excluded, since both acids are weaker than acrylic acid. Methyl has, therefore, in both cases reduced the strength, but to a greater degree in crotonic than in the iso- acid.

Wislicenus assumes similar differences in constitution for angelic and tiglic acids. We get

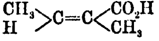
Angelic acid



$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{CO_2H}\\ \mathrm{H}\end{matrix}$

and

Tiglic acid



$\begin{matrix}\mathrm{CH_3}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CH_3}\end{matrix}$

Hence angelic acid again would have to be stronger than tiglic, as has been verified by experience. But it is remarkable that in this case the difference has been found to be much greater than in the first one. Angelic acid has a greater constant than isocrotonic acid, which contains CH_2 less than angelic acid, a fact as unusual as that tiglic acid exhibits a smaller constant than the corresponding saturated acid, valeric, which has for constant 0·00161.

In the same way the values found for the α-chlorocrotonic acids agree with experience. The constants are very nearly in the same ratio as that of those of the two crotonic acids themselves, and the rise effected by the chlorine introduced into the α- position is represented by the factors 36 and 44, which, though markedly smaller, are of the same order of magnitude as the factor for monochloracetic acid.

In opposition to the agreement holding hitherto between theory and experiment, in the case of the β-chlorocrotonic acids, the *allo*- compound proves distinctly weaker than the derivative of crotonic acid. The cause of this discrepancy cannot yet be established. The ratio of the constants for crotonic acid and β-chlorocrotonic acid is 1:7, which is nearly the same as the corresponding factor for propionic acid and β-iodopropionic acid, viz. 6·6. On the other hand, the ratio for the factors of isocrotonic acid and the *allo*-β-chloro- derivative is 1:2·6, and is, therefore, much smaller.

Tetrolic acid is formed from both β-chlorocrotonic acids by splitting off hydrochloric acid; the constant is

Tetrolic acid $CH_3.C{:}C.CO_2H$ . . . 0·246

Though hydrochloric acid is one of the strongest acids, yet the splitting off of its elements from the β-chlorocrotonic acids not only has not lowered the constant, but has raised it considerably. This result makes evident the strongly acid nature of carbon and the basic nature of hydrogen; the removal of four hydrogen atoms from butyric acid, whose constant is 0·00149, has produced a rise in the constant of 160 times its value.

Of other unsaturated acids the following have been measured—

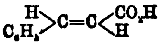
Hydrosorbic acid $C_5H_9.CO_2H$	0·00241
Sorbic acid $C_5H_7.CO_2H$	0·00173
Parasorbic acid $C_5H_7.CO_2H$	0·00173
Ethyl-methacrylic acid $C_5H_9.CO_2H$	0·00111
Atropic acid $CH_2{:}C(C_6H_5)CO_2H$	0·0143
Cinnamic acid $CH(C_6H_5){:}CH.CO_2H$	0·00355
Isocinnamic acid $CH(C_6H_5){:}CH.CO_2H$	0·0156
p-Coumaric acid $CH(C_6H_4.OH){:}CH.CO_2H$	0·0022
o-Coumaric acid $CH(C_6H_4.OH){:}CH.CO_2H$	0·0021
Umbellic acid $CH(C_6H_3(OH)_2){:}CH.CO_2H$	0·00188
α-Bromo-cinnamic acid $CH(C_6H_5){:}CBr.CO_2H$	1·44
β-Bromo-cinnamic acid $CH(C_6H_5){:}CBr.CO_2H$	0·093
Phenylpropiolic acid $C_6H_5.C{:}C.CO_2H$	0·59
o-Nitro-phenylpropiolic acid $C_6H_4NO_2.C{:}C.CO_2H$	1·06

In accordance with the general rule, hydrosorbic acid is stronger than the corresponding saturated compound, which is caproic acid ($k = 0·00145$), while sorbic acid, which contains 2H less, is not stronger but weaker than hydrosorbic acid. It is, therefore, probable that sorbic acid has not one treble linkage, but two double ones, or it may have an altogether different constitution, perhaps one with a closed chain arrangement of the carbon atoms.

Sorbic acid is sometimes obtained in the form of an oil which only when treated with acids or alkalis passes into the crystalline acid. Since it did not seem impossible that this was a case of isomerism, such as that of crotonic and isocrotonic acid, the constant of the liquid parasorbic acid was also measured. It proved identical with that of sorbic acid, and hence, with Fittig and Baringer (*A.* 161, 325 [1871]), these substances must be considered, not as isomeric, but as chemically identical.

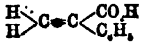
The constant of methylethylacrylic acid is remarkably small; it is smaller than that of the saturated fatty acid, and approaches that of tiglic acid. The acids α-phenylacrylic, or atropic, and β-phenylacrylic or cinnamic, behave as we should expect; the phenyl group causes a much higher value of the constant when it is in the α- than when it is in the β- position. But it is remarkable that cinnamic acid is not only weaker than atropic acid, but even weaker than acrylic acid; in this case, then, the phenyl group lowers the constant.

In the case of cinnamic acid, two 'geometrically isomeric' compounds may be expected, namely—



$\begin{matrix}\mathrm{H}\\ \mathrm{C_6H_5}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{CO_2H}\\ \mathrm{H}\end{matrix}$

and



$\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{C{=}C}\!<\!\begin{matrix}\mathrm{CO_2H}\\ \mathrm{C_6H_5}\end{matrix}$

Quite recently there has been discovered by Liebermann a second cinnamic acid which must be regarded as geometrically isomeric with the ordinary one; it has a much higher constant than the latter, and hence we may conclude that in the new isocinnamic acid the negative phenyl has a closer connexion with the carboxyl than in the old one, and that the new acid may have the second of the above formulæ.

Similarly, there are known two isomeric bromocinnamic acids, which are produced from cinnamic acid dibromide by splitting off hydrobromic acid, and for which the same kind of isomerism holds. Nor can there be any doubt as to which acid corresponds to each formula, the differences in the constants being very great, and in fact it has been made known quite recently by Erlenmeyer that he has obtained Liebermann's isocinnamic acid from the stronger *α*-bromocinnamic acid.

The phenylpropiolic acid formed from the bromoinnamic acids by splitting off hydrobromic acid, is stronger than the *β*- compound, but weaker than the isomeric *α*- compound. The constant is also, as was to be expected, greater than that of tetrolic acid. In *o*-nitro-phenylpropiolic acid the nitro- group in the ortho-position has again been able to exert but a slightly strengthening action, owing to its being at a great distance from the carboxyl.

On comparing cinnamic acid with *p*-coumaric acid, we find that the hydroxyl introduced into the *p*- position again lowers the constant. But, strange to say, a similar effect is produced in the derivatives of cinnamic acid by hydroxyl in the ortho- position; *o*-coumaric acid is also weaker than cinnamic acid. It is in accordance with this that umbellic acid, which contains one hydroxyl in the ortho- position and a second one in the para- position, is weaker than all these acids. It is to be expected that these relations will prove of importance for the complete elucidation of the constitution of these remarkable compounds.

Dibasic acids. The acids of the oxalic series gave the following constants:

Oxalic acid $(CO_2H)_2$	10(?)
Malonic acid $CH_2(CO_2H)_2$	0·158
Succinic acid $C_2H_4(CO_2H)_2$	0·0066
Pyrotartaric acid $C_3H_6(CO_2H)_2$	0·0048
Adipic acid $C_4H_8(CO_2H)_2$	0·0037
Pimelic acid $C_5H_{10}(CO_2H)_2$	0·0036
Suberic acid $C_6H_{12}(CO_2H)_2$	0·0026
Sebacic acid $C_8H_{16}(CO_2H)_2$	0·0023

It has already been explained that the weaker dibasic acids H_2R'' split electrolytically according to the scheme $H + HR''$, and that therefore constants may be calculated for these acids in a manner analogous to that adopted for the monobasic acids. In the case of oxalic acid, however, this is not possible, since the dissociation has proceeded too far; the constant is only estimated approximately, but beginning from malonic acid, the values of the constants can be very well determined.

We see that at first the constants decrease very rapidly; that of malonic acid is about 60 times smaller than that of oxalic acid. From malonic to succinic acid the step is much smaller, 24 : 1, and much smaller from the latter to pyrotartaric acid, 1·4 : 1, and henceforward the numbers vary only by small amounts. The influence which one carboxyl group exerts on the hydrogen of the other decreases, therefore, very rapidly in consequence of the interposition of the carbon atoms; sebacic acid does not surpass by more than twice the fatty acids richer in carbon. Of the numerous isomerides with side carbon chains, the following have been measured:

Methylmalonic acid $CH(CH_3)CO_2H$	0·087
Ethylmalonic acid $CH(C_2H_5)CO_2H$	0·127
Dimethylmalonic acid $C(CH_3)_2CO_2H$	0·077
Methylsuccinic acid $C_2H_3(CH_3)CO_2H$	0·0086
α-Dimethylsuccinic acid $C_2H_2(CH_3)_2CO_2H$	0·0343
β-Dimethylsuccinic acid $C_2H_2(CH_3)_2CO_2H$	0·0245

The three first acids appear at once to be derivatives of malonic acid; their constants do not differ much from that of their parent substance, but all are somewhat smaller. Similarly, the constants of the derivatives of succinic acid approach to the value of the latter, but are all greater. The alcoholic groups have therefore acted in these cases in the ordinary way: an explanation of this has been attempted by Bethmann (*Z. P. C.* 5, 407).

Derivatives of oxalic and of malonic acid:—

Oxamic acid $CO.NH_2.CO_2H$	0·80
Oxaluric acid $CO(NH.CO.NH_2)CO_2H$	4·5
Oxanilic acid $CO(NHC_6H_5)CO_2H$	1·21
o-Chloro-oxanilic acid $CO(NHC_6H_4Cl)CO_2H$	2·03
p-Chloro-oxanilic acid $CO(NHC_6H_4Cl)CO_2H$	1·40
p-Tolyl-oxamic acid $CO(NHC_7H_7)CO_2H$	0·88

The amido- group entering into one of the carboxyls of oxalic acid causes a weakening of the acid to one-twelfth its value; the much more weakly basic urea residue produces a much smaller weakening effect, *viz.* to about half the value. The decrease caused by the residue of aniline is smaller also, to about the eighth part; when chlorine enters into the phenyl of the latter, there again occurs an increase in the acid properties, which increase, however, in consequence of the greater distance, is much smaller than in benzoic acid. But a distinct difference between the ortho- and the para- position still asserts itself. Methyl in the para- position exerts a distinctly weakening effect.

Tartronic acid $CH(OH)(CO_2H)_2$	0·107
Phenylmalonic acid $(C_6H_5)_2C:(CO_2H)_2$	0·408
Malonanilic acid $CH_2CO(NHC_6H_5)CO_2H$	0·0196

Strange to say, in spite of the hydroxyl, tartronic acid is weaker than malonic acid ($k = 0·158$). The replacement of both hydrogen atoms of malonic acid by benzylic radicles raises the constant. Finally, malonanilic acid is about eight times weaker than the parent substance.

Derivatives of succinic acid.

Malic acid $C_2H_3(OH)(CO_2H)_2$	0·0395
Inactive malic acid $C_2H_3(OH)(CO_2H)_2$	0·0399
Dextrotartaric acid $C_2H_2(OH)_2(CO_2H)_2$	0·097
Lævotartaric acid $C_2H_2(OH)_2(CO_2H)_2$	0·097
Racemic acid $C_2H_2(OH)_2(CO_2H)_2$	0·097
Mesotartaric acid $C_2H_2(OH)_2(CO_2H)_2$	0·060
Phenyl-succinamic acid $C_2H_4(CONHC_6H_5)CO_2H$	0·0020

o-Chlorophenylsuccinamic acid $C_2H_4(CONHC_6H_4Cl)CO_2H$.	0·0021
***m*-Chlorophenylsuccinamic** acid $C_2H_4(CONHC_6H_4Cl)CO_2H$.	0·0021
p-Chlorophenylsuccinamic acid $C_2H_4(CONHC_6H_4Cl)CO_2H$.	0·0021
o-Tolyl-succinamic acid $C_2H_4(CONHC_7H_7)CO_2H$ . .	0·0021
p-Tolyl-succinamic acid $C_2H_4(CONHC_7H_7)CO_2H$ . .	0·0020
Succinuric acid $C_2H_4(CONHCONH_2)CO_2H$.	0·00311
Thio-succinuric acid $C_2H_4(CONHCSNH_2)CO_2H$.	0·00333

Oxysuccinic, or malic, acid has a constant six times as great as succinic acid. The factor is somewhat smaller than for the monobasic acids, which may be because a negative radicle carboxyl is already present. The natural optically active acid has exactly the same constant as the inactive acid got from monobromsuccinic acid. The same relation recurs in tartaric acid and racemic acid. Both the dextrorotatory and the lævorotatory acid, as also the inactive racemic acid formed by a combination of these two, are all of exactly the same strength. This result is in accordance with the present views concerning the constitution of these compounds. The dextrorotatory and lævorotatory acids contain their constituents in a perfectly symmetrical arrangement, and must, therefore, have equal co-efficients of affinity. It has been assumed that the optically inactive acids produced from the optically rotating ones consist each of two molecules of the active acids. This is probably correct for the solid crystallised substances, but not for solutions; in these, both compounds are present side by side, uncombined, a conclusion which has also been arrived at in another way by Perkin (*C. J.* 52, 362). The undecomposable inactive mesotartaric acid has, however, another, and that a smaller, constant; theory also ascribes to it a different constitution.

In the preceding table are further contained a number of derivatives of phenylsuccinamic or succinanilic acid. This acid itself is only 3·3 times weaker than succinic acid, while the introduction of the aniline residue into CO_2H of malonic acid decreased the strength 8 times; this indicates that the position of the substituent at a greater distance weakens the effect. The almost complete equality of the constants for all substitution products of succinanilic acid is of great interest; the distance of the benzylic residue from the carboxyl is here too great to allow the substituents to exert their effect over it. The usual assumption, that the molecular forces cease to act at even very small distances, is thereby made more definite, in that such distances are already given by the molecular dimensions.

As already found, the introduction of the urea residue produces a smaller decrease than that due to aniline. Smaller still is the effect of the thio-urea residue.

Dicarboxylic acids of benzene.

o-Phthalic acid $C_6H_4(CO_2H)_2$ . .	0·121
m-Phthalic acid $C_6H_4(CO_2H)_2$ . .	0·0287
Oxyterephthalic acid $C_6H_3.OH.(CO_2H)_2$	0·25
Phthalamic acid $C_6H_4(CONH_2)CO_2H$.	0·0160
Phthaluric acid $C_6H_4(CON_2H_3CO)CO_2H$	0·0290

As we were led to expect, the entry of a carboxyl in the ortho- position produces a somewhat considerable rise in the constant—*viz.* to twenty times the former value. For the meta-position the factor is only 4·8. *p*-Phthalic acid is too insoluble to be measured. But assuming that in oxy-*p*-phthalic acid the hydroxyl acts as strongly as in salicylic acid, the constant of *p*-phthalic acid would be estimated as 0·014 to 0·015, and it would follow that, in accordance with the usual result, carboxyl in the para- position—*i.e.* in the distant one—exerts the least action. A *weakening* effect, such as is exerted by hydroxyl in the para- position, seems to be excluded.

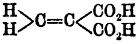
The amide residue in phthalamic acid has lowered the constant to one-eighth its value, but the acid is yet stronger than benzoic acid, and the group $CONH_2$ must be looked upon as negative. The urea residue exerts, as it always does, a much less marked weakening effect.

Unsaturated dibasic acids. The dicarboxylic acids $CH_{2n-2}(COOH)_2$ exhibit very similar isomeric relations to those of the compounds of the acrylic acid series. The following were measured:—

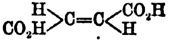
Maleic acid $C_2H_2(CO_2H)_2$ . . .	0·17
Fumaric acid $C_2H_2(CO_2H)_2$ . . .	0·093
Citraconic acid $C_3H_4(CO_2H)_2$ . . .	0·340
Mesaconic acid $C_3H_4(CO_2H)_2$ . .	0·079
Itaconic acid $C_3H_4(CO_2H)_2$ . . .	0·0120

The isomeric compounds are seen to have widely different constants. These results agree very well with the views of van't Hoff and Wislicenus. For fumaric and maleic acids the following formulæ have been adopted:

Maleic acid

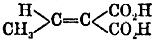


Fumaric acid

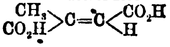


According to this, the two carboxyl groups are much nearer to each other in maleic than in fumaric acid, and the first must be stronger, as is actually the case. Similarly, according to Wislicenus, the formulæ

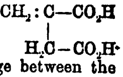
Citraconic acid

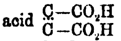


Mesaconic acid



hold, and for the same reason citraconic acid must be stronger than mesaconic acid, which conclusion again agrees with experiment.

Itaconic acid has the formula  $\begin{array}{l} CH_2:C—CO_2H \\ \quad\;\; | \\ H_2C—CO_2H \end{array}$ and therefore no double linkage between the carbon atoms combined with carboxyl. Accordingly, its constant is much smaller; it is only twice as great as that of succinic acid.

It may be mentioned that acetylene dicarboxylic acid  $\begin{array}{l} C—CO_2H \\ C—CO_2H \end{array}$ is so strong that a constant cannot be determined for the first stage of dissociation. The acid is but little inferior to sulphuric acid.

Thiophene and pyridine group.

α-Thiophenic acid $C_4H_3S.CO_2H$ . .	0·030
Pyromucic acid $C_4H_3O.CO_2H$ . .	0·071
Picolinic acid (α) $C_5H_4N.CO_2H$ . .	0·0003
Nicotinic acid (β) $C_5H_4N.CO_2H$ . .	0·00137
Isonicotinic acid (γ) $C_5H_4N.CO_2H$.	0·00109

Lutidinic acid ($\alpha\gamma$) $C_5H_3N.(CO_2H)_2$	0·60
Cinchomeronic acid ($\beta\gamma$) $C_5H_3N.(CO_2H)_2$	0·21
Isocinchomeronic acid ($\alpha\beta$) $C_5H_3N.(CO_2H)_2$	0·43
Chinolinic acid ($\alpha\beta$) $C_5H_3N.(CO_2H)_2$	0·30
$\beta\beta$-Pyridine dicarboxylic acid $C_5H_3N.(CO_2H)_2$	0·15

The replacement of the group C_2H_2 in benzoic acid by sulphur raises the constant to five times its value, provided the carboxyl is placed next to the sulphur. In the β- position the carboxyl is without doubt influenced less, but we have yet no measurement of the constant.

It is remarkable that a similar replacement of C_2H_2 by oxygen, forming pyromucic acid, acts much more strongly than a replacement by sulphur. On account of the magnitude of the constant it is very probable that in pyromucic acid the carboxyl is in a position next to the oxygen.

Differently from sulphur and oxygen, the replacement of C_2H_2 by CNH has a strongly weakening effect on the constant. The values found for the monocarboxylic acids of pyridine correspond fairly with the assumptions which might be made on the basis of the constitutions of these substances; picolinic acid, which contains the carboxyl next to the nitrogen, is by far the weakest; but the β- acid is stronger than the γ- compound, so that in pyridine the β- position proves the place of smallest influence.

The behaviour of the dicarboxylic acids of pyridine is very unexpected. While all monocarboxylic acids of pyridine are weaker than benzoic acid, all dicarboxylic acids are stronger than the strongest dicarboxylic acid of benzene—that is, o-phthalic acid, whose constant is 0·12. A further difference is that the strongest dicarboxylic acids are those which contain carboxyl in the α- position—that is, next to the nitrogen. Then follow the acids which contain carboxyl in the γ- position, and lastly those with carboxyl in the β- position. These relations are the exact reverse of those observed for the monocarboxylic acids; where a decrease of the constant had been observed there, an increase is found here. No plausible hypothesis concerning the cause of these peculiar phenomena has yet been brought forward.

Oxycinchomeronic acid $C_5H_2(OH)^{\alpha}N.(CO_2H)_2$	1·67
Methyl pyridine dicarboxylic acid $C_5H_2(CH_3)^{\alpha}N.(CO_2H)_2^{\beta\beta}$	0·20
Dimethyl pyridine dicarboxylic acid $C_5H(CH_3)_2^{\alpha\alpha}N(CO_2H)_2^{\beta\beta'}$	0·34
Dimethyl pyridine dicarboxylic acid $C_5H(CH_3)_2^{\alpha\gamma}N.(CO_2H)_2^{\beta\beta'}$	0·55

Owing to the entry of hydroxyl in the ortho-position, cinchomeronic acid has had its constant increased to eight times its value. The methyl groups increase the strength of the $\beta\beta$-dicarboxylic acid, and they do so to a greater extent in the γ- position than in the α- position.

Further, several poly-carboxylic acids of pyridine were examined; the constants cannot, however, be calculated, because the dissociation assumes a somewhat complicated character. But it is evident that the relations found in the case of the dicarboxylic acids concerning the influence of the position of the carboxyl hold good in these cases also. The rules found for the dicarboxylic acids were also confirmed in the case of methyl derivatives of the tricarboxylic acids. On the other hand, phenyl on entering into lutidine dicarboxylic acid, whose constant is 0·34, has a weakening effect, the constant for the compound formed being only 0·012. The action here is the reverse of that observed in the case of the fatty acids.

Quinaldinic acid $C_9H_6N.CO_2H$	0·0012
Cinchonic acid $C_9H_6N.CO_2H$	0·0013
Dipyridyl monocarboxylic acid $C_{10}H_7N_2.CO_2H$	0·002
Dipyridyl dicarboxylic acid $C_{10}H_6N_2(CO_2H)_2$	0·032
o-Pyridine benzoic acid $C_{11}H_8N.CO_2H$	0·0005
Phenyl pyridine dicarboxylic acid $C_{11}H_7N.(CO_2H)_2$	0·011

The quinoline carboxylic acids, which have a constitution analogous to that of the pyridine carboxylic acids, are somewhat stronger than these, as the naphthoic acids are stronger than the benzoic acids. Concerning the other acids but little can be generalised.

Amidobenzene sulphonic acids and similar compounds.

o-Amidobenzene sulphonic acid $C_6H_4.NH_2.SO_3H$	0·330
m-Amidobenzene sulphonic acid $C_6H_4.NH_2.SO_3H$	0·0185
p-Amidobenzene sulphonic acid $C_6H_4.NH_2.SO_3H$	0·0581

The results obtained from measurements of the amidobenzene sulphonic acids are somewhat remarkable. While benzene sulphonic acid itself is so strong an acid that its dissociation constant cannot be determined, its amido- derivatives can be measured with ease; the amido- group has, therefore, as it usually does, exerted a weakening effect. But in the case of the carboxylic acids the ortho- position was always that of greatest influence; here it appears as the position of least influence. The weakest of the three acids is the meta- compound, then follows the para- compound, and then the ortho- compound, which comes nearest to the parent substance. The assumption is thus suggested that, by the agency of the group SO_2, the hydrogen is brought to such a distance from the benzene nucleus that it is more influenced by the radicles in the meta- position than by those in the ortho-position.

Diamidobenzene sulphonic acid (2,3) $C_6H_3(NH_2)_2SO_3H$	0·0050
Bromamidobenzene sulphonic acid (2,5) $C_6H_3BrNH_2SO_3H$	7·9
Bromamidobenzene sulphonic acid (3,6) $C_6H_3BrNH_2SO_3H$	0·072
Dibromamidobenzene sulphonic acid (3,4,6) $C_6H_2Br_2NH_2SO_3H$	2·5
Toluidine sulphonic acid (3,4) $C_6H_3(CH_3)NH_2SO_3H$	0·024
Xylidene sulphonic acid (4,2,5) $C_6H_2(CH_3)_2NH_2SO_3H$	0·044

In indicating the constitution, the sulpho- group is put = 1, then follows amide, and then bromine or methyl.

These acids exhibit the usual relations to be expected from the nature of the substituents and their position, and thus do not call for any detailed discussion.

General considerations. The properties of chemical compounds, which can be expressed numerically, may be divided into three groups—the additive, the cumulative, and the constitutive. The first are of such a nature that in chemical compounds their value is the sum of the corresponding values of the constituents; these values have led to the conception of the atomic theory—*i.e.* to the assumption that the components continue to exist in the compounds as such.

The cumulative properties exhibit the peculiarity that, independently of the number and nature of the constituents, their numerical value is the same for certain complex systems. These have led to the conception of the molecular theory—*i.e.* to the assumption that the components of chemical compounds primarily form similar groups or systems, which have an individual existence, and out of which the visible and ponderable substances are built up.

And, finally, there exists a third group of properties, which are neither additive nor cumulative, since even in the case of substances having the same composition they can assume different values. These have led to the assumption that, in addition to the nature and number of the composing atoms, the properties of substances are influenced by still another condition. This condition has, from the time of Berzelius, been considered to lie in the different arrangement of the atoms within the molecule—*i.e.* in the constitution.

Of all the constitutive properties hitherto known—such as boiling-point, melting-point, colour, crystalline form, &c.—not one affords a clear insight into the determining cause, the chemical constitution. It is possible, when the latter has been found, more or less approximately, by purely chemical methods, to establish empirical relations; but these lie on the surface only, and lack generality. The cause of this is the defective development of our conceptions concerning the kind and the amount of the influence which the arrangement of the elementary atoms in the molecule exerts on the properties mentioned.

I believe I am not deluding myself when I affirm that the affinity constants, which represent a property of eminently constitutive nature, are far superior to all others with respect to their theoretical applicability. The result that one and the same atom exerts quite different effects, according to the 'position' which it occupies in the molecule, and that these effects are the greater the more close is the relation of the atom to that of the acid hydrogen, leads to the general inference that these effects are functions of the distance in space of the atoms in question. But thereby, for the first time, is gained a means of taking measurements in space of molecular structures. There is no doubt that long and laborious work is needed before such measurements will lead to results which will give an all-sufficient representation of the form of molecules. But it already seems certain that this goal can be reached.

It has been mentioned, to start with, that k, the affinity co-efficient of acids, appears, generally speaking, as a product whose factors are given by the nature and position of the elementary atoms composing the acid. This follows from the fact that with analogous changes in analogous substances the constants change in the same ratio—*i.e.* that in consequence of these changes the constants of the original substances must be multiplied by the same factor. But these factors are never exactly the same, just because two analogous changes are never exactly the same. If, for instance, we change acetic acid into glycollic acid, and propionic acid into lactic acid, the two changes are, it is true, very much alike; but in the first case the hydroxyl takes up a position next to two hydrogen atoms, in the second case next to one hydrogen atom and one methyl; the hydroxyl is therefore subject to a different influence, and will in consequence necessarily act differently on the carboxyl. The same holds for all corresponding cases. The approximate character of the general relation follows, therefore, as a necessity; the deviations from the type are caused by the nature of the subject, and themselves afford a means for bringing to light their cause, which is the secondary influence mentioned above. What has been said concerning the constitutive properties generally—that they can never be completely represented by a general scheme, because this is contradictory to their nature—holds particularly for the affinity co-efficients. In them the whole variety of nature asserts itself, and within the framework of great and general regularities produces the finest individualisation.

The form of the dissociation-constant as the product of factors $c = c_1.c_2.c_3$ . . . . has a deeper significance, which is recognised on going back to the dissociation-formula itself. This formula is obtained from the mechanical theory of heat in the following form:

$$\log.\frac{p}{p_1 p_2} = \frac{\rho}{R\tau} + C$$

where p_1 and p_2 are the partial pressures of the products of decomposition, p the pressure of the undecomposed substance, ρ the heat of dissociation, τ the absolute temperature, R the gaseous constant, and C is a value which is a function of the temperature only, and which, therefore, at constant temperature can be looked upon as a constant.

In the case in point $p_1 = p_2$, and since p_1 and p must be put proportional to $\frac{m}{v}$ and $\frac{1-m}{v}$, it follows that $\frac{p}{p_1^2} = \frac{(1-m)v}{m^2}$ and thence

$$\log.\frac{(1-m)v}{m^2} = \frac{\rho}{R\tau} + C$$

or

$$\log.\frac{m^2}{(1-m)v} = -\frac{\rho}{R\tau} + C^1.$$

Now the affinity co-efficient is $k = \frac{m^2}{(1-m)v}$; and since, on the other hand, quite generally $k = k_1.k_2.k_3$ . . . . it follows that

$$\log.k_1 + \log.k_2 + \log.k_3 + \ldots\ldots = -\frac{\rho}{R\tau} + C^1.$$

The constant C^1 depends only on the unit adopted and on the point chosen as zero; if, therefore, there appears on the left side of the equation a sum of terms represented by log.k, there must correspond to each of these on the right side a term of the form $-\frac{\rho_n}{R\tau}$, so that $\frac{\rho}{R\tau}$ also resolves itself into a sum of corresponding terms $-\frac{1}{R\tau}(\rho_1+\rho_2+\rho_3+\ \ldots\ .)$ in which one R_n and one ρ_n always correspond to each other.

This means: The natural logarithm of the dissociation-constant or affinity-constant is (save for a constant) proportional to the heat of dissociation of the acid in splitting into ions. Since the value of the dissociation- or affinity-constant is known from experiment to be the sum of a series of terms which depend on the nature and on the position of the constituent atoms, it follows that the electrolytic heat of dissociation also is the sum of a corresponding number of terms each of which is fixed by the nature and position of each individual atom.

Now in this case the heats of dissociation are the exact measures of the quantities of work which are done in the separation of the acid hydrogen atom from the negative ion. This is so because no external work has to be taken into account, and because the condition of the substances dealt with very closely approaches that of ideal gases. Hence the heat of dissociation measures the potential or the force-function of the atomic system at the corresponding point, and we see that this force-function is the sum of the values which, according to their nature and position, the individual atoms contribute to the total value. And thus elements which, like chlorine, sulphur, &c., raise the constant k, cause a decrease of the heat of dissociation, since log.k and ρ have different signs. The amido group, on the other hand, which decreases the constant, raises the heat of dissociation—*i.e.* it increases the amount of work necessary for splitting off the acid hydrogen.

It is by these considerations that the long-mooted question concerning the connection between chemical affinity and the thermal values of reactions has been decided in principle. In this result we see the eminently constitutive property of affinity-quantities brought back again to the additive form. This has been effected by introducing the influence of constitution, or of position in space, into the terms themselves. A similar development awaits the theory of all constitutive properties, as, in fact, we are forced to conceive the combined action of different elements as the sum of various effects.

Electrical theory of chemical affinity. Elsewhere (Affinity, vol. i. p. 67) the laws of chemical affinity have already been explained. Nothing definite could be stated concerning their cause; but it followed from the close connection which was shown to exist between the co-efficients of chemical reacting power of electrolytes, and the values of the electrical conductivities, that an intimate relation exists between these two properties. The prospect is thus opened of carrying out in an exact form the electro-chemical theory of affinity which was rather conjectured than worked out by Davy and Berzelius.

The new view which affords such a possibility is the common cause underlying electrolytic conduction and chemical reactions as recognised by Arrhenius, *viz.* the existence of free ions. On making the assumption, which is justified by this concordance, that chemical processes betwee electrolytes take place only by the agency of th free ions, the laws of chemical affinity, which have been established empirically, can be deduce so as to be in accordance with experiment. T do this we only further need van't Hoff's theor of solutions, and the theory of the laws of dissociation as deduced for gases (*v.* Dissociation in vol. ii.), which laws, thanks to van't Hoff's theory, can also be applied to substances in solution.

The general law of chemical affinity first recognised is that manifestations of this affinity on the part of a definite substance are expressible by a definite co-efficient, dependent on the temperature and dilution, but independent of the nature of the chemical reaction in which the substance participates.

Now, if the reacting power of a substance in solution depends on the number of dissociated ions which are present, it can be seen at once that the above-mentioned law must of necessity hold good. So, for instance, the state of dissociation of an acid determines the velocity with which it must act on methylacetate, acetamide, marble, &c. The nature of the other substance determines a factor only, which in analogous cases is the same.

Hence we must conclude that all acids, for instance, when completely dissociated are equally strong. The strong inorganic acids HCl, HBr, HI, HNO_3, $HClO_4$ must be classed here, as also the sulpho- acids and similar organic acids. No one of these substances exhibits any of the specific differences discussed in former paragraphs for acids of medium strength. They all exert a nearly equal effect when used in equivalent quantities, and approach the maximum conductivity even at moderate dilutions. At a time when the dissociation theory of electrolytes did not exist, the author of this article vainly tried to obtain from benzene-sulphonic acid, by all the means which make weak acids stronger—such as the introduction of halogens, nitro-groups, &c.—acids stronger than the parent substance, which may itself be ranged side by side with hydrochloric acid. This was not possible; all 'strengtheners' remained in this case ineffective. This remarkable fact shows that it is not its special nature, but its electrical condition, which is determinant for the chemical effect of a substance, especially if that substance be an acid.

The greater the number of the molecules which are split into their positively and negatively charged parts, the stronger is the acid; but any ion, when once present in the separated, electrically charged, condition, is as effective as any other. Here, then, we see that Berzelius' conclusion drawn from false premisses, by means of which he attempted to demonstrate the absurdity of Faraday's law—that then the chemical affinity between the ions of all electrolytes would have to be the same—is perfectly correct. The affinity of the most diverse ions is really the same, because it does not depend on their nature but on their electrical charge, and this, according to Faraday's law, is everywhere the same. What does depend on the nature of the ions is the degree to which they dissociate, and herein alone lies the cause of the differences in the affinity-quantities.

In the arguments used so far, it has been assumed that the state of dissociation of the reacting substances is determined by the volume and the temperature, and that the presence of other substances does not alter the state of the one considered. This case, however, only occurs when there are present either one dissociated substance and nothing but non-electrolytes besides, or when all the dissociated substances present are for all practical purposes completely split up. But as soon as several partly dissociated substances are present, the relations become much more complicated.

It is known from the theory of dissociation that when two gaseous substances are present, and the quantities of these substances vary, the product of their active quantities, or of their concentrations, must be constant, constant temperature being presupposed. If, for instance, a given space is filled with the gaseous products of decomposition of ammonium hydrosulphide, the addition of sulphuretted hydrogen will cause a decrease in the quantity of hydrosulphide dissociated, because on increasing the one factor the other must decrease in the same ratio. The same must evidently hold for electrolytes; on adding to a solution which contains the ions A + B an excess of ions A, the quantity of ions B must decrease until the product of the two quantities has again become equal to its original value. Now, it is not very well possible to add ions A only, but an electrolyte can be added which is also dissociated, and which contains the ions A + B′; if B′ is different from B, the two do not influence each other.

We may now ask how two solutions must be constituted in order that their state of dissociation shall not vary when the solutions are mixed. We have the solutions of the electrolytes A + B and A + B′, which contain a common ion A; let their volumes be v and v'. Then, in accordance with the general law of the equilibrium of dissociation, the following equations will hold:

$$\frac{1-\xi}{v} = k\frac{\xi}{v}\cdot\frac{\xi}{v}$$

$$\frac{1-\xi'}{v'} = k'\frac{\xi'}{v'}\cdot\frac{\xi'}{v'}$$

in which the quantities of the electrolytes originally present are put as equal to 1, and the dissociated portions equal to ξ and ξ' respectively. On mixing the solutions, the volume becomes $v+v'$, the dissociation ratios ξ and ξ' remaining unchanged, as supposed. The quantities of the undissociated portions are $1-\xi$ and $1-\xi'$, but the products $\xi.\xi$ and $\xi'.\xi'$ change into $\xi(\xi+\xi')$ and $\xi'(\xi'+\xi)$, since the ion A common to both substances participates in the equilibrium condition of both. We have, therefore,

$$\frac{1-\xi}{v+v'} = k.\frac{\xi}{v+v'}\cdot\frac{\xi+\xi'}{v+v'}$$

$$\frac{1-\xi'}{v+v'} = k'.\frac{\xi'}{v+v'}\cdot\frac{\xi+\xi'}{v+v'}.$$

On dividing each of these equations into each of the corresponding equations given above, it follows that $\frac{\xi}{\xi'} = \frac{v}{v'}$. Therefore, in order that the state of dissociation should not alter on mixing solutions of two electrolytes which have one ion in common (for instance, two acids), the portions dissociated must be in the ratio of the volumes. Writing the equation in the form $\frac{\xi}{v} = \frac{\xi'}{v'}$, the law can also be expressed in this form: when the concentration of the common ion is the same in both solutions, these do not influence each other.

Arrhenius, to whom we owe these considerations, calls solutions which do not influence each other in the sense just mentioned *isohydric solutions*. Since, in accordance with the above formula, it is only necessary for this that the *concentration* of the common ion in the two solutions should be the same, the ratio of the quantities of the two solutions does not enter into consideration; isohydric solutions can be mixed in all proportions without mutually changing their condition.

If, however, two non-isohydric solutions which contain a common ion are mixed, the process can be represented by saying that the one solution withdraws water from the other until both have become isohydric; then they leave each other uninfluenced. This withdrawal of water occurs in the following manner. First, the total concentration of the solution which loses water increases, and thereby the concentration of the ions increases also. But, owing to this, the state of dissociation changes directly, since, in consequence of the smaller volume, the dissociation decreases, and, therefore, the concentration of the ions increases more slowly than the total concentration. Conversely, the concentration becomes less in the portion which takes up water; but, owing to the increase in dissociation, it does so to a smaller degree than corresponds to the volume change.

Since the relation between the volume and the state of dissociation is known for binary electrolytes (p. 194), a formula can easily be deduced which allows us to calculate the characteristic quantities for a mixture of several electrolytes. But it is generally simpler to proceed by way of successive approximation.

Two solutions which are isohydric with a third must be isohydric with each other; because, in order to be isohydric with the third, there must be in both the same concentration of the common ion as is in the third solution.

These laws were all established empirically by Arrhenius (*W.* 30, 51), and it was only lately that he deduced them theoretically from his theory of dissociation (*Z. P. C.* 2, 284 [1888]). The examination of these relations is best conducted by making measurements of electrical conductivities. Since the conductivity of a compound in solution is proportional to the number of free ions, it can easily be recognised whether two substances with a common ion—two acids, for instance—are isohydric; if the conductivity of the mixture is equal to the sum of the conductivities of the components, the solutions are isohydric; if this is not the case, the two numbers differ from each other more or less. To quote an example: with a phosphoric acid solution, of specific conductivity $l = 225{\cdot}6$, was mixed an equal volume of hydrochloric acid solution $l = 225{\cdot}9$; the mixture gave $2l = 469{\cdot}0$, while the sum of the two values is $451{\cdot}5$; the observed conduc ivity was too great by 17·5. Further, the same phosphoric acid solution mixed with an equal volume of a more dilute hydrochloric acid, $l = 185·1$, gave for the conductivity of the mixture $2l = 407·4$; this is smaller by 3·3 than the sum 410·7. Finally, hydrochloric acid of $l = 168·8$ gave for the mixture $2l = 394·4$, the sum being 394·4; both solutions were isohydric. By such experiments as this Arrhenius arrived at the laws stated above.

It need scarcely be mentioned that any other property of solutions which depends on the molecular condition of the dissolved substance could likewise have been used for determining the relations of isohydricity. The best of these properties would be measurements of the velocities of reaction — for instance, those of the inversion of sugar — these being proportional to the state of dissociation; but the freezing-points, vapour pressures, &c., could also have been used.

So far the only case considered has been that in which the mixed electrolytes contain a common ion. If this is not the case, new phenomena appear, which we will now consider in greater detail. It has already been pointed out that the theory of free ions leads to a view of the processes of the formation and mutual decomposition of salts which is very different from that generally accepted. It has been shown that, neglecting the small undissociated portions, the process of neutralisation between the strong acids and bases consists exclusively in the formation of water from the ions H and OH. The cause why these ions coalesce to form undissociated water lies in the fact that water is an extremely stable compound, which, under ordinary circumstances, is only very slightly split into ions. If, therefore, such ions anywhere appear simultaneously, they combine directly to form undissociated water.

The phenomena take a quite similar course when a strong acid—hydrochloric, for instance—acts on the salt of a weak acid—sodium acetate, for instance. The former solution is almost exclusively composed of ions H and Cl, the latter of ions Na and $CH_3.CO_2$. Since the sodium chloride also is almost completely dissociated when in dilute solution, the ions Na and Cl are already present in the same condition as in sodium chloride solution, and there exists no tendency to the formation of this compound. But, in addition, there are present the ions H and CH_3CO_2, and these cannot exist side by side without for the most part combining. Hence a corresponding quantity of undissociated acetic acid will be formed, as is actually shown by experiment. But while formerly this fact was ascribed to a specially great affinity between the chlorine and the sodium, and the acetic acid was allowed to play a passive part, being supposed to be 'expelled' by the hydrochloric acid, we now see that the entire cause of the process lies in the action of the acetic acid. Owing to the great affinity of its ions, it is formed whenever its ions meet, while the components of the 'strong' reagents, chlorine and sodium, remain perfectly indifferent in the process.

The conditions under which chemical equilibrium is established between four substances, formed by a combination in pairs of two positive and two negative electrolytes, must now be established in a general manner. We assume we have produced four solutions of the substances A_1B_1, A_1B_2, A_2B_1, and A_2B_2, so that those solutions which contain a common ion are isohydric. When this is the case we can, it is true, mix the isohydric solutions in all proportions; but if we mix all four solutions the simple law stated above evidently no more holds, and we must ask in what proportion the mixture must be made in order that no change in the state of dissociation should occur. Let a, b, c, and d be the relative volumes of the four solutions in which this occurs, and let α, β, γ, and δ be the undissociated quantities of the four substances. We can represent the dissociated quantities by ha, hb, hc, and hd, since, in consequence of the assumption made, there must in all cases be equal concentration of the ions. The equations of dissociation of the solutions thus become

$$\frac{\alpha}{a} = k_1\left(\frac{ha}{a}\right)^2 \qquad \frac{\beta}{b} = k_2\left(\frac{hb}{b}\right)^2$$

$$\frac{\gamma}{c} = k_3\left(\frac{hc}{c}\right)^2 \qquad \frac{\delta}{d} = k_4\left(\frac{hd}{d}\right)^2$$

or, $\alpha = k_1h^2a$, $\beta = k_2h^2b$, $\gamma = k_3h^2c$, $\delta = k_4h^2d$.

If we suppose the four volumes to be mixed, new equations will make their appearance which have the form $\frac{\alpha}{a+b+c+d} = k_1\frac{h(a+b)(a+c)}{(a+b+c+d)^2}$, &c., and which can be brought to the form

$$\alpha = \frac{k_1h^2(a^2+ab+ac+bc)}{a+b+c+d},$$

$$\beta = \frac{k_2h^2(b^2+ab+bd+ad)}{a+b+c+d}, \text{ \&c.}$$

The quantities α, β, γ, and δ are to remain unchanged, according to the assumption. Now, by dividing the corresponding equations by each other, the same equation follows from each pair

$$ad = bc,$$

i.e. the volumes a, b, c, d of the four solutions must be such that the products of the volumes of such pairs of solutions as contain no common ion must be equal to each other.

Now, the volumes a, b, c, and d are proportional to the active or dissociated portions of the four substances present. Calling the total quantities of the latter, p, p_1, q, and q_1, the values a, b, c, and d are proportional to m_1p, m_2p_1, m_3q, and m_4q_1, and hence we get from $ad = bc$ the equilibrium formula

$$m_1p \,.\, m_3q = m_2p_1 \,.\, m_4q_1$$

This equation represents not only Guldberg and Waage's formula for chemical equilibrium, but it also contains the extension, made by Ostwald, that every co-efficient of the Guldberg and Waage equation, $k_1pq = k_2p_1q_1$, is made up of two factors each of which depends only on the nature of the ions.

But the equation goes still further than this extension. In the theory of affinity the co-efficients m_1, m_2, &c. have been considered as constant to a first approximation. But from what has been said it follows that they are not constant; they depend on the state of dissociation of the four substances, and are rather complicated functions of the dissociation-constants, of the quantities, and of the total volume. The various deviations from the simple laws which were brought to light by experiment find here their appropriate explanation. Thus it follows that in the case of slightly dissociated acids the degree of dissociation must be considerably lowered by the presence of the normal salts of these acids, which salts are themselves considerably dissociated. The corresponding fact, that such mixtures act much less strongly than the quantity of free acid present in them would do, was known long before theory explained it.

Arrhenius has subjected his investigations on the saponification of ethyl acetate by means of ammonia in the presence of different salts (*Z. P. C.* 1, 110) to an examination from the standpoint of these newly-established ideas (*ib.* 2, 289), and has everywhere found them to be in complete agreement with experiment. He has also re-examined a great number of older investigations on conditions of chemical equilibrium in the light of his theory (*ib.* 5, 1), and here also the discrepancies found when considered from the point of view of the older theory have for the most part disappeared (*v.* also *Z. P. C.* 9, 487).

Electromotive forces. Contact theory or chemical theory?[1]

The laws of electromotive force, or of differences in potential produced on the contact of different substances, are not nearly so well known as those of electrical conductivity. It is true the knowledge of the phenomenon itself is as old as that of galvanic electricity, since Volta had already carried out the first approximate measurement of it, but up to the present day no agreement has been arrived at between the different investigators concerning even the chief phenomena.

Volta screwed a disc of zinc coated with isolating varnish on to his straw-electrometer; on the top of this he placed a similar disc of copper, connected the two discs metallically, and after the connection had been broken he took off the copper disc by means of an insulating handle. The electrometer then proved to be charged; examination showed that the straws were charged with positive electricity.

This phenomenon indicates that the substances used—that is zinc, copper, and the isolating coating—charge each other electrically on contact. Volta assumed that, of the three contacts, only the one between copper and zinc was electromotively active; the contact between the metals and the isolating layer of resin was regarded by him as indifferent. Though neither then, nor up to the present day, has a proof of this assumption been brought forward, it has yet met with fairly universal acceptance, and it often passes as a fact not to be doubted.

On the further assumption, which certainly is incorrect, that liquids also—such as water or salt solutions—show no differences of potential with the metals, Volta constructed his electric pile by superposing alternately two metals and a moist card disc. By this he expected an intensification of the electrical effects, since the electricity of the metal lying underneath was to communicate itself through the moist discs to the one lying above, without any change, and so the effects of the individual pairs of metals were to be added together. Volta did, in fact, obtain the expected intensification—a proof that great discoveries may be made on the basis of quite false hypotheses.

Fabbroni first refused to accept the assumption that the tension of the voltaic pile has its seat only at the point of contact of the metals, and numerous other investigators have taken the same line. Faraday especially, whose work in electrochemistry ranks with the most important done in this subject, was an opponent of Volta's views. He attributed the production of the electric current solely to the chemical processes present, and transferred the cause of the production of electricity to the places at which these processes occur—*i.e.* the point of contact between the metals and the electrolytes.

The contention thus aroused between the contact theory and the chemical theory of the galvanic cell has lasted to the present day, and even now it is not completely decided. But most of the discussions raised have certainly originated in the insufficient lucidity with which the questions have been stated.

In so far as a galvanic current can be produced only by using electrical energy, it can be maintained, to begin with, that in order to cause a galvanic *current* there must be present a corresponding source of energy. If other kinds of energy are excluded, as is the case in an ordinary galvanic cell, it can further be said that chemical energy changes into electrical energy, and that, therefore, a theory of the electric *currents* produced by the voltaic cell must in any case be a chemical one.

But to an electric current there appertain two factors: a quantity of electricity, and a difference of potential. The first is given by the law of Faraday. Since in electrolytes the motion of electricity takes place only simultaneously with the motion of the ions, equivalent quantities of the different ions carrying equal quantities of electricity, a current in a galvanic cell can again not be produced without a corresponding chemical process. From this point of view, also, the theory must be a chemical one. As regards the other factor of the current energy—*i.e.* the difference of potential—an unequivocal decision, as in the preceding cases, can certainly not be pronounced easily. The experiments on this subject, taken alone, have proved that all substances, when separated from each other after close contact, show themselves to be electrically charged. The smallest differences suffice for this. It has been long known, for instance, that black and white silk stockings which have been pulled over each other are electrically charged after separation. Even in such homogeneous materials as crystals of mica or calcite, the two parts obtained by cleavage of the layers are found to be in different electrical conditions at the original point of contact.

It is imperative, therefore, to accede to the proposition of the 'contact theory,' in so far as to admit that a process occurs at the surface of contact when two surfaces touch, in consequence of which the surfaces are at different potentials after separation. We do not know what the nature of this process is. Helmholtz supposes the different substances to possess a different attraction for electricity, in consequence of which there is brought about a separation of the electricity at the planes of contact; then when the bodies are separated they appear electrically charged. A difficulty with respect to this theory is found in the electrical phenomena attending the cleavage of crystals, where a difference in attraction seems excluded.

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[1] A complete discussion of this question by O. Lodge is to be found in *P. M.* [5] 19.

In order that the equilibrium of electricity may be changed when two bodies charge themselves oppositely on contact, the expenditure of a certain quantity of energy is required. The source of this energy has to be sought in the change which the surfaces of the bodies undergo owing to their mutual contact.

In order that this difference of potential may cause an electric current, two things are needed. Firstly, the bodies touching must be conductors, as otherwise the electricity cannot move; and secondly, a cause must be present which will maintain unchanged the condition of the surfaces in contact, in consequence of which condition the arrangement of the electricity is changed; otherwise a charging motion of the electricity could take place once only, but not a continuous current. The current can be produced by mechanical action, and then the phenomena of frictional electricity appear, or the renewal of the surfaces occurs by chemical action, and we deal with galvanic cells.

When considered from this point of view also, the chemical processes appear as the causes of galvanic currents, and a final theory of these currents will doubtless be much more a 'chemical' than a 'contact' theory.

Galvanic cells. The simplest conditions for examining the relations between chemical and electrical energy are found in the so-called *constant galvanic cells*, of which the Daniell cell is a type. This cell consists of a copper plate in a solution of copper sulphate, and a zinc plate in a solution of zinc sulphate; both solutions are in contact with each other. Such a galvanic cell has an electromotive force of about 1·09 volts, which does not change appreciably when the metals are connected by a conductor, and the galvanic current is thus allowed to pass for a longer or a shorter time.

The chemical process in such an element is also of the simplest kind: zinc dissolves to zinc sulphate, while copper is separated from the copper sulphate. Hence the same process takes place as when a piece of zinc is brought into a copper sulphate solution.

The chemical energy which is available in this process can easily be measured by experiment; it proves to be 50,100 cal. for the reaction

$$Zn + CuSO_4Aq = Cu + ZnSO_4Aq.$$

Now, since (p. 180) the unit of electrical energy, volt × coulomb, is equal to 0·2356 cal., this quantity of heat corresponds to 212,600 electrical units.

Now, of the two factors making up the electrical energy of the voltaic cell, one is given by Faraday's law. One gram-equivalent of a metal carries (p. 180) 96,540 coulombs. Since copper and zinc are divalent, the above equation refers to 2 gram-equivalents; when, therefore, 65 g. of zinc dissolve in the Daniell cell, 193,080 coul. are transferred. Dividing this value into the number 212,600 (volt × coulomb), we get 1·10 volts for the electromotive force of the Daniell element, a number which agrees well with the observed value.

This calculation was first carried out by W. Thomson with the help of numbers due to Joule. From the agreement between observation and calculation, the inference was drawn that the assumption made in this case—namely, that the chemical energy transforms itself completely into electrical energy—was universally correct. From this was deduced the possibility of calculating, on the basis of thermochemical data, the electromotive force of all constant elements, and further, the electromotive force of all elements in which the chemical process is known. It was only necessary to multiply the heat of the reaction referred to one *equivalent* (not molecular weight) by $\frac{0·2356}{96540} = 0·00000244$. It would also follow that the electromotive force of all cells would be proportional to the heat of the chemical reaction.

This theory could not, however, be maintained. On the one hand, theoretical doubts were raised, and that specially by Braun (*W.* 5, 188), against the premisses that the chemical energy of the galvanic cell was always completely transformed into electrical energy; and, on the other hand, experience proved that as a rule the assumed proportionality between heat of reaction and electromotive force did not exist. Raoult (*A. Ch.* [4] 4, 392) discovered a number of cells, some of which produced less, and some produced more, energy than corresponded to the heat of reaction of their chemical changes; and at a later time it was proved—chiefly by F. Braun and Alder Wright (*P. M.* [5] 19, 1), by means of direct measurement—that only in rare cases do the chemical and electrical energy exactly correspond to each other.

The simple theory must, therefore, be abandoned, and without assuming that the chemical energy is wholly transformed into electrical energy, we must seek to discover a relation between the two. Such a formula has been found by W. Gibbs and H. von Helmholtz (*B. B.* 1882). The following statement is a simple way of deducing this equation. Let there be given a galvanic cell whose heat of reaction calculated for one equivalent is W. Let its electromotive force at the absolute temperature τ be ϵ. On raising the temperature by $d\tau$ the electromotive force is changed by $d\epsilon$.

Now let us carry out the following cycle. The cell is heated from τ to $\tau + d\tau$. Then let the quantity of electricity q, by means of which one equivalent of the reacting substance undergoes chemical decomposition, pass through the cell, the electromotive force remaining $\epsilon + d\epsilon$, and the temperature being kept constant. Now let the temperature be brought to τ and, the electromotive force being ϵ, and the temperature being constant, let the same quantity of electricity q be passed through the element in the opposite direction. Thereby the element returns exactly to its initial condition.

According to the mechanical theory of heat, the portion of heat transformable into work, in a reversible cycle taking place in the temperature-interval $d\tau$, is $\frac{d\tau}{\tau}$ of the total quantity of heat produced. Now, the work is given by $qd\epsilon$, and the total heat which has been communicated to and taken from the cell is $\epsilon q - W$. If an electric current alone were produced, the quantity of heat would be ϵq. But since a chemical process also takes place, which yields a portion of the heat—namely, the heat of reaction, W—it is only necessary to communicate the difference $\epsilon q - W$.

We have then the equation—

$$\frac{d\tau}{\tau} = \frac{qd\epsilon}{\epsilon q - W}$$

or

$$\epsilon = \frac{W}{q} + \frac{1}{\tau} \cdot \frac{d\epsilon}{d\tau}$$

The former equation was $\epsilon = \frac{W}{q}$; we see, therefore, that a correcting term must be added, and that this term is dependent on $\frac{d\epsilon}{d\tau}$, that is, on the change of electromotive force with change of temperature. In the case that $\frac{d\epsilon}{d\tau} = 0$, the new equation is the same as the old one; in the Daniell cell the temperature co-efficient is, in fact, nearly equal to zero, and thus it is explained that in this case the chemical energy is equal to the electrical energy.

The equation has been examined in many ways. At first it gave only partially correct results, and in some cases observation and calculation differed from each other. The differences occurred, however, only in cells which contained mercury compounds, and the cause was the use of a wrong number for the heats of formation of these compounds. When this error was corrected by Nernst (*Z. P. C.* 2, 23) the discrepancies disappeared; and a very careful investigation by H. Jahn (*W.* 34, 755), in which the thermal and electrical quantities were measured simultaneously, has fully confirmed the correctness of the Gibbs-Helmholtz formula.

The formula has been deduced primarily for constant galvanic cells, and when deducing it the conditions assumed have been expressed; the chemical process resulting from the passage of the quantity of electricity q (which, however, can be as small as we will) must be reversible, by allowing the same quantity of electricity q to pass through the element in the opposite direction. In order that a galvanic cell should fulfil this condition, it is generally requisite that each metal should be surrounded by its corresponding salt. Therefore, when the salt is soluble, the metal must stand in a solution of the salt. In the case of insoluble salts it generally suffices to cover the metallic surface with the solid salt; in this case, either the salt of another metal with the same acid (which salt is not precipitated by the first metal), or the free acid itself, serves as the electrolyte.

The action in a Daniell cell is as follows. Individual atoms of the metal pass from the zinc as positively charged ions into the solution of the sulphate. Since no free electricity can exist within the solution, the copper ions of the copper sulphate must go to the copper plate, where they give up their positive electricity, passing into ordinary metallic copper. Owing to this action, a motion of the positive electricity from the zinc to the copper takes place in the solution; on connecting both metals by a wire the current passes continually through it, corresponding quantities of zinc and copper being dissolved, and precipitated, respectively. If the cell is not closed, the zinc becomes charged negatively, owing to the exit of positive ions, and the copper positively, owing to their entrance; and this goes on until the attraction of the zinc for the positive ions, and their repulsion by the copper, is so great that neither can zinc pass into solution nor can copper separate out. The capacity of the ions being enormous, this is brought about by even extremely small numbers of them.

Nernst, who has studied these changes in detail (*Z. P. C.* 4, 129), assigns to the metals which are in contact with electrolytes definite *solution pressures*, just as volatile liquids or solids have definite vapour pressures. This pressure is the cause of zinc tending to pass into solution. The solution pressure of copper is very much smaller than that of zinc. Hence when the Daniell cell is newly set up, both metals will at first send positive ions into the solution. But, since no free electricity can exist in the interior of the solution, that metal which has the greater pressure will maintain the preponderance; its ions will pass into solution, and, in order that no free electricity may accumulate in the liquid, an equal number of copper ions must leave the solution, and be precipitated in the metallic state.

Similar arguments hold for all reversible elements. By their help, and with the help of the theories of electrolytic solutions expounded above, a great number of special cases referring to galvanic cells can be deduced theoretically. The results thus obtained have, on the whole, been confirmed by experiment; but details cannot be entered into here.

Besides the constant galvanic cells of the type just described, which are *reversible*, there still exists a great number of cells which, though practically constant, are not reversible. The constancy of these cells rests on the fact that the nature of the surfaces in contact is not altered by the chemical processes. When metal dissolves at the surface of the zinc, and when metal deposits at the surface of the copper, the nature of the bounding surfaces is not thereby influenced; this cell is also reversible, because on sending a current through in the opposite direction zinc is precipitated and copper dissolved, but the surface again undergoes no alteration.

Cells of the type of that of Grove, which consists of zinc in sulphuric acid and platinum in nitric acid, are also constant. On working this cell, zinc dissolves, expelling the hydrogen ions from the sulphuric acid; these hydrogen ions go to the nitric acid, whose own hydrogen ions go to the platinum; at the moment when they give up their positive electricity there, and pass into ordinary hydrogen (which, however, is in the nascent state), they are oxidised by the nitric acid to water, and the platinum surface remains unaltered. But such elements are not *reversible*. When an opposite current is passed through the cell, since the platinum ions cannot pass into solution, the ions NO_3 of the nitric acid separate out at the platinum, while hydrogen appears at the zinc; both these actions change the condition of the bounding surfaces, and thereby simultaneously change the electromotive force also.

Finally, there still remains the large group of the non-constant cells. These are distinguished by the fact that even when the current passes through them in the direct way, the ions separated out produce an alteration in the bounding surfaces, or in one of them at least. To these belongs Volta's cell, which consists of zinc and copper in salt water, and all the other similar combinations. A type still in use is Smee's cell, which consists of zinc and platinum in dilute sulphuric acid. On closing the circuit, zinc ions enter into the solution, expelling the hydrogen, which gives up its electricity at the platinum, whereby it first combines with or dissolves in the metal, and when that is saturated escapes in the gaseous form. In consequence of this, the surface of contact between the acid and the platinum is altered, and the electromotive force also changes, until saturation with hydrogen has taken place; after this point has been reached the electromotive force of Smee's cell remains practically constant. If the cell is left with the circuit open, the hydrogen gradually disappears, partly through diffusion into the air, partly through combination with the free oxygen of the air, induced by the catalytic action of the platinum. Thus, the cell again gradually resumes its original electromotive force. Such cells are, therefore, quite workable in cases where only small quantities of electricity are required at long intervals.

The seat of the electromotive forces. Volta found that no galvanic pile, giving a current, could be produced from metals only. When considered from the point of view of the principles of energy, such behaviour follows necessarily, because, no continuous source of energy being present in a circuit of metals alone, no current can be produced.

The cause of this may be of a two-fold nature. Either there exist no differences of potential between metals, or these follow a definite law, which involves that in a closed circuit these differences just neutralise each other. With Volta, we will assume the latter alternative, of which the former is only a special case. If, then, we have several metals A, B, C. . . and if we call the differences in potential between A and B, A and C, B and C, &c., in succession $(a-b)$, $(a-c)$, $(b-c)$ . . . the law is that we must always have $(a-b)+(b-c)+(c-d)+\ldots+(y-z)=(a-z)$. The difference of potential of a series of metals depends only on the nature of the first and the last metal, and not on the nature of the intervening metals.

This result necessarily follows if the values a, b, c . . . in the quantities $(a-b)$ &c. are considered as the potentials of the individual metals referred to a zero value which must be fixed arbitrarily. For the zero value of potential we generally use the potential of the earth, or, more correctly speaking, that of a large metallic mass which is in connection with the earth, as are, for instance, iron water-pipes. It can, therefore, be assumed that every metal connected with the 'earth' assumes a definite value of potential which depends only on the nature of the metal. These values of potential are the same for every metal, whether the different metals are in contact with each other or not.

In order to measure these differences of potential, the experiment of Volta mentioned before (p. 212) has been improved upon, in that instead of a dividing layer of resin one of air is used; and, dating from the time that R. Kohlrausch (*P.* 75, 88) thus carried out the first experiments, a great deal of similar work has been done.[1] But in this case also we are dealing, not with one, but with three separating surfaces—namely, copper-zinc, zinc-air, air-copper, and only when we make the assumption that the differences of potential at the last two surfaces are zero, are we enabled to judge from the measurements of the total difference of potential as to the difference between the metals.

The legitimacy of this assumption has formed the subject of much discussion. Considering the universality of differences in potential between heterogeneous substances, the absence of a difference between metal and air would be very strange, and we are quite entitled to demand a proof of it from the champions of this view. But, on the contrary, it seems as if the following fact proved the existence of such differences of potential. All the investigators who have undertaken such measurements complain of the extraordinary inconstancy in the differences of potential observed. On placing two freshly-cleaned plates opposite to each other and measuring their difference, one is sure to find different values after a little time. If the surfaces are again cleaned, the original values approximately recur. Therefore, it is not the point of contact of the two metals (besides, this can be made unalterable by soldering), but their surfaces with respect to air, which are the seat of the changes. Let us now assume that at a definite moment the difference of potential of both plates towards air is equal to zero; since another value is observed after some time, the difference of potential of the metals towards air cannot now be zero, *i.e.* between metals and air there exist differences of potential. How great these are cannot as yet be determined. There is nothing against the assumption that these make up the greatest part of the apparent differences of potential between the metals (measured in air). It is true an attempt has been made to eliminate the influence of the air by making the experiment *in vacuo*. But since we have learned by observation of the electrical phenomena in vacuum tubes, how difficult—how impossible, even—it is to withdraw from a substance the last remnants of air condensed on it and in it, these experiments cannot be looked upon as affording any conclusive proof.

Other methods for solving the difficulties must be sought. Unfortunately, there does not exist a single process quite free from objection. The following consideration still appears to be the best:—

When a given quantity of electricity q is brought from a potential A to a higher potential $A+a$, a quantity of work aq is required. Therefore, when we lead a current through two metals which touch in one place, and which there exhibit a difference of potential *a*, an absorption or a production of energy will occur at the place of contact, according to the direction of the current; and, if there is no other source of energy, this energy-change will be produced from, or will be added to, the heat which is present, as the case may be. In the case of metals such a phenomenon is actually known; it is the effect discovered by Peltier (*A. Ch.* 56, 371 [1834]). If the strength of the current, and the total heat produced, are measured, the corresponding difference of potential can be calculated. Such experiments have been made by Le Roux, and again quite recently, with great accuracy, by H. Jahn (*W.* 34, 755), and the results have shown the values to be very small; they are mostly only a few thousandths of a volt.

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[1] Compare O. Lodge, *l.c.*

It is true we must not pass over in silence the following objection made against the validity of this argument. Since we know nothing definite concerning the nature of the electric current, the possibility is not excluded that it may be connected with movements of energy of other kinds. It has been especially assumed as probable by several authors that, simultaneously with the electric current, a heat-current flows through the conductor. If so, the quantity of heat flowing with the unit quantity of electricity might be different in different conductors; and at the point of contact of the metals, in addition to the thermal exchange resulting from the difference of potential, there might occur a further exchange of heat resulting from the difference in the 'thermal capacity of electricity.' Since these two quantities need not have a necessary connection, it would not be permissible to draw any conclusion from the Peltier effect—that is, from the sum of two independent effects—as to the magnitude of the difference of potential.

Without attempting to decide this difficult question here, I should like to draw attention to a circumstance which makes it probable that the second effect, if present at all (which so far has not been proved), must probably be of the same order of magnitude as the difference of potential corresponding to the Peltier effect. According to the second law of the mechanical theory of heat, the carrying of a definite quantity of heat Q from a lower to a higher temperature involves work which is given by $Q\frac{T_1 - T_2}{T_1}$. If, therefore, we pass an electric current through a wire whose temperature varies, it follows that, if heat is carried with the current, in places of rising temperature a corresponding quantity of work must be expended, *i.e.* an opposing electromotive force must there assert itself. Indications of such a force appear to manifest themselves in the so-called Thomson effect (supposing that this effect does not find its explanation in differently heated portions of one metal having differences of potential to each other), but in any case the quantities of work, or the differences of potential, indicated by this phenomenon are extremely small (of the same or of a smaller order of magnitude as those corresponding to the Peltier effects), so that the assumption of an appreciable carrying of heat by means of electricity (for which, at any rate, we lack the power of forming a conception) seems excluded.

From this it is evident that though nothing quite certain is known concerning the differences of potential between different metals, yet preponderating reasons favour the assumption that such a thing does exist, but that its magnitude does not exceed a few thousandths of a volt, and particularly that it does not attain the order of magnitude of 1 volt. But, varying slightly with the nature of the metals, such a value has been observed by means of the air-condenser method.

As regards differences of potential between various electrolytes, such differences certainly do exist. This can be inferred from the fact that there exist 'liquid chains,' *i.e.* combinations of different liquids, which produce an electric current. If, for instance, we put into a series of beakers water, concentrated hydrochloric acid, concentrated soda solution, and water, and if we connect these by small syphons or by moist threads, then the two quantities of water at the ends exhibit a difference of potential which may attain to 0·5 volt.

In such liquid chains we have always to deal with three distinct differences of potential at least; designating the three liquids named above by A, B, and C, there exist in the chain the differences of potential $(a-b)$, $(b-c)$, and $(c-a)$, whose sum is observed. There is no combination of the liquids by which we could succeed in obtaining as many independent observations as there are differences of potential, so that it is impossible to determine by measurements on liquid chains only the individual differences of potential.

This determination has, however, been achieved in another way. Since in electrolytes the electricity moves only with the ions, differences in potential between two liquids in contact can only be produced if the different positive and negative ions distribute themselves unequally. A cause for such an inequality lies in the different velocities of migration of the ions (p. 92), and, in an extensive investigation, W. Nernst has shown (*Z. P. C.* 4, 129) how thereby the actually observed differences of potential can be theoretically calculated in a great number of cases. The fundamental idea of these calculations is the following. When any solution is brought into contact with pure water, forces make themselves apparent at the surface of separation, which forces can be calculated by van't Hoff's theory (pp. 184–5); for 'normal' solutions (which contain one gram-molecular weight per litre) they are equal to the pressure of about 22 atmospheres, and they are proportional to the quantity of substance in the solution. Owing to the osmotic pressure, the molecules of the substance are forced into the water. The velocity of their motion is determined by the resistance which they encounter, and this depends on their form as well as on the nature of the solvent.

This statement contains a physical theory of hydro-diffusion (Nernst, *Z. P. C.* 2, 613), and from it the law of Fick follows directly, that the velocity of diffusion at any point is proportional to the change in concentration at that point. From this we see at once how a separation must occur in the diffusion of dissolved substances, because those molecules which are endowed with greater mobility or suffer less friction outstrip the slower ones. The same laws hold for each kind of molecules, only the constants are different.

These arguments can only be applied immediately to electrolytes in solution if both ions have equal rates of motion. This condition is very nearly fulfilled in the case of potassium chloride, and this substance conforms, therefore, to the simple law of diffusion.

It is now possible, in the case of electrolytes, to determine the resistances which the ions encounter, as well as to measure the impelling forces. If the ions are moved past each other by *electrical* forces of separation, they encounter exactly the same resistance, and since in the electrical conductivity we have a measure of the velocity of the corresponding motion of the ions, it is possible, as first shown by F. Kohlrausch (*W.* 6, 160), to calculate the magnitude of the resistances from a knowledge of the impelling force and of the velocity attained. On introducing this resistance (which, owing to the smallness of the molecules, is enormously great) into the equation for the velocity of diffusion, indicated above, Nernst has found (*l.c.*) that the velocities of diffusion agree very well with the results of experiment.

In the case of electrolytes whose ions do not migrate with equal velocities the phenomena become much more complicated. If, for instance, we imagine hydrochloric acid, in which the hydrogen ion travels about six times more quickly than the chlorine ion, to be brought into contact with water, the quicker hydrogen atoms will, to start with, pass into water, and the chlorine atoms will remain behind. But since the hydrogen atoms are charged with positive electricity, the water will become positively electrified, while the acid, owing to the preponderance of chlorine atoms, becomes charged negatively. But the further exit of hydrogen atoms is thus rendered more difficult, owing to the electro-static effect, while from a similar cause the chlorine atoms are subject in addition to the osmotic pressure, and also to an electric impelling force, and are thus driven into the water. The consequence is that both ions influence each other's velocity until they again migrate at equal rates.

At the same time, we see that every electrolytic solution whose ions travel with unequal velocities on contact with water—or, speaking more generally, on contact with a solution of different concentration—at once acts as the cause of difference of potential, and also that the more dilute solution will always assume the sign of the ion which has the greater migration velocity. The exact expression which has been deduced by Nernst (*l.c.* p. 138) is

$$\epsilon_1 - \epsilon_2 = 0{\cdot}0000860 \quad \tau \quad \frac{u-v}{u+v} \, log. \frac{p_1}{p_2}$$

Where $\epsilon_1 - \epsilon_2$ is the difference of potential (in volts) of two solutions in which the osmotic pressures of the (positive as well as negative) ions are p_1 and p_2; u is the velocity of the positive, v that of the negative, ion; τ is the absolute temperature, while *log.* stands for the natural logarithm.

We see that for $u = v$ the electromotive force becomes zero, and it becomes the greater the greater the difference between the migration-velocities of the two ions. Further, we see that as regards the electromotive force, only the ratio $\frac{p_1}{p_2}$ of the two pressures, and not their absolute values, enters into consideration. By increasing the concentration n times in both solutions, the difference of potential does not change. If one of the solutions is pure water, we get $p_2 = 0$, and the electromotive force becomes infinitely great. Since 'pure water' in this sense does not exist, such values cannot come under our observation. But yet we see that liquid chains with 'water' can give very different values according to the degree of purity of this liquid.

The preceding formula is the fundamental expression for all kinds of liquid chains, since in the combination of any solutions the corresponding differences of potential are superposed. It would take us too far afield to enter into the different cases; in the memoir of Nernst, a number of cases are discussed theoretically as well as experimentally. But on the whole it may be concluded that the differences in potential apparent on contact of approximately equally concentrated solutions of the most varied kind, vary within fairly small limits, which probably do not surpass 0·01 volt.

Now, since we cannot suppose that differences of potential of the order of magnitude of those observed in galvanic cells exist either between metals alone, or electrolytes alone, we are obliged to regard the surfaces of contact between the metals and the electrolytes as the real seat of the electromotive forces. This result quite corresponds with what was to be expected from the relations between the chemical and electrical energies. This is so because these surfaces of contact are the only seat of the processes by which energy becomes available in the chains, *i.e.* they are the result of the chemical changes. Since, on the one hand, the cause of the galvanic current of the chains has to be sought in the transformation of chemical into electrical energy, and since, on the other hand, a galvanic current can be produced only when a difference of potential exists, it does not seem very logical to wish to separate in space, and in their nature, the more approximate and the less approximate causes of the same phenomenon, as is done in the assumption that the difference of potential is to be sought at the surface of contact of the metals.

The question now arises again, whether some means does not exist for directly measuring the differences of potential between metals and electrolytes. The answer is that up to the present only one such means is known. A second independent way for arriving at these numbers does not as yet exist, and hence it has hitherto been impossible to put to the proof the results obtained by that method.

The method in question is based on the phenomena exhibited by mercury surfaces when in contact with electrolytes. Lippmann (*P.* 149, 561; *A. Ch.* [5] 5,494) has shown that there is a close connection between the condition of the surface of mercury touching an electrolyte and the electrical state of the system. If, for instance, mercury is covered with dilute sulphuric acid, and the surface of contact between the two is then increased, a galvanic current is produced, because the mercury becomes less positive on expansion. This can be observed most easily by allowing mercury to drop out of a funnel with a small orifice immersed in dilute sulphuric acid. On connecting the mercury in the funnel and that collected below the sulphuric acid by means of a galvanometer, a current passes from the lower mercury to the higher; in the sulphuric acid the reverse occurs.

This phenomenon is reciprocal. On leading a current through the surface of contact between mercury and sulphuric acid the surface tends to diminish or to increase, according to the direction of the current—*i.e.* the capillary tension at this point changes. As is always the case, both phenomena are in such a relation that they oppose each other—*i.e.* when the surface is made larger the current has the direction such that if it alone were active it would tend to make the surface smaller, and *vice versâ*.

Helmholtz (*W.* 16, 35 [1882]) has given a theory of these phenomena which is based on the following considerations. When a metal and an electrolyte are in contact, they generally possess a varying difference of potential. Owing to this circumstance, the opposite electricities must accumulate on both sides of the bounding surfaces, since they are prevented from combining by the cause which produces the difference of potential (and which, without making a definite assumption, can be designated as a different attraction of the substances for the electricity). The result is the formation of an 'electric double layer,' which will exhibit a similar arrangement to the charge of a Franklin plate.

But such a double layer will have the property of tending to increase its surface as much as possible, since the similarly electrified particles present at each side repulse each other, and therefore tend to stretch the surface. Hence the development of such a double layer will act in opposition to the surface tension, which seeks to decrease the surface, and the actually observed surface tension is the difference between the real tension and the electric force.

When a surface so constituted is made larger, the electric layers are thereby extended, and their difference of potential decreases. But since, as is known from experience, a constant difference of potential is always formed at the boundary, which difference of potential does not depend on the size of the surface of contact, electricity will flow from the mercury as well as from the electrolyte to replace the loss, and in this way the current is produced.

If, on the other hand, the difference of potential of the electric double layer is changed, the surface tension must change also. It must get smaller when the difference of potential is made larger, and larger when it is made smaller.

By leading electric currents of varying electromotive force through a system consisting of two masses of mercury in sulphuric acid—one of which had a very small, the other a very large, surface of contact with the acid—Lippmann was able to follow the change of surface tension at the small bounding surface which accompanied the change in the difference of potential at that surface. Because, since the change in the difference of potential between a metal and an electrolyte is proportional to the *density* of the current (current strength divided by the cross-section), the resulting difference of potential practically restricted itself to the small bounding surface, which was surpassed in extension some thousand times by the large one. It was found that when the mercury of the small surface was connected with the positive pole of the external cell, the surface tension decreased. On the other hand, when negative electromotive forces acted, the surface tension increased until the external force was 0·9 to 1·0 volt; beyond that it again decreased.

In accordance with Helmholtz's theory, we must infer from this that the difference of potential between mercury and sulphuric acid is of such a kind that the former becomes charged positively—*i.e.* that the positive electricity of the double layer is on the side of the mercury, and the negative electricity is on the side of the electrolyte. If the difference of potential is increased by addition of positive electricity to the mercury, the electric repulsion increases, and therefore the surface tension decreases. If, however, negative electricity is added, the charge of the double layer decreases and the surface tension increases. On making the successive additions of negative electricity larger and larger, the difference of potential of the double layer eventually becomes zero; the surface tension has reached its greatest value, and, beyond this, a new double layer of opposite sign is produced. When this state is reached, the surface tension must again decrease.

According to the experiments of Lippmann, the maximum of surface tension is reached when the external electromotive force is 0·9 to 1·0 volt. Then no more double layer is present at the small surface of the mercury, and the metal and electrolyte have the same potential. Since this condition is separated from the ordinary one by about 0·9 volt, *it follows that the usual difference of potential between dilute sulphuric acid and mercury is 0·9 volt.*

This result is confirmed by the following experiment of Pellat (*C. R.* 104, 1099). When the surface of contact between mercury and sulphuric acid is increased, a motion of electricity is produced, owing, as has been mentioned above, to the stretching of the double layer. But this must disappear when, by the use of a difference of potential of about 1·0 volt, the double layer has been made to disappear; and, in fact, under these conditions, Pellat, on changing the surface, could observe no current.

Another confirmation can be obtained in the following manner. When mercury is dropped very quickly out of a fine point into an electrolyte, it must, after a short time, as Helmholtz has shown, assume the potential of the latter (*W.* 16, 35), because if, for instance, the mercury were at the beginning positive, every falling drop would form a double layer at its surface, which would take positive electricity out of the mercury, and which would make its positive potential smaller and smaller till it became equal to that of the liquid.

But it is to be remembered that the mercury in contact with sulphuric acid spontaneously becomes positively charged; everything will depend, therefore, on allowing the formation of drops to take place as quickly as possible, in order that the discharge may preponderate over the charge. Experiments by W. Ostwald (*Z. P. C.* 1, 583 [1887]) have shown that the discharge can be achieved to a great extent, but not completely; there still remain over, even with the best dropping electrodes which have yet been made, differences of some hundredths of a volt. But within these limits the experiment confirms the conclusion which Helmholtz had drawn—the difference of potential between the dropping electrode and the mercury at rest in sulphuric acid amounts in 'normal' sulphuric acid solution to 0·81 volt, while the maximum of surface tension (that is, the true difference of potential) lies at 0·86 volt.

Finally, another inference, which must be drawn from the theory of Helmholtz, has been confirmed by the same author. If the maximum of the surface tension of mercury, as obtainable by means of suitable electromotive forces, actually is the real surface tension of mercury in contact with aqueous liquids, free from auxiliary effects, then it must have the same value whatever be the nature of the electrolyte, while experience shows that the natural surface tension changes considerably with the nature of the electrolyte. This also was confirmed; while the natural surface tension in different solutions varied between 485 and 561, the maximum values were 610 to 644, and were, therefore, practically constant.

All these facts speak for the correctness of Helmholtz's theory of the electric double layers, and leave us, therefore, with the final conclusion that the electromotive force required for producing the maximum of surface tension of mercury in contact with an electrolyte is equal to the ordinary difference of potential at this bounding surface (but with inverted sign). But it must be again emphasised that this is the only group of phenomena from which the values considered can be deduced. An examination of the results by means of another entirely independent method has not yet been feasible.

If, now, the difference of potential between mercury and sulphuric acid is known, the difference of potential between all other metals and sulphuric acid can be measured by experiments which are easily carried out. For this purpose the electromotive force of the combination *mercury, sulphuric acid, and metal* alone need be measured; this is the sum of the differences of potential of mercury-sulphuric acid and sulphuric acid-metal, and since the first of these is known the other follows by difference. But here it is supposed that no appreciable difference of potential exists between the metals. Again, if the difference of potential between mercury and any other electrolyte is determined, either by the maximum surface tension or by means of the mercury-dropping electrode, the difference of potential of these electrolytes against any other metals can also be determined. In this manner, therefore, the whole subject of the differences of potential between metals and electrolytes has been made amenable to measurement.

But few trustworthy measurements of this kind have as yet been made; in the following table some numbers are given:—

	HCl	HBr	HI	H_2SO_4
Zn . .	−0·54	−0·46	−0·30	−0·62
Cd . .	−0·24	−0·18	−0·08	−0·22
Sn . .	+0·02	+0·12	+0·28	−0·02
Pb . .	+0·03	+0·10	+0·26	−0·04
Cu . .	+0·35	+0·35	+0·36	+0·46
Bi . .	+0·41	+0·47	+0·60	+0·46
Sb . .	+0·51	+0·60	+0·54	+0·48
Ag . .	+0·57	+0·51	+0·45	+0·73
Hg . .	+0·57	+0·50	+0·44	+0·86

The values refer to 'normal' solutions of the electrolytes mentioned, and indicate the potential of the metal when that of the electrolyte is put equal to zero.

We see that those metals which dissolve in the acids become negative; the others become positive. The values are also in very nearly the same order as the corresponding heats of reaction, but, as a calculation shows, they are not proportional. The nature of the electrolyte has generally a smaller influence than that of the metal, but there are cases where the reverse is true.

It should be mentioned that nearly the same numbers are obtained when salts of the acids, with metals which are not precipitated by the metal under examination, are used instead of the acids themselves. The difference of potential between the metal and the electrolyte depends, therefore, chiefly on the negative ion of the latter. From the numbers in our possession it is seen, for instance, that in the Daniell cell, whose difference of potential is 1·08 to 1·10 volt, the greater part of this (0·62 volt) is present at the bounding surface between zinc and zinc sulphate, and the smaller part at the surface (0·46 volt) between copper and copper sulphate.

No further conclusions of more general interest have as yet been drawn from these numbers.

Galvanic polarisation. When two metal plates are introduced into an electrolytic liquid and a galvanic current is made to pass through the electrolyte by means of the plates, these plates generally become the seat of a new electromotive force which acts in opposition to the current already active. This phenomenon is called *galvanic polarisation*, and it may be perceived by connecting the plates with a galvanometer immediately after breaking the primary current.

The cause of this phenomenon is to be found in the change which is produced by the current at the boundary surface between the metal and the electrolyte. There the ions of the electrolyte separate out, and cause changes of the most manifold kind.

The simplest case occurs when the metal plates are surrounded by the solution of a salt which contains the same metal, for such a system scarcely exhibits the phenomenon of polarisation at all; such electrodes are 'unpolarisable.' The reason is that in this case the changes occurring at the electrodes do not change the condition of the bounding surfaces. If, for instance, we have zinc in zinc sulphate, zinc is separated out at the cathode, and this combines with the metal present without changing it, and at the anode SO_4 separates out, which then dissolves zinc and forms zinc sulphate. The only effect is that the zinc sulphate solution becomes more concentrated at the anode, and accordingly a small concentration-current can be observed, whose electromotive force is, however, very inconsiderable.

Such a system of unpolarisable electrodes differs from all similar combinations in that it allows any, even the smallest, current to pass through. Polarisable electrodes do not behave thus. If, for instance, two platinum plates are placed in dilute sulphuric acid, and a current of small electromotive force—say, 0·1 volt—is allowed to pass, we observe by the galvanometer that at first a motion of electricity takes place, but that this ceases after a very short time. It is a phenomenon such as a condenser exhibits on being charged, with this difference, that the capacity of such electrolytic condensers appears to be very great. On increasing the electromotive force, a corresponding quantity of electricity answering to a greater charge of the condenser always enters, but no permanent current is produced until the electromotive force is somewhat more than 2 volt; then a more copious passage of the current suddenly takes place, and simultaneously gaseous oxygen and hydrogen appear at the electrodes.

We must, therefore, represent the phenomenon to ourselves in the following way. Between the electrolyte and the platinum plates there exists originally some one difference of potential, and in consequence the double layers form there. Now, on allowing the electromotive force to act, on the one side the difference of potential of the double layer is increased, on the other it is diminished. The corresponding process to this is the condensing charge. On increasing the difference of potential, there is a moment at which the condenser no more isolates under the influence of the electro-static effects; a passage of electricity from the metal to the ions (or *vice versâ*) occurs, corresponding to the disruptive discharge of the condenser, and the ions, deprived of their electric charges, separate out. When sulphuric acid is the electrolyte, the ions are H_2 and SO_4; the latter substance is not stable, and reacts with the water present to form sulphuric acid and oxygen, the latter escaping in the gaseous state.

From this we see that a difference of potential of definite magnitude must exist when the electricity is to leave an ion in order to travel to a metal; until this difference of potential is reached, the system acts at the electrode like an isolator. But why does this not occur with unpolarisable electrodes? The answer to this question follows from the consideration of the processes occurring at these electrodes. Let us again take zinc plates in zinc sulphate, and let us lead positive electricity into one plate. This electricity can at once enter into the solution, by using as its vehicle a corresponding number of zinc atoms, which travel with it as positively charged zinc ions. At the other zinc plate an equal number of zinc ions can also deposit at once, and since there exists no difference of potential between zinc and zinc these can at once deliver up their electricity. Here, therefore, no cause exists for condensing effects. It is not, however, as if no difference of potential existed between the metals and their solutions; such differences, in fact, are present, and hence also corresponding double layers are formed, which at one side are made up of ions. But these do not act as condensers, free communication of their ions between the metal and the electrolyte being possible, and consequently the difference of potential, independent of the current, maintains itself at an unaltered value.

Beside the unpolarisable electrodes and those polarisable at both sides, there still exist combinations in which polarisation occurs only at one side, mostly at the cathode. This takes place, for instance, with copper plates in dilute sulphuric acid. At the cathode, when the electromotive force is sufficient, hydrogen separates out, just as it does at a platinum plate. But at the anode, on the other hand, copper sulphate is formed by the ion SO_4 acting on the copper—*i.e.* the ion SO_4 need not give up its negative electricity there, since in its stead positive electricity fixed to copper comes out of the plate. Hence, no polarisation occurs here.

From what has been said an explanation follows of the cause of the polarisation current, which occurs after breaking the primary current and connecting both plates in the opposite direction. It is, in brief, the discharge of the electrolytic condenser. Looking at the process more in detail, we see that when the charge in the double layers is formed, the electricity led in has remained in the electrodes, equal quantities of the opposite electricities having collected from the electrolyte on the electrodes—the electricity being, of course, bound to the ions. On the primary current being broken, and the electrodes being connected with each other, the electricities present in these neutralise each other, and the ions, which are no longer fixed, form the carriers of the current in the electrolyte. This lasts until the original condition of equilibrium has re-established itself.

In accordance with what has been said, the measurement of galvanic polarisation refers almost exclusively to the maximum value it can assume, or to the value of the difference of potential at which the double layer condenser no more isolates.[1] The measurement of this quantity is somewhat difficult; because, when carrying out the simple experiment indicated above—*i.e.* when increasing the primary current up to decomposition, interrupting it, and afterwards connecting the electrodes with an electrometer—we observe that (in consequence of the secondary effects) the electromotive force of polarisation decreases very rapidly. We are, therefore, not sure whether a considerable portion of the polarisation has not already been lost in the time which elapses before the measurement. But there exists a means of obtaining information concerning the magnitude of the possible error. If the change of connections is carried out more and more quickly, increasing values at first are observed. But these approach

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[1] It must be observed that complete isolation does not occur; a small amount of percolation of electricity takes place when the maximum value is not reached. But, as Helmholtz has shown, this phenomenon is a consequence of electrolytic convection, and is of a secondary character.

to a maximum, and when the number of current reversals reaches about 100 per second a further rise in the velocity no longer produces an increase, as was found by Raoult (*A. Ch.* [4] 2, 326), and the value observed under these conditions may be regarded as the correct one.

Other methods are based on making measurements of current strengths and resistances in the primary circuit, and on calculating from this the electromotive force of polarisation. These become uncertain by the fact that, owing to the processes occurring at the electrodes, the resistance of the cell undergoes variations during the passage of the current, which variations cannot be determined. Finally, we can use electrometric methods, by measuring the difference of potential between the electrode to be polarised and an auxiliary electrode through which no current passes, both before closing the circuit and while the current passes; the difference between the two magnitudes is the polarisation required. But difficulties, which have not yet been removed, appear in the practical application of this ingenious method, which was pointed out by Fuchs (*P.* 156, 158).

Because of these difficulties only a small number of trustworthy measurements of the electromotive force of the maximum polarisation have as yet been made. Consequently, no certain relations with chemical conditions have been discovered as yet.[1] Though an attempt has been made to calculate the electromotive force of polarisation in a manner similar to that of the galvanic cell, from the thermal effects appertaining to it, the same objections can be raised against it as in the former case (p. 213): the observed electromotive force is generally different from that calculated.

It is especially remarkable that the maximum forces of polarisation corresponding to one and the same chemical process may be very different according to the nature of the metal. If we form galvanic cells of zinc, dilute sulphuric acid, and different metals—such as copper, silver, gold, platinum—or of charcoal, and if we close the circuit in the cells, the same process occurs in all. zinc sulphate is formed, and, to make up for it, hydrogen is expelled from the sulphuric acid. The latter appears at the metal, and polarises it. It is found that the electromotive forces of these cells, even after they have completely polarised themselves, are distinctly different; according to the nature of the second metal, a greater or less portion of the energy liberated by the reaction $Zn + H_2SO_4 = ZnSO_4 + H_2$ is transformed into electrical energy.

The cause of this can be understood after what has already been explained. The electricity must overcome unequal differences of potential in passing from the H ions to the different metals; hence different portions of the total available energy are used, and only the residue of this energy finds its expression in the electromotive force of the cells. We see, then, that the electromotive force cannot possibly bear the simple relation to the heat of reaction which was formerly supposed to be the case. But it is possible that the equation of Gibbs and Helmholtz (p. 214) is applicable to galvanic polarisation also; if this is so we shall be able, from a knowledge of the electromotive force and its changes with the temperature, to draw conclusions as to the thermal changes due to the processes which primarily participate in the polarisation. W. O.

VI. FREEZING-POINTS OF SOLUTIONS, METHODS BASED ON; *v.* MOLECULAR WEIGHTS, vol. iii. p. 417; and ELECTRICAL METHODS, this vol. p. 186.

VII. OPTICAL METHODS.—**Section 1: REFRACTION AND DISPERSION.** When a ray of light passes at an angle from a rarer into a denser medium, it is always reflected towards the perpendicular, the sine of the angle of incidence being in a constant ratio to the sine of the angle of refraction, namely the ratio of the velocities of wave propagation in the two media. This constant ratio is called the index of refraction, and is generally represented in England by the Greek letter μ, and on the Continent by n: $\mu = \frac{\text{sine } i}{\text{sine } r}$. The angle of incidence being in such case greater than the angle of refraction, the index of refraction will be greater than 1. The reverse will be the case when the ray passes from a denser to a rarer medium.

The refraction of a ray of light is, however, always accompanied by another phenomenon—*dispersion*, as the ray is made up of a number of vibrations of different velocities which are affected diversely in passing from one medium to another. This causes the ray of common or white light to be spread out into a number of coloured rays corresponding to vibrations of different rapidity. In all precise determinations, therefore, a definite point of the spectrum thus formed must be measured for refraction, and two such points for dispersion. The work of early observers on the refraction of light is usually wanting in precision in this respect, the records being commonly described as having reference to the bright or yellow part of the spectrum, or to the extreme red; while they furnish no data at all for calculating the dispersion. Moreover, as each colour occupies a certain breadth in the spectrum, and the boundaries of the colours are not well defined, it is by no means certain that two observations made on the same colour will refer to exactly the same part of the spectrum. In more recent observations the most conspicuous lines of the solar spectrum, such as A, D, F, H, are adopted, or, if artificial light be used, the α, β, and γ lines of the hydrogen spectrum; these are recorded as μ_A, μ_D, &c.; μ_α. μ_β, μ_γ. The greater part of the English data of recent times are given for the solar lines, while foreign observers have generally adopted the hydrogen lines.

Refraction and dispersion equivalents. The index of refraction, minus unity, when divided by the relative density (d) and multiplied by the atomic weight if an element is examined, or by the molecular weight if a compound is examined (P), is usually represented by the formula $P\frac{\mu - 1}{d}$ in England and $P\frac{n - 1}{d}$ on the Continent, and is termed the refraction-equivalent. It will be expressed in this article by the simple letter R. When Lorenz's formula is used,

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[1] See, however, a recent investigation by M. Le Blanc (*Z. P. C.* 8, 299).

$\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{P}{d}$, the refraction-equivalent so calculated will be distinguished as R. The part of the spectrum to which the observation refers will be indicated by adding the sign for infinity, or the letters of the solar or other lines observed, as R_∞, R_A, R_a, &c. The dispersion-equivalent represents the difference between the refraction-equivalents of two selected portions of the spectrum; thus the dispersion-equivalent for H – A will be expressed as $\frac{(\mu_H-1)}{d}-\frac{(\mu_A-1)}{d}$, or, more briefly $\frac{\mu_H-\mu_A}{d}$, multiplied by P; or R_H-R_A.

The index of refraction of solids is generally ascertained by the method of total reflection, unless they are transparent, and can be cut into the form of a prism; that of gases is best determined by interference. The refraction of liquids is most conveniently arrived at by placing the substance in a hollow prism, with sides of plate glass; on the prism being so adjusted that the incident and emergent rays make equal angles with the refracting surfaces, the minimum deviation will be arrived at. Let D be the deviation, *i* and *r* the angles of incidence and refraction, and *a* the refracting angle of the prism; then

$$\frac{\text{sine } i}{\text{sine } r}=\frac{\text{sine } \frac{1}{2}(a+D)}{\text{sine } \frac{1}{2}a}=\mu.$$

Newton, acting upon the emission theory, proposed $\frac{\mu^2-1}{d}$ as representing the absolute refractive power of any substance, and this formula met with general adoption till recent times. Gladstone and Dale (*T.* 1863), as the result of a long series of experiments with different substances at various temperatures, found that the refractive index, minus unity, multiplied by the volume, gave nearly a constant. To $\mu-1$ they accordingly gave the name of 'refractive energy' as really representing the influence of the substance itself on the rays of light; and to $\frac{\mu-1}{d}$ that of 'specific refractive energy.' This empirical formula has been adopted by most subsequent investigators; and Sutherland (*P. M.* [5] 27, 141) has lately advocated it on mathematical, as well as on physical, grounds. It holds its position side by side with the theoretical formula we have now to consider.

Lorenz's formula. H. A. Lorentz, of Holland (*W.* 9, 641), and L. Lorenz, of Copenhagen (*W.* 11, 70), came almost simultaneously to the conclusion, from purely theoretical considerations, based, in the case of the former, on the electro-magnetic theory, that $\frac{\mu^2-1}{(\mu^2+2)d}$ must express the relation between the velocity of the transmission of light and the density of the medium through which it is propagated. Landolt (*B.* 15, 64) tested the comparative merits of this formula, and that which he had previously adopted—viz. $\frac{\mu-1}{d}$—and found that so far as liquids were concerned there was nothing to choose between them, but that Lorenz's formula showed much less difference between the specific refractive energy of a liquid and that of its vapour. This is shown in the following table, in which it will be also noticed that the difference with the rise in temperature is uniformly plus in the one case, and minus in the other. Weegmann (*Bonn.* 1888) experimenting at 10°, 20°, and 30°, noted the same rise in the one case and fall in the other.

Substance	State	Temp.	$\frac{\mu_D-1}{(\mu_D+2)d}$		$\frac{\mu_D-1}{d}$	
Water .	Liquid	10°	0·2062		0·3338	
	"	20°	0·2061	0·0001	0·3336	0·0002
	Vapour	100°	0·2068	0·0007	0·3101	0·0235
Ethyl alcohol	Liquid	10°	0·2804		0·4582	
	"	20°	0·2807	0·0003	0·4581	0·0001
	Vapour	100°	0·2825	0·0018	0·4237	0·0344
Ethyl ether .	Liquid	10°	0·3026		0·4935	
	"	20°	0·3029	0·0003	0·4930	0·0005
	Vapour	100°	0·3068	0·0039	0·4599	0·0331
Ethyl acetate	Liquid	10°	0·2547		0·4174	
	"	20°	0·2549	0·0002	0·4172	0·0002
	Vapour	100°	0·2683	0·0134	0·4024	0·0148
Ethyl iodide	Liquid	10°	0·1557		0·2663	
	"	20°	0·1558	0·0001	0·2658	0·0005
	Vapour	100°	0·1571	0·0013	0·2356	0·0302
Chloroform .	Liquid	10°	0·1790		0·3000	
	"	20°	0·1791	0·0001	0·2996	0·0004
	Vapour	100°	0·1796	0·0005	0·2694	0·0302
Carbon disulphide .	Liquid	10°	0·2805		0·4977	
	"	20°	0·2809	0·0004	0·4970	0·0007
	Vapour	100°	0·2898	0·0089	0·4348	0·0622

In the case of liquid and solid phosphorus, as well as of other highly refractive bodies, the empirical formula appeared to give the best results. Landolt also found the simpler formula best adapted to his process of optical analysis subsequently described. But while he found that the refraction-equivalents (*i.e.* the specific refractive energy multiplied by the atomic weight in the case of elements, or by the molecular weight in the case of compounds) of substances calculated by Lorenz's formula are about one-third smaller than the numbers calculated by the formula previously adopted by him, the values which he obtained for the elements carbon, oxygen, hydrogen, and chlorine did not bear the same proportion. Adopting Brühl's figures for R_a (as described later on), the values according to Lorenz's formula vary from about ½ to ¾ the values found by using the other formula. Thus:—

	Old Formula	Lorenz's Formula
Carbon	5·0	2·48
Hydrogen	1·3	1·04
Oxygen, alcoholic . .	2·8	1·58
" aldehydic . .	3·4	2·34
Chlorine	9·8	6·02
Increase for double carbon bond	2·4	1·78

Brühl, however, in 1886 (*A.* 235, 1), maintained that the statement of Landolt, that the two formulæ lead practically to the same conclusions in respect to chemical constitution and the refraction of light, cannot any longer be accepted in its general sense. In this paper Brühl contended that the expression of the molecular refraction hitherto used—viz. $P\frac{\mu-1}{d}$, is generally adapted only to the paraffinoid series of carbon compounds, and for unsaturated compounds of weak dispersive power; and that in these cases even the results are not altogether satisfactory. For the investigation of the relations between the refractive power and the constitution of bodies, Brühl claimed that in future Lorenz's formula must be used. The tables appended to the paper certainly show better proportionate results for R_a by this formula, especially in the case of the most dispersive substances; but in using these tables it must be borne in mind that the values assigned to the elements under the two formulæ are not strictly comparable. Nasini (*Lincei, Rc.* 3, 128) stated that he and Bernheimer did not consider that, from a chemical point of view, any great preference should be given to Lorenz's formula over the formula $\frac{\mu-1}{d}$, as the newer formula was insufficient to represent every relation between the chemical constitutions of the substances and their refractive powers. Ketteler does not accept the Lorenz formula as altogether satisfactory; in place of it he has proposed $\frac{\mu^2-1}{(\mu^2+x).l}$, where x is a variable quantity depending on the nature of the substance, but averaging about 3·5 instead of 2. Sutherland (*P. M.* [5] 27, 141) objects to Lorenz's formula on the ground that it assumes a mean wave length, whereas the wave length must vary in passing from ether to matter; and he maintains that while the formula holds good for both the liquid and gaseous states, it fails when change of density is produced by change of pressure. On the other hand, he thinks that Gladstone's formula meets the last requirement, but fails to bridge over the great gap in density between liquid and vapour. Ketteler (*Z. P. C.* 2, 905) suggests an equation of the form $(n^2-1)(v-\beta)=M$, where β is the volume actually occupied by the ponderable molecules, v that of the space in which they are contained, and M a molecular function depending on the constitution of the medium. M may have one of two values, both of which are definite constants, the one for the liquid and the other for the gaseous state. The value of β may be obtained by varying the temperature, the pressure, or the constitution of the media examined. Sutherland says that this formula gives for compressibility results less satisfactory than those given by that of Gladstone.

Zehnder (*W.* 34, 91) investigated the influence of pressure upon the index of refraction of water at different temperatures, and on comparing the results with the co-efficient of compressibility, he came to the conclusion that the formula $\frac{\mu-1}{d}$ was practically exact—much more so than that of Lorenz. Röntgen and Zehnder (*W.* 44) have since applied the same inquiry to CS_2, and C_6H_6, ether, and a series of alcohols, with the result that in the cases of all these substances neither formula is sufficiently exact, the experimental figures occupying very nearly the mean place between those given by the two formulæ.

Perkin (*C. J.* 61, 287) in studying magnetic rotation at widely different temperatures, observed a slight reduction as the temperature was raised. Dale and Gladstone (as long ago as 1868) had observed that the specific refractive energy of substances was similarly affected; Nasini and Bernheimer (*G.* 15, 59) in 1885, and Ketteler (*W.* 33, 506, 662) in 1888, also found small differences in the same direction. Perkin accordingly made a series of experiments to see if the changes in $\frac{\mu-1}{d}$ due to temperature vary with different classes of substances, as they do in the case of the magnetic rotation. The results seem to corroborate this, though not very definitely. On trying Lorenz's formula, he found the refraction rise with increase of temperature, and he came to the conclusion that this formula is not suitable when dealing with high temperatures.

Guye (*Ar. Sc. Genève*, 23, 197, 204) pointed out a relation between the constants of the equation of Van der Waals and that of the formula of Lorenz for the refraction of light. He maintained that the relation of the absolute critical temperature to the critical pressure, which he termed the 'critical co-efficient,' is proportional to the molecular refraction, and that it furnishes a valuable means of determining the molecular constitution of bodies at the critical point. By a comparison of the data given by a number of observers for forty different substances he obtained the result that the critical co-efficient (K) is in proportion to R_∞ as 1 to 1·8. The experimental difficulties connected with the determination of K, and the fact that Guye had not always the data for reducing R observed to R_∞, rendered the final results less uniform than they might be otherwise; but the extreme range of his factor varied from 1·6 to 2·0, giving 1·8 as a mean. Guye found, however, certain classes of bodies which gave a different factor to that above mentioned. Such gases as O, N, and CO, gave a factor ranging from 1·1 to 1·4. Water gave 1·1, and methylic alcohol 1·1 to 1·2. He also recorded some which are exceptionally high, but in most of these cases the results of the experiments seem untrustworthy in consequence of chemical action having taken place. Having determined his factor, he was able to divide by it the recognised refractions of the elements according to Brühl, and so to get what he termed the 'atomic critical co-efficient,' from which he could build up the critical co-efficient of any substance of which the theoretical constitution was determined.

Dispersion formulæ. As the observations of Gladstone extended to the solar line A, his calculations were but slightly affected by dispersion; whereas nearly all the Continental observers have used the hydrogen light, and have no actual measurements below the line α. They have, therefore, usually sought to get rid of the effect of dispersion by adopting one or other of the suggested formulæ for calculating the theoretical ray of infinite wave length, and have worked out their results both for the observed line α, and for the assumed limit. The simplest of these methods, and on that account the one most generally adopted, is that of Cauchy. It is usually expressed by the formula

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots$$

in which λ represents the wave length of any given line of the spectrum. As this formula contains three unknown quantities, it requires for their determination three simultaneous equations; but the third term is often dispensed with to reduce the amount of calculation required. By the process of elimination, the values of A, B, and C are obtained, A being Cauchy's co-efficient of refraction, and B and C the co-efficients of dispersion. This theory accords fairly with the experimental data for substances of moderate dispersive power, though by no means well with the data for substances of high dispersive power, such as oil of cassia. Wüllner (*A.* 133) considered that this formula was sufficiently exact for bodies of low dispersive power when two constants were used; but that for highly dispersive substances, such as carbon disulphide, it was necessary to go to the third term, as the difference between the observed value of μ_β and that calculated from μ_α and μ_γ amounted to as much as 0·0022; while on using three terms the calculation was correct to the fourth decimal place. He also tried the formula of Christofle

$$n = \frac{n_0\sqrt{2}}{\sqrt{1+\frac{\lambda_0}{\lambda}} + \sqrt{1-\frac{\lambda_0}{\lambda}}}$$

in which n_0 and λ_0 signify two selected constants, and n is the corresponding index of refraction of the wave length λ; this also gave results which were not sufficiently accurate. Taking the observed indices for the lines α and γ of carbon disulphide at 0° as 1·631066 and 1·692148, this formula gave 1·669397 for β, while the observed value was 1·669076. At 20° the calculated value for β was as much as ·000494 too high. Langley (*P. M.* [5] 17, 194) has discussed the relative merits of Biot's, Cauchy's, and Redtenbacher's formulæ, and has come to the conclusion that while each of them is sufficiently exact within the limits of the visible spectrum, they soon begin to give too small results for μ when that limit is passed. Biot's formula

$$\frac{1}{n^2} = a + b\left(\frac{n^2}{\lambda^2}\right) + c\left(\frac{n^4}{\lambda^4}\right) + k\left(\frac{\lambda^2}{n^2}\right)$$

gives more trustworthy results than either of the others.

Redtenbacher's formula $\frac{1}{n^2} = a + b\lambda^2 + \frac{c}{\lambda^2}$ has the serious objection that it reached a minimum at a point corresponding to $n = 1{\cdot}5647$ in the prism which he employed, so that for every value of n greater than 1·5647 it gave two different values for λ. Langley has experimentally determined wave lengths in the invisible prismatic spectrum far beyond the extreme limit possible according to Cauchy's formula. Brühl, after working out his results for R_∞ as well as for R_α, has latterly (*A.* 235, 1; 236, 233) come to an adverse conclusion as to the utility of Cauchy's co-efficient of refraction for getting rid of the effect of dispersion, and he even asserts that when three terms are used the results are less to be relied upon for this purpose than when two terms only are employed. The following table shows the differences in Cauchy's A when calculated with two and three terms respectively, from the observed indices μ_α and μ_γ in the former case, and from μ_α, μ_β, and μ_γ in the latter; and also μ_β as observed, compared with the same index of refraction as calculated by Cauchy's formula from μ and μ_γ, showing in this case a difference of from one to five units in the third place of decimals:—

Substance	Cauchy's A		μ_β	
	2 terms	3 terms	Observed	Calculated
Benzoyl chloride .	1·51906	1 52700	1·56964	1 57097
Orthotoluidine .	1·53715	1·54160	1·58945	1·59069
Cinnamic alcohol .	1·54307	1·55253	1·59993	1·60151
Aniline . . .	1·54741	1·55689	1·60434	1·60592
Furfurol . . .	1·48269	1·49816	1·54566	1·54824
Cinnamic aldehyde .	1·55966	1·58256	1·65090	1 65622

In the case of substances of small dispersion, Brühl regards the use of Cauchy's formula as superfluous; with substances of medium dispersion, the results are generally preferable to those for the line α, though not to any great extent; but with substances of great dispersive power the differences are too great to be neglected in considering questions of chemical structure.

Nasini (*Lincei, Atti*, 18 [3]) comes to the same conclusion, that Cauchy's co-efficient of refraction ought to be rejected in studies of this nature, and that his co-efficient B is still more misleading if it be regarded as a measure of dispersion. N. (*Lincei, Atti*, 19 [3]) had already tested the merits of several formulæ, and given the preference to that of Lommel as affording better results than those arrived at by Cauchy's formula with two terms. The following table will show the differences between μ_β as observed, and as calculated by these two formulæ:—

Substance	μ_β observed	Calculated		Difference	
		Cauchy	Lommel	Cauchy	Lommel
Benzene. .	1·51339	1·51404	1·51369	0·00065	0·00030
Aniline . .	1·60434	1·60592	1·60522	0·00158	0·00088
Methyl-α-naphthol .	1·64597	1·6477	1·64678	0·00173	0·00081
Dimethyl-naphthalene	1·63200	1·6330	1·6324	0·00100	0·00010

Weegmann (*Bonn.*, 1888) gives reasons why Cauchy's formula for the limit of the spectrum is not to be relied upon; and maintains that his B, or co-efficient of dispersion, must not be taken as a measure of dispersive power, but that it should in any case be divided by the relative density.

Helmholtz has proposed the formula

$$n^2 - 1 = Q\frac{\lambda^4}{\lambda^2 - \lambda^2_m} - P\lambda^2$$

in which n and λ represent the index of refraction and the corresponding wave length, and Q, P and λ^2_m are three constants dependent upon the nature of the medium. Ketteler has subsequently proposed another, viz.

$$n^2 - 1 = \frac{A}{\lambda^2 - B} + \frac{C}{\lambda^2 - D} + \dots$$

Brühl has tested the comparative merits of both these formulæ, as well as that of Cauchy. Taking Gladstone and Dale's observations of a solution of phosphorus in carbon disulphide, he calculated the values of the lines B, D, F, and G from the observed values of A, E, and H, and again those of A, B, E, and G from those of D, F, and H. The following table shows the differences in the two cases between the observed and calculated values (*A.* 236, 233);

Line	λ	μ observed	Cauchy	Helmholtz	Ketteler	Cauchy	Helmholts	Ketteler
A	7·606	1·9209	...	...	...	+19	+48	+108
B	6·372	1·9314	−3	−5	+2	+ 9	+21	+ 47
D	5·893	1·9527	−2	−4	...	...	...	...
E	5·271	1·9744	...	...	−4	−5	−6	−9
F	4·862	1·9911	+8	+9	...	...	...	...
G	4·304	2·0361	+1	+2	−7	−7	−6	...
H	3·956	2·0746	...	...	...	...	...	...

Dispersive power. The difference between the indices of refraction of the rays of the spectrum of any refracting medium is termed the 'dispersion'; and by the dispersive power of a substance is expressed the ratio of the co-efficient of dispersion to the index of refraction of the mean ray minus unity. Thus taking the full length of the visible spectrum as extending from A to H, and F as the mean ray, the dispersive power would be represented by the formula, $\frac{\mu_H - \mu_A}{\mu_F - 1}$.

Ketteler (*Theoretische Optik*, Braunschweig, 1885) has proposed two formulæ for dispersion based upon theoretical grounds:

$$\frac{\mu_n{}^2 - 1}{\mu_m{}^2 - 1} \text{ and } \frac{\mu_n{}^2 - \mu_m{}^2}{\mu_n{}^2 - 1}$$

when n is a ray more refractive than m. Costa (*G.* 19) regards these as having the advantage over the formula $\frac{\mu_n - \mu_m}{d}$ on account of their being independent of the density of the medium.

Early experiments. Newton, Herschel, Young, Wollaston, Brewster, and others determined the indices of refraction of a large number of solids and liquids, in most cases for the yellow or brightest part of the spectrum. The index for the solids ranged from 1·111 for tabasheer to 2·974 for chromate of lead, and for liquids and soft solids from 1·0570 for ether expanded by heat to thrice its volume, to 1·678 for disulphide of carbon, and about 1·8 for chloride of antimony (*Encyc. Brit.*, 8th edit. Optics, 558).

Arago and Fresnel applied the method of interference to the comparison of the refractive indices of moist and dry air, with the result that moist air was found to be rather less refractive than dry air. Dulong determined the indices of refraction of a considerable number of gases and vapours.

Dulong, together with Arago, Biot, and others, adopted the formula of Newton $\frac{\mu^2 - 1}{d}$, and came to the following conclusions; that the refractive power of a mixture of gases is equal to the mean of the refractive powers of the constituent gases calculated for the pressure to which each gas is actually subjected in the mixture, and that the refractive power of a compound gas is not equal to the mean of those of the component gases, but is sometimes greater and sometimes less.

Höck also found this formula to apply to some mixtures of liquids, and Schrauf (*P.* 133, 479) has more recently supported the same mode of calculating the refractive power; but Ketteler (*P.* 124, 390) found that liquid sulphurous acid was not accordant with the known refraction of the gas as arrived at by the formula $\frac{\mu^2 - 1}{d}$, while the two came into agreement when he adopted the modern formula for the specific refractive energy $\frac{\mu - 1}{d}$.

Jamin (*A. Ch.* [4] 3, 49) made careful experiments on the influence of the presence of aqueous vapour in the atmosphere upon the refractive index, and he found that the difference between the refractive indices of dry air and air saturated with aqueous vapour was only ·000000726, a quantity so small that it may be safely neglected in the calculation of atmospheric refraction for astronomical purposes.

Ketteler (*B. B.* 1865) adopted Jamin's interference refractor for the measurement of the index of air, CO_2, CN, H, and SO_2, for the line D. He calculated the lithium and thallium lines from the wave length of the sodium line, according to the proportional number of rulings that coincide, it being found that this is independent of density and is a true function of the wave lengths.

RELATIONS BETWEEN PHYSICAL AND CHEMICAL PROPERTIES AND REFRACTION OF LIQUIDS.

Dale and Gladstone (*T.* 1858. 887) made an elaborate series of experiments on what they then termed the sensitiveness of liquids, or the effect of temperature on the refractive index. The principal conclusions they arrived at were that both the index of refraction and the length of the spectrum, $\mu_H - \mu_A$, diminish as the temperature rises, and that the sensitiveness of a substance is independent of its specific refractive or dispersive power. These conclusions were the result of observations on CS_2, Et_2O, H_2O, P, alcohols, &c. The following table and the table on p. 226 give the data for CS_2 and H_2O:—

Carbon disulphide (b.p. = 43°)

Temp.	μ_A	μ_D	μ_H	Sensitiveness	$\mu_H - \mu_A$	Dispersive power
0°	1·6217	1·6442	1·7175	0·0045	0·0958	0·1489
5°	1·6180	1·6397	1·7119	0·0051	0·0939	0·1467
10°	1·6144	1·6346	1·7081	0·0043	0·0937	0·1477
15°	1·6114	1·6303	1·7035	0·0042	0·0921	0·1462
20°	1·6076	1·6261	1·6993	0·0041	0·0917	0·1463
25°	1·6036	1·6220	1·6942	0·0038	0·0906	0·1460
30°	1·5995	1·6182	1·6896	0·0042	0·0901	0·1457
35°	1·5956	1·6140	1·6850	0·0037	0·0894	0·1456
40°	1·5919	1·6103	1·6810	0·0042	0·0891	0·1459
42·5°	1·5900	1·6082	1·6778		0·0878	0·1443

The sensitiveness is reckoned from the indices of the line D, and the dispersive power represents $\frac{\mu_H - \mu_A}{\mu_D - 1}$. The sensitiveness indicates an anomaly in water, which has also been observed by others.

Gladstone and Dale (*T.* 1863. 317) extended the same inquiry to the following five points:—(1) the relation between sensitiveness and the change of volume by heat; (2) the refraction and dispersion of mixed liquids; (3) the refraction, dispersion, and sensitiveness of different members of homologous series; (4) the

Water						
Temp.	μ_A	μ_D	μ_H	Sensitiveness	$\mu_H - \mu_A$	Dispersive power
0°	1·3291	1·3330	1·3438	0·0001	0·0147	0·0429
5°	1·3290	1·3329	1·3436	0·0002	0·0146	
10°	1·3288	1·3327	1·3434	0·0003	0·0146	0·0439
15°	1·3284	1·3324	1·3431	0·0004	0·0147	
20°	1·3279	1·3320	1·3427	0·0003	0·0148	0·0445
25°	1·3275	1·3317	1·3420	0·0006	0·0145	
30°	1·3270	1·3309	1·3415	0·0006	0·0145	0·0438
35°	1·3264	1·3303	1·3410	0·0006	0·0146	
40°	1·3257	1·3297	1·3405	0·0009	0·0148	0·0449
45°	1·3250	1·3288	1·3396	0·0008	0·0146	
50°	1·3241	1·3280	1·3388	0·0009	0·0147	0·0448
55°	1·3235	1·3271	1·3380	0·0012	0·0145	
60°	1·3223	1·3259	1·3367	0·0010	0·0144	0·0441
65°	1·3218	1·3249	—	0·0012	—	
70°	1·3203	1·3237	1·3344	0·0012A	0·0141	0·0435
80°	1·3178	—	1·3321		0·0143	

refraction, dispersion, and sensitiveness of isomeric liquids; (5) the effect of chemical substitution on these optical properties. As to the first point of the inquiry, they came to the conclusion that the specific refractive energy $\left(\frac{\mu-1}{d}\right)$ is a constant not affected by temperature. They made the reservation, however, 'that there is some influence, arising wholly or partially from dispersion, which gives rise to the slight progression of most of the calculated products, and perhaps to the non-inversion of the sensitiveness of water at 4°, remarked on already by Jamin and ourselves.' As to the second point of inquiry, it was found 'that the specific refractive power of a mixture of liquids is the mean of the specific refractive powers of its constituents,' subject to some slight exceptions, as in the case of sulphuric acid and water. The inquiry into the refraction, dispersion, and sensitiveness of different members of homologous series showed a progressive increase in the specific refractive energy as the series advanced; but that the influence of each addition of CH_2, which is observable throughout the series of the methyl group, does not necessarily hold good with reference to substances of quite another type. The observations on isomeric bodies showed that some of them are widely different in their optical properties; but that those which have a close chemical relationship show an identity in their optical properties also. In the last branch of the inquiry it was sought 'to determine the amount of change in the optical properties which results from a replacement of one element by another, the type remaining the same,' in order to 'attain to a knowledge of the influence of the individual elements on the rays of light transmitted by them.' The general conclusion of Gladstone and Dale was that 'every liquid has a specific refractive energy composed of the specific refractive energies of its compound elements, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when mixed with other liquids.' This opened up a question which has since occupied the attention of many observers.

Landolt (*P.* 117, 122, 123) took up the inquiry, adopting the formula $\frac{\mu-1}{d}$ used by Gladstone and Dale, and applied it in the first instance to an investigation of the values of C, H, and O. He simplified the investigation by multiplying the specific refractive energy by the molecular weight of the compound, which gave P $\frac{\mu-1}{d}$ as the molecular refractive power, or refraction-equivalent, terms which had already been applied by Berthelot and Schrauf to the formula P $\frac{\mu^2-1}{d}$. By comparing series of homologous compounds, acids of the series $C_nH_{2n}O_2$, alcohols of the series $C_nH_{2n+2}O$, and esters of the series $C_nH_{2n}O_2$, L. obtained the increment due to each addition of CH_2 as shown in the following selection from his data:—

—	Substance	S.G. $\frac{18}{18}$	μ	$\frac{\mu_a-1}{d}$	R_a	Diff. CH_2
Acids $C_nH_{2n}O_2$	Formic	1·2211	1·3693	0·3024	13·91	7·20
	Acetic	1·0514	1·3699	0·3518	21·11	7·46
	Propionic	0·9963	1·3846	0·3860	28·57	7·65
	Butyric	0·9610	1·3955	0·4116	36·22	7·83
	Valerianic	0·9313	1·4022	0·4319	44·05	7·56
	Caproic	0·9252	1·4116	0·4449	51·61	7·79
	Œnanthylic	0·9175	1·4192	0·4569	59·40	
Alcohols $C_nH_{2n+2}O$	Methyl	0·7964	1·3279	0·4117	13·17	7·53
	Ethyl	0·8011	1·3605	0·4501	20·70	7·60
	Propyl	0·8042	1·3794	0·4717	28·30	7·81
	Butyl	0·8074	1·3940	0·4879	36·11	7·78
	Amyl	0·8135	1·4057	0·4987	43·89	
Esters $C_nH_{2n}O_2$	Methyl acetate	0·9053	1·3592	0·3967	29·36	6·81
	Ethyl acetate	0·9015	1·3705	0·4110	36·17	
	Methyl butyrate	0·8976	1·3869	0·4311	43·97	7·35
	Ethyl butyrate	0·8906	1·3940	0·4424	51·32	
	Methyl valerate	0·8809	1·3927	0·4458	51·71	7·49
	Ethyl valerate	0·8674	1·3950	0·4554	59·20	
	Ethyl formate	0·9078	1·3580	0·3944	29·18	6·99
	Ethyl acetate	0·9015	1·3705	0·4110	36·17	
	Methyl butyrate	0·8976	1·3869	0·4311	43·97	7·74
	Methyl valerate	0·8809	1·3927	0·4458	51·71	
	Ethyl butyrate	0·8906	1·3940	0·4424	51·32	7·88
	Ethyl valerate	0·8674	1·3950	0·4554	59·20	

The mean of Landolt's comparisons gave the value R = 7·60 for CH_2. Dealing in the same manner with compounds differing by one atom of carbon, by two atoms of hydrogen, and by one atom of oxygen, respectively, he assigned to the several elements the following refraction-equivalents; C = 5·00; H = 1·30; O = 3·00. Subsequent investigations would lead one to reject several of the substances which he brought into comparison.

Landolt also adopted a modification of Biot and Arago's formula for mixtures of gases, by substituting *n* for n^2 throughout, so that

$$\frac{N-1}{D}P = \frac{n-1}{d}p + \frac{n'-1}{d'}p' + \ldots$$

N, D and P representing the index of refraction, density, and 'molecular weight' of the mixture, and the small letters the same values of the several substances forming the compound. In this manner he calculated the value of n_a or μ_a, for mixtures of liquids as shown in the follow-

ing table. It will be seen that the calculated and observed values correspond very closely.

—	p	Observed d	Observed μ_a	Calculated μ_a
Methyl alcohol	96	0·7964	1·3279	
Amyl „	88	0·8135	1·4057	
Mixture .	184	0·8038	1·3640	1·3644
Ethyl alcohol	92	0·8011	1·3605	
Amyl „	88	0·8135	1·4057	
Mixture .	180	0·8065	1·3822	1·3821
Ethyl alcohol	46	0·8011	1·3605	
Amyl „	176	0·8135	1·4057	
Mixture .	222	0·8104	1·3961	1·3960
Acetic acid	60	1·0518	1·3706	
Butyric „	88	0·9610	1·3953	
Mixture .	148	0·9930	1·3850	1·3847
Ethyl alcohol	46	0·8011	1·3605	
Formic acid	46	1·2211	1·3693	
Mixture .	92	0·9602	1·3610	1·3612
Oil of bitter almonds. .	106	1·0474	1·5391	
Formic acid	46	1·2211	1·3693	
Mixture .	152	1·0876	1·4900	1·4900

Landolt subsequently (*A.* 4, *Suppl.*) reversed the process, and applied it to the quantitative analysis of mixed liquids by means of their refractive-indices and specific gravities. The following will serve as instances of the percentage results obtained:—

—	μ_a	d	$\frac{\mu_a-1}{d}$	Percentage Calculated	Percentage Actual
Amyl alcohol .	1·4057	0·8135	0·4987	47·4	47·8
Methyl „ .	1·3279	0·7964	0·4117	52·6	52·2
Mixture .	1·3640	0·8038	0·4529	100·0	100·0
Acetic acid .	1·3706	1·0518	0·3523	40·3	40·5
Butyric „ .	1·3955	0·9610	0·4116	59·7	59·5
Mixture .	1·3850	0·9930	0·3877	100·0	100·0
Ethyl alcohol .	1·3606	0·8011	0·4501	49·8	50·0
Formic acid .	1·3693	1·2211	0·3024	50·2	50·0
Mixture .	1·3610	0·9602	0·3760	100·0	100·0
Oil of bitter almonds . .	1·5391	1·0474	0·5147	69·8	69·7
Formic acid .	1·3693	1·2211	0·3024	30·2	30·3
Mixture .	1·4900	1·0876	0·4505	100·0	100·0

Halogen compounds. Landolt's values for the refraction-equivalents of C, H, and O are:

Carbon . .	R_∞	4·86	R_a	5·00
Hydrogen . .	„	1·29	„	1·30
Oxygen . .	„	2·90	„	3·00

Adopting these values, Haagen (*P.* 131, 117) deduced values for Cl, Br, and I from some of their organic liquid compounds, and then deduced values for other elements from observations of R for their chlorine compounds. The following are the results he obtained for R_∞ and R_a:—

Element	R_∞	R_a
Chlorine . . .	9·53	9·79
Bromine . . .	14·75	15·34
Iodine	23·55	24·87
Sulphur . . .	14·74	16·03
Phosphorus . . .	14·60	14·93
Arsenic . . .	18·84	20·22
Antimony . . .	—	25·66
Silicon . . .	7·81	7·90
Tin	18·64	19·89
Sodium . . .	4·71	4·89

Refraction-equivalents of the elements. Gladstone (*T.* 159, 13; *Pr.* 18, 49) applied Landolt's $P\frac{\mu-1}{d}$ to inorganic compounds in order to arrive at the refraction-equivalents of the several elements, and also to determine whether or not any of the elements had more than one definite refraction-equivalent. As most of his observations were made upon crystalline salts, many of which were doubly refracting, Gladstone adopted the plan of dissolving them in water, or alcohol, and deducting from the R of the solution the R due to the solvent. This mode of operation was supported by the consideration that in the cases of rock-salt and sugar, where the refraction-equivalent of the substance has been obtained both in the solid and dissolved condition, it is found to be the same. On comparing a series of salts of K and Na, it was evident that, while the refraction-equivalents of the compounds differed very widely, according to the nature of their negative constituents, the refraction-equivalents of the compounds of Na differed *pari passu* with those of the K compounds, and hence it was concluded that the negative constituent has the same effect on light, whichever metal it is united with. Values were arrived at for forty-six of the elements, a number which has been subsequently somewhat increased; and more recent investigations have led to slight modifications in the figures. The latest list is as follows:—

Element	At. w.	R_A
Aluminium . . .	27·5	7·7
Antimony . . .	120	24·5
Arsenic	75	15·4
Barium	137·2	15·8
Beryllium . . .	9·1	5·1
Bismuth	208	38·2
Boron, in borates . .	11	about 4
Bromine	80	15·3
Cadmium . . .	111·6	13·1
Cæsium	132	19·1
Calcium	40	10·0
Carbon	12	5·0
„ doubly linked .	„	6·1
Cerium	138·2	19·6?
Chlorine	35·2	9·9
Chromium . . .	52·4	15·4
„ in chromates .	„	about 22
Cobalt	58·7	10·4
Copper	63·4	11·5
Didymium . . .	145	23·3
Fluorine	19	1·6?
Gold	196·2	23·1
Hydrogen . . .	1	1·3
Iodine . . .	127	24·5
Iron, in ferrous compounds . . .	56	11·6
Iron, in ferric compounds . . .	„	19·4
Lanthanum . . .	138	22·9
Lead	207	24·3
Lithium	7	3·5
Magnesium . . .	24	6·7
Manganese . . .	55	11·7
„ in permanganates	„	about 25

Element	At. w.	R_A
Mercury	200	19·4?
Nickel	58·7	10·0
Nitrogen	14	4·1
„ in bases, oxides, &c.	„	5·1
Oxygen, singly linked	16	2·8
„ doubly linked	„	3·4
Palladium	106	21·6?
Phosphorus	31	18·3
Platinum	195	24·7
Potassium	39·1	7·85
Rhodium	103·4	23·4?
Rubidium	85·4	12·1
Selenion	78	30·1
Silicon	28	7·4
„ in silicic acid	„	about 6
Silver	108	13·2
Sodium	23	4·4
Strontium	87·5	13·0
Sulphur	32	16·0
„ singly linked	„	14·1
Thallium	203·6	20·4
Tin	118	27·0?
„	„	18·6?
Titanium	48	24·6
Uranium	237·6	19·4
Vanadium	51·3	24·8?
Zinc	65·3	9·8
Zirconium	90	21·3

Anomalies were pointed out in the refraction-equivalents of the hydracids, and of the benzenoid carbon compounds. With regard to the specific refractive energy it was remarked:—First, hydrogen has more than double the energy of any other element, even in the lowest number that can be assigned to it. Second, phosphorus, vanadium, titanium, and sulphur have singularly high energies, and they are substances that present certain chemical analogies. Third, there are several pairs of analogous elements having nearly the same energy; thus bromine and iodine, arsenic and antimony, potassium and sodium, manganese and iron, nickel and cobalt. Fourth, an element in altering its valency alters its energy. Fifth, if the metals are arranged in the order of their energies, they are, with few exceptions, in the inverse order of their atomic weights.

Benzenoid hydrocarbons.—The anomalous refraction and dispersion of the hydrocarbons already referred to was treated in a paper by Gladstone (*C. J.* 23, 147), the tables in which indicated that the values for all these bodies and their derivatives were largely in excess of the normal, calculating R_A of carbon at 5·0. The refraction-equivalents of the typical hydrocarbons were expressed as in the following table; but while the physical fact indicated has been fully verified by subsequent research, the particular numbers in the third column have been modified, and a plus has been assigned to the olefines.

A similar table is given illustrating the increased influence on light of carbon which is combined with two atoms of hydrogen or one of oxygen, in a series of oxidised bodies obtained from essential oils, differing from one another only in the quantity of hydrogen.

Hydrocarbons	Typical Formula	R
Paraffins	C_nH_{2n+2}	Normal
Olefines	C_nH_{2n}	„
Terpenes	C_nH_{2n-4}	„ + 3
Benzenes	C_nH_{2n-6}	„ + 6
Naphthalene	C_nH_{2n-12}	„ + 14
Anthracene	C_nH_{2n-8}	„ + 17

Bedson and Williams (*B. A.* 1881. 155) tested the question whether the specific refraction of a solid body could be determined from the refractive power of its solution as stated by Dale and Gladstone, as this method had been called in question by Janovsky (*Sitz. W.* 82, 148). They found the specific refractive energy for the ray of infinite wave length, calculated from solutions of NaCl, $Na_2B_4O_7$, H_3BO_3, and $NaPO_3$ to be in substantial accord with the results derived from observations on the solids. They also found that the specific refraction of liquid phenol is practically identical with the value calculated from solutions in alcohol and in acetic acid.

In taking the index of refraction of solid $NaPO_3$, B. and W. immersed it in a liquid of greater refractive power, and then added a feebly refractive liquid until the refractive power of the mixture appeared to be the same as that of the solid suspended in it. The index of refraction of the mixture was then determined. The result being found satisfactory, the prisms of rock-salt and of fused borax were also tried by the same process, as well as in the ordinary way, and with similar results.

Double values of carbon and oxygen. Brühl, in 1879 and 1880 (*A.* 200, 139; 203, 1, 255), conducted a long investigation into the chemical constitution of carbon compounds in reference to their relative densities and their power to refract light. Taking up the observations of Gladstone, and also referring to some of the anomalous results in the tables issued by Landolt, whose mode of investigation suggested that the grouping of the atoms exercised a certain influence upon the refraction of light, Brühl set himself to inquire: What is the typical peculiarity which must be common to all the bodies that refract light in an abnormal manner? He usually determined the indices for the three H lines, μ_α, μ_β, and μ_γ, and for the Na line μ_D, and calculated the refraction-equivalents both for the line α, and for Cauchy's A, viz. R_∞. The following table is so arranged that between each horizontal line the first-named substance has the highest molecular weight, while those below differ only in having a smaller quantity of hydrogen, and, therefore, contain doubly-linked carbon atoms.

It will be observed that the density, the index of refraction, and the co-efficients of refraction and dispersion of Cauchy always increase with the diminution of H, and that the loss in specific refractive energy which is suffered by the disappearance of two atoms of H is at least fully made up by the consequent double linking of the carbon atoms. For the calculated values of the refraction-equivalents, Brühl has adopted the following values for the elements, viz.—for R, C=5·0, H=1·3, O=3·0, Cl=9·8, Br=15·3,

Substance	Formula	S.G. $\frac{20^\circ}{4^\circ}$	μ	Cauchy's A	Cauchy's B	$\frac{\mu_\alpha - 1}{d\frac{20^\circ}{4^\circ}}$	R_α Observed	R_α Calculated
Propyl alcohol	C_3H_8O	0·8044	1·38315	1·37542	0·34630	0·4767	28·60	28·4
Allyl alcohol	C_3H_6O	0·8540	1·41051	1·39881	0·50453	0·4807	27·88	25·8
Propyl aldehyde	C_3H_6O	0·8066	1·36157	1·35344	0·35065	0·4483	26·00	25·8
Acrolein	C_3H_4O	0·8410	1·39620	1·38010	0·69427	0·4711	26·38	23·2
Propyl ether	$C_3H_7(OC_3H_7)$	0·7386	1·36758	1·35975	0·33758	0·4977	43·80	43·6
Allyl ether	$C_3H_5(OC_3H_5)$	0·7651	1·38565	1·37547	0·43882	0·5041	43·35	41·0
Propyl acetate	$C_3H_7(C_2H_3O_2)$	0·8856	1·38235	1·37427	0·34832	0·4317	44·04	44·0
Allyl acetate	$C_3H_5(C_2H_3O_2)$	0·9276	1·40205	1·39151	0·45458	0·4334	43·34	41·4
Propyl chloride	C_3H_7Cl	0·8898	1·38659	1·37813	0·36474	0·4345	34·11	33·9
Allyl chloride	C_3H_5Cl	0·9379	1·41245	1·40007	0·53369	0·4398	33·64	31·8
Isobutyric acid	$C_4H_8O_2$	0·9490	1·39093	1·38259	0·35971	0·4119	36·25	36·4
Methacrylic acid	$C_4H_6O_2$	1·0153	1·42815	1·41400	0·61013	0·4217	36·27	33·8
Amylene (34° to 35°)	C_5H_{10}	0·6476	1·37330	1·36352	0·42173	0·5764	40·35	38·0
Valerylene	C_5H_8	0·6786	1·39763	1·38565	0·51660	0·5680	39·85	35·4
Hexane	C_6H_{14}	0·6603	1·37337	1·36538	0·34462	0·5655	48·63	48·2
Diallyl	C_6H_{10}	0·6880	1·39180	1·38589	0·52733	0·5787	47·45	43·0
Benzene	C_6H_6	0·8799	1·49668	1·47562	0·90816	0·5645	44·03	37·8
Triethylamine	$C_6H_{15}N$	0·7277	1·39801	1·38803	0·43179	0·5470	55·25	55·3
Aniline	C_6H_7N	1·0216	1·57948	1·54741	1·38319	0·5672	52·75	44·9

N = 5·8; the first three being the values given by Landolt, the two halogens those by Haagen, and that for N being determined by Brühl himself. From the observations recorded in the foregoing table and others, Brühl has arrived at the following conclusions:—That the closing of the chain of atoms in the form of a ring, with which so marked an increase in the density and index of refraction is associated, exercises a very special influence on the power of the substances to disperse light; that the mol. refraction of the substances in which the existence of one or more pairs of doubly-linked carbon atoms is recognised is greater than the sum of the refractions of the constituent atoms by 2·0 in the case of Cauchy's limit, and 2·3 in the case of the line H_α for each such pair. For combinations of the acetylene type, including the propargyl derivatives, he gives a rather lower value, viz.: 1·8 and 1·9 respectively. These data give the following atomic refractions for carbon, viz.—

	R_∞	R_α
C′	4·86	5·00
C″	5·86	6·15
C‴	5·76	5·95

Nasini and Bernheimer (*Lincei, Atti*, 18) do not, however, admit Brühl's views as to the constitution of the propargyl compounds, as well as some of the other conclusions at which he has arrived. They give tables of observations on naphthol compounds, styrol, cinnamic alcohol, anethol, anisol, thymol, and diamylene, and have worked out the results by the two ordinary formulæ for R_α and R_∞, and also for R_∞ and $\mathbf{R}_\infty$, as well as showing the small differences both in specific refraction and specific disperson due to differences in temperature. The principal conclusions at which they arrive are as follows:—The statement that every double bond, and only every double bond, causes the mol. refraction to increase by a constant quantity is not confirmed by complete series of substances, because in compounds containing only four or five double bonds the increase in refraction indicates a much greater number. That the increase in mol. refraction grows step by step as the compounds become poorer in H; but no proportion exists between the increased values and the number of pairs of atoms of H that is lost; nevertheless, a simple relation exists with the other structural changes in the formula, expressed by double bonds, closed chains, &c. That the augmentation increases more or less rapidly from the paraffins to the olefines, and thence to the benzenes, and again to the naphthalenes, but by what law is not evident, and is not capable of expression by our structural formulæ. They consider it established, however, that the principle is approximately valid, that in every series of compounds each atom in the molecule furnishes its fixed contribution of refraction, and that in the paraffin series the mean values of the atomic refractions coincide with those derived directly from the elements themselves. They remark that even in the paraffin series the constancy of the atomic refractions is not absolute; because the more the mol. w. increases the greater is the difference between the calculated and experimental values. For other series the same values no longer apply, being too low, and hence other constants are required.

Kanonnikoff (*Bl.* [2] 36, 557) has published observations confirming Brühl's calculation of the increase due to the double bond between carbon atoms, and of the loss in specific refractive energy due to the elimination of two atoms of hydrogen being counterbalanced by the increase due to the consequent double linking of the carbon atoms.

Landolt (*P.* 117, 122) had determined the refraction of oxygen from a comparison of the refraction-equivalents of various substances the empirical formulæ of which differed by one atom of oxygen; and from acids of the formula $C_nH_{2n}O_2$ by deducting the value of n times CH_2. The results were somewhat discordant, the first series giving a mean value for oxygen of 2·76, and the latter of 3·0. The former of these manifestly represented the atomic refraction of oxygen in hydroxyl; and if oxygen varied in its refraction according to its valency it is evident that a general average resulting from these two modes of determination could not be taken. Brühl shows that, adopting Landolt's second plan for arriving at the value of oxygen in the aldehydes and ketones of the formula $C_nH_{2n}O$, the R_α for oxygen will average 3·4; and that chloral, butyl-chloral, and the oxychlorides give substantially the same result. On the other hand, deducting the refraction-equivalents of the aldehydes from those of their corresponding acids, of the alcohols from the glycols, and of the acids from the oxyacids, he obtains 2·75 as the mean value for oxygen. An approximate result, 2·80, is obtained if, from the ethers, $C_nH_{2n}O_2$, the value of n times CH_2 + the higher value (3·4) for one atom of oxygen be deducted. For oxygen united to carbon by a double bond, Brühl therefore assigns the refraction-equivalent 3·4 for the line α; and for oxygen in hydroxyl, or generally for oxygen united to two other atoms, he gives the value 2·8; he represents the former as O″ and the latter as O′.

$$\text{Hence } C{=}O = 5{\cdot}0 + 3{\cdot}4 = 8{\cdot}4.$$
$$C{-}O = 5{\cdot}0 + 2{\cdot}8 = 7{\cdot}8.$$

Whether, however, the increased result of the double linking of the carbon and the oxygen is due to one of the elements only, or whether both of them share in it, he leaves an open question, though he regards the latter as the more probable. If two atoms of H are removed from a substance without involving the double linking of carbon atoms, as in the case of an alcohol being converted into an aldehyde or ketone, there follows a very marked reduction of the specific refractive energy. This reduction, however, becomes less and less marked as the quantity of C increases in the higher members of the series. When the removal of two atoms of H involves the double linking of the C, the loss of refractive energy is more than compensated by the increase due to the doubly-linked C.

A comparison of a considerable number of isomeric bodies of the paraffinoid series of acids shows that the indices of refraction of the primary and normal compounds are a little greater than those of the secondary and iso-compounds, and that the densities are proportional. In the case of unsaturated compounds of similar empirical composition, however, the double linking of the carbon atoms increases the refractive power more than the density.

In a subsequent paper (*A.* 235, 1), Brühl treated of the molecular refraction of organic liquids of high dispersive power. He arrived at the conclusion that the dispersion of different substances stands in no clearly recognisable relation either to their refraction or chemical constitution; and that it cannot be numerically expressed. This, however, is contested by Gladstone (*Pr.* 42, 401), who, while admitting that there are difficulties in the investigation of dispersion which are not felt in dealing with refraction, still holds (1) 'that dispersion, like refraction, is primarily a question of the atomic constitution of the body: the general rule being that the dispersion-equivalent of a compound is the sum of the dispersion-equivalents of its constituents; (2) that the dispersion of a compound, like its refraction, is modified by profound differences of constitution, such as changes of atomic valency; (3) that the dispersion frequently reveals differences of constitution at present unrecognised by chemists, and not expressed by our formulæ.' Brühl held that the differences which still appear between the calculated and experimental values when Lorenz's formula is used, and which he showed to be less in proportion than when the old empirical formula is used, are principally due to the influence of dispersion, and that they would in great measure vanish if this disturbing cause could be overcome; that with substances with a dispersion equal to about that of cinnamic alcohol the molecular refraction for the line α would serve as a help to the determination of the chemical constitution, but beyond that limit the numerical results are too uncertain to be of use except as collateral evidence; that there is a direct and simple proportion between the number of unsaturated groups of atoms in any compound and the increase of the molecular refraction $\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{p}{d}$ over the value derivable from the empirical chemical formula; that the effect on refraction of the acetylene combination, which he represents by ≡, is analogous to that of the ethylene, or doubly-linked carbon, =, and that it is somewhat greater, but not twice as great, as the latter.

Gladstone questions Brühl's assumption that both cinnamic alcohol and cinnamic aldehyde have four pairs of doubly-linked carbon atoms, on the ground that they have widely-different dispersions; also that allyl paracresolate and anethol are similarly constituted, for the same reason. He also thinks that the evidence as to the constitution of cymol and hexahydro-naphthalene from Brühl's observations is not conclusive as to the one having three pairs, and the other two pairs, of doubly-linked carbon atoms, seeing that they have nearly the same dispersion. Nasini (*Lincei*, *Rc.* 3, 164) in like manner holds that these particular compounds do not justify the conclusions that Brühl has come to respecting them, and agrees with G. that the dispersion may be a constant, and a much more sensitive one than the specific refraction; and that as such it is affected more and varies more by certain little differences of composition and constitution of which the specific refraction does not feel the influence.

Brühl (*Z. P. C.* 1, 6) maintains that Erlenmeyer's constitutional formula, with five ethylene combinations, correctly represents the structure of naphthalene, and those derivatives in which hydrogen is replaced by monovalent elements. But the results of the observations on which he bases this conclusion all show a larger increment than can be accounted for by this formula; the excess he attributes mainly to the influence of dispersion. In this and all the other inquiries he has adopted Lorenz's formula, and the solar line C, without attempting to get rid of the influence of dispersion by the use of Cauchy's co-efficient of refraction. In the same paper he formulates the following six propositions:—(1) Isomerides of similar atomic arrangement (*Stellungsisomere*) have similar specific and molecular refractive powers; on the other hand, those isomerides which show differences of saturation (*Sättigungsisomere*) have various specific and molecular refractive powers; (2) polymeric combinations never show similar specific refractive energy, or multiple molecular refraction corresponding to the molecular weights; (3) transformations of multiple linkings of atoms into simple ones have as their result a diminution of refraction, equally, whatever the kind of chemical change may be (polymeric or isomeric change); (4) the optical effect of the accumulation of multiple linkings is the same, whether it produces open chains (amylene—diamylene) or ring formations with one or more groups of rings (as in paraldehyde, cymhydrene, menthol, &c. in the one case, and in turpentine and cajeputol in the other); (5) the molecular refraction of a fully saturated body is very nearly that of the sum of the refractions of the atoms of the empirical chemical formula, each of these being reckoned as united by single bonds—all those are to be regarded as saturated bodies in which there is no multiple linking of the atoms, such as the true paraffins, or derivatives of the general formula $(C_nH_{2n+2}) - xH_2$; (6) all unsaturated bodies show an increased refraction which is proportional to the number of ethylene, acetylene, or carbonyl combinations present; the proportion, as a rule, is the more exact the less the substances in question are distinguished by a specially great dispersion. While holding to the opinion that the monovalent elements have virtually each but one refraction equivalent, and that the change of valency in the others is the chief cause of their variable refraction, Brühl considers that exact values cannot be obtained, because the mode of the grouping of the atoms may not be altogether without influence.

In the meantime, Gladstone (*C. J.* 45, 241) had brought together a large number of observations on organic compounds, both liquids and solutions of solids, and placed against them the refraction-equivalents calculated on the basis of the following values for the elements:—

Carbon, saturated . . .	R_A 5·0
„ in C_nH_n	5·95
„ doubly linked . . .	6·1
Hydrogen	1·3
Oxygen, singly linked . . .	2·8
„ doubly „ . . .	3·4
Nitrogen	4·1
„ in bases, NO_2, &c. . .	5·1
Chlorine	9·9
Bromine.	15·3
Iodine	24·5
Sulphur, singly linked . . .	14·1
„ doubly linked . . .	16·0

Gladstone's observations confirm Landolt's original determination for H, and also for C in saturated compounds. Gladstone points out that the hydrocarbons of the formula C_nH_n scarcely come up to Brühl's previous estimate of the higher value of C, so that in these cases he has adopted the figure 5·95 instead of 6·1, as the difference is more than he considers can be accounted for either by dispersion or by the distance from the boiling-points. In the case of those substances where the C atoms outnumber those of H, all of which show an inordinately high refraction and are at the same time enormously dispersive, Gladstone points out that Kanonnikoff's view that the increase is due to dispersion alone is not established by that observer's own figures for the theoretical limit of the spectrum according to Cauchy's formula. He admits, however, that if the limit were carried back considerably further, though still fairly within what Langley's observations would allow, the values would so far approximate as to render it not impossible that the refraction-equivalent of C might prove to be the same in these compounds as in the benzenoid series, or wherever it is doubly linked. As to the halogens, the figures in the table are generally consistent with the values which were originally assigned by him to Cl, Br, and I, viz. 9·9, 15·3, and 24·5 respectively. These numbers are very nearly the same as those arrived at independently by Haagen, viz. 9·8, 15·3, and 24·8. The values for O are taken from Brühl's original determinations, though the evidence of the alcohols rather favours his old estimate of 2·9 for the line A.

With regard to the phenomena of dispersion, Gladstone points out 'that the double linking of carbon atoms, while it does not much affect the specific refraction, widens the spectrum greatly, to such an extent indeed that where there are three pairs of such carbon atoms the specific dispersion is about double that of a saturated compound; where, however, the carbon atoms are actually in excess the dispersion becomes far more rapid. This is evident throughout, but the following typical hydrocarbons may illustrate it:—

Hexane .	C_6H_{14}	sp. ref.	0·5626,	sp. disp.	0·0242
Amylene .	C_5H_{10}	„	0·5708	„	0·0300
Benzene .	C_6H_6	„	0·5595	„	0·0486
Napthalene	$C_{10}H_8$	„	0·5870	„	0·0782
Difluorene	$C_{26}H_{18}$	„	0·6057	„	0·1108

or the following alcohols:—

Isobutyl alcohol	$C_4H_{10}O$	sp. ref.	0·4878,	sp. disp.	0·0209
Allyl alcohol	C_3H_6O	„	0·4731	„	0·0275
Phenol	C_6H_6O	„	0·5090	„	0·0476
Naphthol	$C_{10}H_8O$	„	0·5487	„	0·0832

'The effect of the halogens in lowering both the specific refraction and dispersion is very marked, and that of NO_2 is still more remarkable.'

Gladstone (*C. J.* 59, 290, 589) has since published other long series of observations; including a record of experiments on the effect of changes of temperature on the refraction of some highly-refractive substances, which seem to confirm the opinion previously expressed by Dale and himself. Among the substances contained in these tables the benzyl and benzal camphors of Haller call for special notice, as they have a very high refraction, and a dispersion which is altogether excessive. The latter compound has in like manner a very high rotatory power. The hydracids in aqueous solution are shown to have not only a higher value than the normal, a fact which has long been observed, but also that the value rises with dilution; and that in the dispersion the excess is still more striking. The same fact was observed by Perkin in regard to the molecular magnetic rotation of these acids dissolved in water, both as to the initial excess, and to its increase with the dilution up to a certain point where it remained nearly constant.

Other investigators have availed themselves of the optical properties in order to determine the constitution of compound bodies, or to confirm the views arrived at on other grounds. Knops (A. 248, 175) has determined the indices of refraction of the methyl, ethyl, and propyl salts of fumaric, maleic, mesaconic, citraconic and itaconic acids. A comparison of these acids with their ethereal salts leads to the conclusion that fumaric and maleic acids contain only one doubly-linked carbon atom; and that fumaric acid stands in the same relation to maleic acid as mesaconic acid does to citraconic acid.

Kanonnikoff (*J. pr.* [2] 31, 321, 497) has made a long series of observations on solutions of solids, of which he tabulates seventy-nine different substances, using water, alcohol, benzene, and chloroform as the solvents. As a preliminary inquiry, he reviewed the work of former investigators, and in some cases added experiments of his own to confirm previous conclusions: that the refractive energy of a substance is not changed in passing from the state of a liquid to that of a gas or vapour; that the same applies to bodies in passing from the solid to the liquid condition; that the refraction-equivalent of a mixture of liquids is the sum of the refraction-equivalents of its constituents; and that if the refraction-equivalent of a mixture and that of one of the components, together with the proportion of the same, is known, the refraction-equivalent of the other component can be calculated; that the same law applies to solutions of solid bodies, and that like results will be obtained whatever the solvent may be; that a derivative will be comparable with the substance from which it is derived, though the one may be a liquid and the other a solid body, as in the case of mesaconic acid and ethyl mesaconate. From the results of the observations above referred to, K. has determined the refraction-equivalents of fourteen of the elements, as follows:—

Element	R_C	R_∞	Element	R_C	R_∞
Lithium . .	3·16	3·00	Magnesium .	7·03	6·47
Sodium . .	4·22	4·00	Calcium .	9·32	9·05
Potassium .	7·75	7·40	Zinc . .	9 80	9·40
Copper . .	—	11·30	Strontium .	11·61	11·25
Rubidium .	12·04	11·60	Cadmium .	13·03	12·66
Silver . .	13·05	12·53	Barium .	15·84	15·28
Cæsium . .	19·55	18·70	Mercury .	19·20	17·90

K.'s values for the solar line C will be found to be generally slightly lower than those determined by Gladstone for the line A. The refraction-equivalents for the theoretical limit of the spectrum were also calculated by Cauchy's formula from observations of the lines α and β of hydrogen. K. also gave determinations of refraction-equivalents of thirty organic liquids, showing the excess due to the double linking of the carbon atoms wherever this occurred.

Nasini (*Lincei*, *Rc.* 1, 1) points out that the suggestion thrown out by Gladstone that there may be a third and higher value of carbon when its four bonds are satisfied by other carbon atoms, is supported qualitatively by the researches of Bernheimer and himself, but not quantitatively, and that, therefore, this hypothesis is not a sufficient explanation of the facts. He argues as follows: naphthalene derivatives have two such atoms, while cinnamic alcohol has but one, whereas the values differ but very little. Anethol with one such carbon atom has a much greater excess than the naphthalene derivatives, while styrol shows so slight an excess, that on this hypothesis it could hardly be allowed to have any carbon atom in this condition. He compares two pairs of isomeric bodies, both as to refraction and dispersion,

Substance	R_α	$\frac{\mu_\beta - \mu_\alpha}{d}$
Allyl phenylate . .	70·45	0·0173
Cinnamic alcohol .	73·83	0·0220
Allyl paracresolate .	78·79	0·018
Anethol . . .	82·95	0·0257

from which he infers that when the allyl group is directly united to the benzene nucleus the molecular refraction greatly increases, whereas when the union takes place through the intervention of oxygen no augmentation takes place; so far, therefore, while supporting the hypothesis of Gladstone, he does not find any proportionality between the number of such carbon atoms and the increase of refraction.

Nasini (*Lincei*, *Rc.* 3, 164) criticises some of the conclusions of Brühl in the paper on the molecular refraction of organic liquids of high dispersive power (*A.* 235, 1) already referred to; and in particular he points out that the elimination of dispersion, if that were possible, would not get rid of the discrepancies between the observed and calculated values for the refraction of substances of high refractive power, and he cites observations on a series of substances in which he finds the constant fact that on adding a saturated side chain to an aromatic nucleus the specific dispersion diminishes while the refractive power increases.

Costa (*G.* 19) has made observations with the special object of testing the effect on dispersion of adding saturated side chains to a benzene or naphthalene nucleus. For this purpose he used compounds of amyl with benzene, thymol, eugenol, resorcin, and naphthol, and found in each case a still further increase in the refraction-equivalent than could be accounted for by the nucleus itself, while at the same time the specific dispersion showed a decrease.

Dispersion equivalents. In the same way that Gladstone arrived at the refraction-equivalents of the elements, he has sought also to determine the dispersion-equivalents of several of them; and (*Pr.* 42, 401) he has given the results of his observations upon nine of them, together with the values for the combinations CH_2 and NO_2. The values are as follows:—

Substance	R_A	Disp. Eqt. H–A
Phosphorus . .	18·3	3·0
Sulphur, doubly linked	16·0	2·6
„ singly „	14·0	1·2
Hydrogen . . .	1·3	0·04
Carbon . . .	5·0	0·26
„ . . .	6·1?	0·51
„ . . .	6·1	0·66
Oxygen, doubly linked	3·4	0·18
„ singly „	2·8	0·10
Chlorine . . .	9·9	0·50
Bromine . . .	15·3	1·22
Iodine . . .	24·5	3·65
Nitrogen . . .	4·1	0·10
CH_2	7·6	0·34
NO_2	11·8	0·82

It will be observed that G. gives three dispersion equivalents for C, which he considers pretty well established, and he raises the question whether there may not be an intermediate refraction-equivalent corresponding to the dispersion-equivalent 0·51, which is found in such bodies as the allyl compounds and olefines. In his previous paper (*Pr.* 31, 327), G. suggested that there is a still higher refraction-equivalent of C in those cases in which it has four bonds satisfied by other C atoms, as in naphthalene and pyrene. Whatever may be the truth of this view, it appears that the dispersion-equivalents of these bodies are enormously high — much beyond what is recognised in the above table.

Brühl (*Z. P. C.* 7, 2, 140) has since modified his views upon the subject of dispersion; and has worked out carefully the atomic dispersions of some of the most important elements that enter into organic compounds. In the course of this investigation he has been led to revise his previous figures for the refraction as well as the dispersion. They now stand as follows:—

	Symbol	R_a	$R_\gamma - R_a$
Carbon, singly linked .	C'	2·365	0·039
Hydrogen . . .	H	1·103	0·036
Oxygen (hydroxyl) .	O'	1·506	0·019
„ (ether) . .	$O\!<$	1·655	0·012
„ (carbonyl) .	O''	2·328	0·086
Nitrogen, linked singly with C . . .	N'	2·76	0·19
Chlorine . . .	Cl	6·014	0·176
Bromine . . .	Br	8·863	0·348
Iodine	I	13·808	0·774
Ethylene bond . .	=	1·836	0·23
Acetylene bond . .	≡	2·22	0·19

It will be observed that B. retains Lorenz's formula; and that he takes the difference between the refraction of the hydrogen lines γ and a as his measure of dispersion. He now acknowledges that the molecular dispersion can be regarded and employed in like manner with the molecular refraction as a specific expression of the material composition of chemical bodies; and that the dispersion is decidedly more sensitive to structural influences than the refraction. His inquiries have convinced him that refraction and dispersion are in no general sense correlative properties; but that certain structural peculiarities that have much influence upon refraction have little upon dispersion, while others have the opposite effect, and, as a rule, exercise a much stronger influence upon the dispersion. It is evident that this must be so, from the very high relative dispersion of O'' as compared with that of O' or $O\!<$, and the large proportionate dispersion due to the ethylene bond. This figure, ·23, B. does not, however, recognise as a constant value. These revised values have since been used by him in his inquiries into the relations between the optical properties and chemical constitution of epichlorhydrin, the aldehydes and benzoyl (*B. B.* 24, 656), in which he draws attention to the concurrence of the evidence derived from chemical, calorimetrical, and optical investigations.

Essential oils. Gladstone (*C. J.* 17, 1; 25, 1) gave a long list of observations in which he recorded the circular polarisation as well as the index of refraction. The power of the oils in rotating the plane of polarisation appears to be very diverse, both in degree and direction; but he suggests that a comparison of the specific gravity and of the length of the spectrum may in some cases be of service in determining the genuineness or otherwise of the oils. The hydrocarbons obtained from these oils (of which a long table is given) divide themselves into two great groups, which are more fully investigated in the second paper.

Subsequently (*C. J.* 49, 609) the effect of the higher refraction and dispersion of C when united by double bonds was applied to the determination of the structure of the essential oils. Taking 2·2 as the increased refraction for the solar line A, and 0·8 as the increased dispersion, H—A, due to one pair of doubly-linked carbon atoms, the terpenes indicate, both by their refraction and dispersion, that they contain only one pair of carbon atoms doubly linked, thus corroborating the views of those who, on chemical grounds, have held that a terpene requires the addition of only two atoms of hydrogen, or their equivalent, to saturate it. The refraction and dispersion of solid inactive camphene also show that this substance does not contain more than one pair of doubly-linked carbon atoms, which is consistent with the fact that it combines with only one molecule of hydrochloric acid, and is directly converted by oxidation into camphor $C_{10}H_{16}O$, which is certainly a saturated compound both by chemical and optical evidence. In the same way, the citrenes give a refraction and dispersion indicative of the presence of two pairs of doubly-linked carbon atoms. Allied to these are several hydrocarbons having different amounts of hydrogen, and the number of doubly-linked carbon atoms varying accordingly. Thus, while citrene $C_{10}H_{16}$ has two pairs, cymene $C_{10}H_{14}$ has three, while menthene $C_{10}H_{18}$ has but one pair of doubly-linked carbon atoms, and cymhydrene $C_{10}H_{20}$ has none, being a saturated body. Pentene and isoprene C_5H_8 are identical in their optical properties, and indicate that no less than four of the five carbon atoms are doubly linked, which accords with the fact that these compounds combine with four atoms of bromine or two molecules of hydrochloric acid. The following table will illustrate the foregoing conclusions :—

Hydrocarbons	Experimental		Pairs of C atoms doubly linked	Theoretical	
	Specific refractive energy	Specific dispersive energy		Specific refractive energy	Specific dispersive energy
Cymhydrene . . .	0·543	0·0246	none	0·543	0·0243
Menthene	0·548	0·0313	one	0·547	0·0298
The terpenes . . .	0·537	0·0295	do.	0·537	0·0296
Terebenthene . . .	0·537	0·0294	do.	,,	,,
Camphene	0·528	0·0269	do.	,,	,,
The cedrenes . . .	0·538	0·0296	do.	,,	,,
The citrenes . . .	0·551	0·0334	two	0·553	0·0354
Isoterebenthene . . .	0·552	0·0337	do.	,,	,,
Caoutchene . . .	0·554	0·0366	do.	,,	,,
Cymene	0·560	0·0406	three	0·558	0·0413
Isoprene	0·592	0·0470	four	0·585	0·0472

The advance in these experimental figures with the double linking is evident, though it is obscured in the first two cases by the larger amount of hydrogen contained in cymhydrene and menthene. The influence of the double linking upon the specific dispersive energy is apparent at a glance, and renders this property more valuable than the refractive energy in determining the rational constitution; though, of course, it is in the agreement of the two that the most conclusive evidence must be sought.

Kanonnikoff (*Bl.* [2] 36, 557) had already pointed out the differences between the calculated and observed refraction equivalents for the following substances :—

Substance	R_∞	Calculated	Difference
Peppermint camphor .	77·6	77·1	+ 0·5
Cajeputene hydrate .	74·8	74·5	+ 0·3
Terebenthene hydrate, lævogyrate . .	77·1	74·5	+ 2·6
French terebenthene, lævogyrate .	71·7	69·2	+ 2·5
Hydrocarbon from *oleum camillæ* . .	71·9	69·2	+ 2·7
Hydrocarbon from *oleum thymiani* .	71·4	69·2	+ 2·2
Isoterebenthene . .	73·6	69·2	+ 4·4
Carvol	74·8	69·4	+ 5·4
Cymene from camphor .	72·0	66·6	+ 5·4

K. has drawn the conclusion that the first two contain no double bond, that the two terebenthenes and the two hydrocarbons contain one double bond, that isoterebenthene contains two, and that carvol and cymene contain three, double bonds.

Carbon. Schrauf (*W.* 22, 424) made observations on the refraction of a Brazilian diamond of the first water, the S.G. of which was 3·516, with the following results :—

μ_{Li} 2·408449
μ_{Na} 2·417024 and 2·417227
μ_{Tl} 2·425487

These figures give $R = 4·8$, a result slightly lower than his earlier observations on the diamond, in which the index for the red part of the spectrum is recorded as 2·434, and the S.G. 3·55.

Selenion. Sirks (*P.* 143, 429) made observations on the refraction and dispersion of solid Se. By pressing a small quantity of melted Se between two glass plates, he prepared a thin film of the substance, which exhibited Newton's interference bands. From these he was able to calculate the index of refraction for the solar lines A, *a*, B and C, with an estimated error not exceeding 0·003; and for D, with some difficulty and uncertainty, to the second place of decimals only. The values obtained were:—μ_A 2·654, μ_a 2·692, μ_B 2·730, μ_C 2·787, μ_D 2·98. From these S. calculated the dispersion as compared with water, calcspar, and CS_2, the figures in each case being reduced to the standard of $\mu_C - \mu_A = 100$:—

	$\mu_a - \mu_A$	$\mu_B - \mu_a$	$\mu_C - \mu_B$	$\mu_D - \mu_C$
Water . .	36	31	33	88
Calcspar . .	36	30	34	90
Disulphide of carbon . .	34	31	35	99
Selenion . .	29	30	42	146

Comparing Se with CS_2, he found that while in the case of CS_2 $\mu_D - \mu_C$ differed very slightly from $\mu_C - \mu_A$, in the case of Se $\frac{\mu_D - \mu_C}{\mu_C - \mu_A} = 1·46$.

In testing Cauchy's and Christofle's formulæ for the index of the ray of infinite wave-length by the above observations, the former gave 2·733 and the latter 2·433. It will be observed that Cauchy's co-efficient of refraction is somewhat higher than the observed value for the solar line B, which is 2·730, the co-efficient of dispersion in this particular case being a minus quantity.

Phosphorus. Gladstone and Dale (*P. M.* 1859) measured the index of refraction of both solid and liquid P, an element remarkable not only for its very high refractive power, but for an unprecedented amount of dispersion. For solid P at 25° they obtained for μ_A 2·1059, for μ_B 2·1442, and for the extreme limit visible in the violet portion of the spectrum 2·3097. Assuming the latter to be equivalent to μ_H, the length of the spectrum $\mu_H - \mu_A = 0·2038$. For liquid P at 35° they obtained the following:—

μ_A	μ_D	μ_F	μ_G	End of violet
2·0389	2·0746	2·1201	2·1710	2·2267

The change from the solid to the liquid state is attended with a considerable diminution of density, the ratio between the density and the refraction being about the same in the two conditions. The R_A of P is taken at 18·3 from the above observations on liquid P, but Gladstone points out (*C. J.* 23, 101) that when combined with O it seems to have a much smaller refraction, HPO_3 giving a less value (18·0) than the P it contains, while H_3PO_4 also has a refraction-equivalent of only 23·6.

Sulphur. It was pointed out by Gladstone in 1869 (*T.* 159, 9) that while S, whether solid or liquid, has a refraction-equivalent of 16·0 or 16·3 for the solar line A, the equivalent for S deduced from CS_2 was 15·85; that the difference between KCN and KCNS gave a value of 16·24, and that S_2Cl_2 gave a similar figure. On the other hand, however, it was evident that in the two gases $H_2S = 14·28$, and $SO_2 = 14·91$, or in liquefied $SO_2 = 14·59$, the refraction-equivalent of S cannot amount to 16·0, nor yet in H_2SO_4, which has a refraction-equivalent of only 21·9.

Wiedemann and Nasini have subsequently given considerable attention to the values of S in combination. Wiedemann (*W.* 17, 577) investigated the sulphur substitution products of the carbonic esters, and obtained the following results:—

		d	μ_{Li}	μ_{Na}	μ	R_∞	$\mathbf{R}_\infty$
I.	$CO\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5}$	0·975	1·3837	1·3858	1·3876	45·66	27·80
II.	$CO\genfrac{}{}{0pt}{}{OC_2H_5}{SC_2H_5}$	1·0285	1·4479	1·4515	1·4544	56·95	34·11
III.	$CO\genfrac{}{}{0pt}{}{SC_2H_5}{SC_2H_5}$	1·085	1·5168	1·5237	1·5287	69·15	40·57
IV.	$CS\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5}$	1·0325 ?	1·4563	1·4601	1·4632	57·82	34·56
V.	$CS\genfrac{}{}{0pt}{}{OC_2H_5}{SC_2H_5}$	1·085	1·5301	1·5370	1·5431	70·26	41·23
VI.	$CS\genfrac{}{}{0pt}{}{SC_2H_5}{SC_2H_5}$	1·152	1·6105	1·6210	—	82·73	47·56

From these figures it will be seen (1) that the index of refraction rises whenever an atom of O is replaced by an atom of S, and that so much the more, the more S there is already in the compound; (2) that the refractive indices of the combinations which contain the radicle CS are greater than those of their analogues containing CO; (3) that the refractive index likewise increases if, besides the radicle, first one and then a second atom of S replaces O, and in the latter case more than in the former; (4) the isomeric bodies II. and IV., as well as III. and V., have quite different indices of refraction, and in both cases the compound that has the S in the radicle has the higher index. This indicates that the position of the S in the compound influences, in a very distinct manner, the value of the index of refraction. From the refraction-equivalents given above W. obtains the value 14·04 for S′ in the compounds II. and III.; and for S″ 15·20, 16·31, and 17·45 respectively. Using Lorenz's formula he gets the value of 7·94 for S′, and 9·09, 9·44, and 9·88 for S″. Whichever formula be adopted, the figures show that the atomic refraction of S, like that of O, is greater when S is doubly linked to an atom of carbon. It should be observed that the above results are based upon the recognised values of C, H, O′, and O″, which give

$$CO\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5} = R_\infty\ 45·91, \text{ and } \mathbf{R}_\infty\ 27·76;$$

and also that W. takes as the value of S′ the mean derived from the observations II. and III. If Wiedemann had adopted a direct comparison of the actual observations, the values of S″ would approximate more closely according to the old formula, and less closely according to Lorenz's formula.

Nasini (*G.* 13, 296; *Lincei, Rc.* 1, 1) has determined the value for S in various compounds. From sundry organic sulphides and mercaptans he obtained the atomic refraction of S corresponding to alcoholic oxygen. From CS_2, and from the compound $CS(OC_2H_5)_2$, he deduced the refraction of S corresponding to aldehydic oxygen:—

Sulphur	R_a	R_∞	$\mathbf{R}_a$	$\mathbf{R}_\infty$
S′ (singly linked) .	14·10	13·53	7·87	7·65
S″ (doubly linked) .	16·05	15·09	9·02	8·84

But when examining other compounds, such as H_2SO_4, SO_3, and SO_2, N. found that whatever hypothesis he adopted as to their constitution—or, in other terms, whatever value he took for the atomic refraction of O—he obtained values for S, not very discordant among themselves, but totally different from those given above. Treating the sulphur as divalent, R_∞ varied from 8·10 to 9·01; as tetravalent, from 6·94 to 8·43; as hexavalent, from 6·63 to 7·85. Calculating by Lorenz's formula, $\mathbf{R}_\infty$ ranged from 5·24 to 6·27 in the first case, from 4·51 to 4·91 in the second, and from 3·13 to 3·79 in the third. Some observations recorded by Kanonnikoff (*J. R.* 15, 434) substantially support these figures.

Nasini and Scala (*Lincei, Rc.* 1886. 617, 623) record observations on the sulphocyanides, which show that the mustard-oil compounds have refractive and dispersive powers in excess of those of their isomerides, while phenylic isosulphocyanide has a specific refraction and dispersion far above the calculated values—exceeding, in fact, oil of cassia or CS_2. In this combination the union of the group S=C=N, endowed with a high refractive power, with the phenylic group, also highly refractive, appears to produce a heightening of the refrangibility, a phenomenon which N. regards as analogous to the increase in refraction which he observed when in the benzene group an unsaturated side chain is joined to an unsaturated carbon atom. In compounds containing four atoms of S there is an excess of refraction above what is estimated from the value of S in CS_2, the monothiocarbonates of Et and Pr giving a value of 17·4 and 17·5 for the refraction-equivalent of sulphur.

Nasini a. Costa (*Ist. Ch. Rome*, 1891) made further studies of S and its compounds. They conclude that the oxygen compounds, which are generally distinguished by a low refractive and dispersive power as compared with those not oxygenated, may be divided into two principal groups: those which may be regarded as derived from SO_2 have the higher, and those derived from SO_3 have the lower, refractive and dispersive powers. Kanonnikoff (*S. Ph. Ch. Russ.* 16, 129) assumed that the refraction of S varies with the change of valency, and assigned the following values for R_a:—

S divalent 14·10
S tetravalent 8·72 (in sulphones)
S hexavalent 4·85 (in H_2SO_4)

but this is not accepted by N. and C. They find that the accumulation of S in the molecule is almost always accompanied by an increase in the refractive and dispersive power. In this respect, though not in others, S appears to have much analogy with carbon. Throughout this investigation N. and C. tested the dispersion formula of Ketteler, $\frac{\mu_a^2-1}{\mu_b^2-1}$, in which *a* and *b* represent rays of different wave-length, and found that it gave very uniform results; but from a physico-chemical point of view they do not regard this fact as an argument in favour of the formula.

Sulphuric acid. Van der Willigen published (*Ar. N.* 8) a long series of very careful determinations of the indices of refraction of mixtures of H_2SO_4 and H_2O, in various proportions for all the principal lines of the solar spectrum from A to H inclusive. These show a progressive increase in refraction and dispersion with every addition of H_2SO_4, until a maximum is reached at a point corresponding, apparently, with the monohydrate of the acid, after passing which the refraction and dispersion suddenly decline, while the density of the mixture continues to increase. Out of the seventeen series of determinations at different concentrations, the seven most conc. are given below, the central one of the series representing the nearest approach to the maximum. The indices are all reduced to a temperature of 18·3°. The specific gravity given in the line below is for 0°, water at the same temperature being taken as 1·0. In the cases of the two G's and the two H's, the higher one in each corresponds with the lines so designated by Fraunhofer.

μ	63·69 p.c. SO_3	71·97 p.c. SO_3	81·41 p.c. SO_3	85·93 p.c. SO_3	88·97 p.c. SO_3	91·43 p.c. SO_3	04·72 p.c. SO_3
A	1·40819	1·41930	1·43049	1·43279	1·43151	1·42918	1·42683
a	1·40928	1·42042	1·43168	1·43385	1·43270	1·43035	1·42781
B	1·41016	1·42133	1·43263	1·43476	1·43357	1·43114	1·42868
C	1·41112	1·42227	1·43360	1·43579	1·43444	1·43198	1·42944
D	1·41342	1·42466	1·43596	1·43807	1·43669	1·43426	1·43163
E	1·41618	1·42740	1·43877	1·44081	1·43944	1·43701	1·43431
b	1·41669	1·42793	1·43928	1·44130	1·43996	1·43749	1·43484
F	1·41838	1·42967	1·44103	1·44311	1·44168	1·43922	1·43649
G	1·42058	1·43186	1·44327	1·44534	1·44392	1·44144	1·43869
G	1·42233	1·43364	1·44507	1·44706	1·44569	1·44316	1·44037
H	1·42421	1·43561	1·44703	1·44901	1·44759	1·44512	1·44229
H	1·42567	1·43696	1·44841	1·45040	1·44883	1·44640	1·44347
S.G.	1·55438	1·64925	1·76066	1·80676	1·83123	1·84485	1·84994

Van der Willigen pointed out that the formula $(100-p)\frac{n^2-1}{d}+p\frac{n'^2-1}{d'}=100\frac{n''^2-1}{d''}$ will not apply to mixtures of H_2SO_4 and water, where $100-p$ and p are the respective weights of the two mixed liquids, *n*, *n'*, and *n''* the indices of refraction, and *d*, *d'*, *d''* the densities of the two liquids and the mixture respectively. Dale and Gladstone had formerly stated that the same was the case in respect of their formula.

Nickel and iron carbonyls. Ludwig Mond has prepared $Ni(CO)_4$ and $Fe(CO)_5$, both liquids of a highly-refractive character. The former has been examined optically by Nasini (*Lincei, Rc.* 7, 411), and the latter by Gladstone. R_a for the nickel compound was found to be as high as 57·7, which, deducting 8·4 for the value of each CO, gives $R_a = 24·1$ for the metal itself, instead of about 10·0, as determined from the chloride, sulphate, and nitrate. This would seem to confirm the hypothesis that the refractive power varies with change of valency, increasing with the increased power of combination. In this compound the Ni is regarded by Mond a. Nasini as octovalent, and as justifying Mendeléeff in placing it in Group VIII. of his system of classification. Gladstone, on the other hand, is disposed to think that the metal in both compounds is, as usual, divalent, and that it is the

CO which has a greatly increased value. He obtained for $Fe(CO)_5$, $R_A = 67\cdot38$, $R_D = 69\cdot40$. These figures show not only a very high refraction, but also very great dispersive power.

Silver iodide, bromide, and chloride. Wernicke (*A.* 142, 560) measured the refraction and dispersion of light by these salts in two different ways: (1) by examining the light reflected from glass plates covered with a layer of these salts, by means of a spectroscope, and noting the position of the dark interference-bands; (2) by direct measurements of small prisms made of the fused salts. The portion of the spectrum observed ranged from the solar line C to G. The dispersion $\mu_G - \mu_D$ was about twenty-seven times that of water in the case of the iodide; that of the other two salts is much less, though considerably greater than that of flint glass. AgI seems capable of existing in two conditions: at temperatures above 138° it gives a short spectrum limited to the red, yellow, and green, while below that temperature it gives a spectrum twice as long, showing all the colours. W. believes that AgI is partly dissociated at the higher temperatures.

Bromine. Weegmann (*Diss.* Bonn, 1888) determined the refraction-equivalent of Br by Lorenz's, as well as by the older, formula, for both the hydrogen lines, α, and Cauchy's limit, from a series of ethylene and acetylene compounds, adopting Brühl's values for C, H, and the ethylene linking. The following are his figures for Br compared with those arrived at by Brühl:—

Bromine	R_∞	R_a	R_∞	R_a
Weegmann .	14·78	15·38	8·56	8·83
Brühl . .	14·81	15·39	8·70	8·95

Fluorine. The writer of this article has collated the observations made by various observers on bodies containing F in order to arrive at the refraction-equivalent of this element (*P. M.* 1885. 481). Those of Brewster on cryolite, of Brewster, Wollaston, Fizeau, Stefan, and Kohlrausch on fluorspar, and of Gladstone on aqueous solutions of KF, give a refraction-equivalent for F varying from 0·29 to 0·32. Those of Topsöe and Christiansen on crystalline silicofluorides of Cu, Ni, Zn, Mg, and Mn, of the formula $RSiF_6.6H_2O$, give a refraction-equivalent for F varying from 0·62 to 0·84; while $(NH_4)_2SiF_6$ gives 0·59 for F. The latter figures must be accepted with caution, as a very slight difference in the values ascribed to the other elements will account for the whole of the discrepancy. It is evident, however, that in any case the refraction-equivalent is of exceedingly small amount, and that the specific refraction, even if the highest value be taken, can scarcely be the half of that of any other element known.

J. H. and G. Gladstone (*P. M.* 1891. 1) have investigated the optical properties of fluorbenzene and allied compounds. The molecular refraction for C_6H_5F, for six lines of the solar spectrum, is given in the following table; from this is deducted the value for benzene less one atom of H, leaving a small balance as the atomic refraction of fluorine.

These figures are remarkable as giving a negative value for the dispersion $R_H - R_A$, namely the quantity, −0·28. According to Lorenz's formula $R'_A = 0\cdot92$ and $R'_H = 0\cdot84$, showing in like manner a negative dispersion. The observations of Baille, Stefan, and Sarasin on fluorspar, and those of the authors on solutions of KF and NH_4F, all distinctly confirm the foregoing evidence as to the anomalous dispersion; while a comparison of the refraction of the three lines C, D, and F of the solid silicofluorides measured by Topsöe and Christiansen, and the author's observations on aqueous solutions of H_2SiF_6, seem to point in the same direction.

	R_A	R_C	R_D	R_F	R_G	R_H
C_6H_5F	42·92	43·33	43·70	44·68	45·61	46·40
C_6H_5	42·29	42·70	43·17	44·20	45·17	46·05
F	0·63	0·63	0·53	0·48	0·44	0·35

Liquefied gases. Bleekrode (*Pr.* 37, 339) adopted a special apparatus for measuring the indices of refraction of liquefied gases, consisting of a modification of a Faraday tube, forming a vessel having two parallel side plates, free from leakage even at high pressures. By observing, through a microscope provided with a graduated scale and a micrometer screw, test objects, such as lepidoptera scales, attached to the inner surface of the glass plates of the cell, the variation in the focus between the direct observation and that through the cell and liquid was found, and, with a correction for the effect of the glass, he obtained the data from which to calculate the index of refraction according to the equation $\frac{D}{D-d} = \mu$, in which D represents the thickness of the layer of liquid and *d* the apparent displacement of the test object. The observations were taken both with a sodium flame and with daylight, and the calculated probable error of the result amounted to ± 0·003. The first table on p. 238 gives the results of B.'s observations compared with those of Dulong, Ketteler, Croullebois, and Lorenz on the same substances in the gaseous state; the specific refraction is calculated by both the formulæ in common use.

B. drew attention to the remarkably low S.G. of ethylene, as the lightest fluid substance known; his determinations gave 0·335 at -8°, 0·361 at 6°, and 0·386 at 3°. B. also gave determinations of the indices of refraction of the following substances taken by the same process; and commented on the high indices of the organo-metallic compounds as inconsistent with the opinion expressed by early observers that a high index of refraction is indicative of a body being combustible.

Substance	Temp.	μ_D
Hydrobromic acid . .	10°	1·325
Do. . .	15°	1·330
Hydriodic acid . . .	16·5°	1·466
Bromine	13°	1·571
Methylamine . . .	17·5°	1·342
Dimethylamine . . .	17°	1·350
Trimethylamine. . .	16°	1·353
Zinc ethyl	12·5°	1·485
Zinc methyl . . .	14°	1·474
Aluminium ethyl . .	6·5°	1·480
Aluminium methyl . .	12°	1·432

Substance	Liquid		$\frac{\mu-1}{d}$		$\frac{\mu^2-1}{\mu^2+2}\times\frac{1}{d}$	
	S.G.	μ_D	Liquid	Gas	Liquid	Gas
Sulphurous anhydride	1·359	1·351	0·252	0·236	0·153	0·157
Cyanogen	0·866	1·327	0·378	0·350	0·234	0·233
Hydrocyanic acid	0·697	1·264	0·379	0·368	0·238	0·246
Nitrous oxide	0·870	1·204	0·235	0·255	0·150	0·170
Carbonic anhydride	0·863	1·196	0·227	0·221	0·145	0·147
Hydrochloric acid	0·854	1·257	0·300	0·277	0·190	0·185
Chlorine	1·33	1·367	0·270	0·240	0·169	0·160
Ammonia	0·616	1·325	0·528	0·490	0·327	0·327
Ethylene	0·361	1·180	0·498	0·526	0·321	0·350
Hydrogen phosphide	0·622	1·323	0·519	0·500	0·322	0·333
Hydrogen sulphide	0·91	1·390	0·429	0·413	0·262	0·275

Liveing and Dewar (*P. M.* 1892. 205) have determined the refractions of three liquefied gases, at their respective boiling-points, by direct observation through a hollow prism. They obtained the following results for the sodium line D:—

	μ_D	R_D	R_D
Oxygen	1·2236	3·182	2·024
Nitrous oxide	1·3345	11·587	7·163
Ethylene	1·3632	17·556	10·752

Alums. The indices of refraction of some of the alums have been measured by several observers, amongst them Grailich, Fock, Kohlrausch, Stefan, Topsöe, and Christiansen. The most complete series of observations on inorganic sulphuric alums is that of Soret (*Ar. Sc. Genève*, 12, 553; 14, 96; 20, 517), including those containing Rb, Cs, In and Ga. His mode of determination was by total reflection, which he considered the best adapted for the purpose; he gave indices which he calculated to be correct to two units in the fourth place of decimals. His observations were given for eight rays of the solar spectrum, viz. the lines *a*, B, C, D, E, *b*, F, and G. He remarked on the very low value of the index of refraction of the Na—Al alum. He gave the following comparative table for μ_D, showing that the different series of alums vary in general with much regularity. The horizontal lines contain the same metal, and the vertical lines the same metal or alkaline radicle.

	NH_4	K	Rb	Cs	Tl
Aluminium	1·4594	1·4564	1·4566	1·4586	1·4975
Indium	1·4664	—	1·4638	1·4652	—
Gallium	1·4683	1·4653	1·4658	1·4649	1·5066
Chromium	1·4842	1·4814	1·4815	1·4810	1·5228
Iron	1·4848	1·4817	1·4823	1·4838	1·5236

Calculating for each salt the difference between its μ_D and that of the ammoniacal alum on the same horizontal line, Soret obtained:—

	NH_4–K.	NH_4–Rb	NH_4–Cs	NH_4–Tl
Aluminium	+0·0030	+0·0028	+0·0008	−0·0381
Indium	—	0·0026	0·0012	—
Gallium	0·0030	0·0025	0·0034	0·0383
Chromium	0·0028	0·0027	0·0032	0·0386
Iron	0·0031	0·0025	0·0010	0·0388

These figures show a close accord, except in the case of Cs, in which the Ga and Cr compounds appear to be too low. Soret did not consider that the impurity in the specimens, if any existed, could be due to the Cs.

Gladstone (*P. M.* 1885. 162) worked out the refraction-equivalents from the data given in the first named of Soret's papers, and also from those by Topsöe and Christiansen, in order to test his former conclusions that a salt has the same specific refraction whether it is in a solid form or in solution, and that the refraction-equivalent of a compound body is the sum of the refraction-equivalents of its constituents. As to the first point, in the case of the two alums given below he found the specific refractions, after deducting the amount due to the solvent, to be in substantial accord:—

	Dissolved	Crystallised
Ammonium-aluminium alum	0·2780	0·2784
Sodium-aluminium alum	0·2613	0·2604

To test the second point, the alums were regarded as compounds of the sulphates of two metals of different kinds with twenty-four molecules of water. Taking the R_A of water in the uncombined state at 5·926—and taking the observations of Kanonnikoff, Topsöe, and Christiansen, as well as his own, of the several sulphates—Gladstone arrived at the results given in the following table. The other observers did not take the A line, but their observations have been reduced to A for purposes of comparison. The agreement between the calculated and observed refraction-equivalents is as near as might be expected, except in the case of Cs.

Substance	R_A calculated	R_A observed and reduced	
		Soret	Topsöe and Christiansen
Ammonium-aluminium alum	252·0	252·2	—
Sodium " "	239·3	238·5	—
Methylamine " "	267·2	267·7	—
Potassium " "	245·1	246·8	—
Rubidium " "	254·0	253·7	—
Caesium " "	268·0	262·3	—
Ammonium-chromium alum	264·0	265·9	—
Potassium " "	257·1	261·2	—
Rubidium " "	266·0	266·7	—
Caesium " "	280·0	275·5	—
Ammonium-iron alum	270·6	269·1	268·6
Potassium " "	263·7	265·0	261·4
Rubidium " "	272·6	273·2	—
Caesium " "	286·6	276·0	—

Gladstone also sought, by means of Soret's observations, to determine the refraction-equivalents of In and Ga, and (*B. A.* 1892) he gave the following constants:—

	At. W.	R_A
Indium . . .	113·4	13·7
Gallium . . .	69·9	11·6

These figures, however, can only be looked upon as approximate, as all experimental errors are accumulated on these residual numbers.

Perrot (*Ar. Sc. Genève*, 1880) has made a series of observations on the refraction and dispersion of an isomorphous series of biaxial crystals—the double sulphates of Zn with K_2, Rb_2, $(NH_4)_2$, Cs_2, K_2, and of Mg with Rb_2, and in each case $6H_2O$. He has followed the plan adopted by Soret in his observations on the alums. The results conform satisfactorily to the values computed on the same principle as that adopted by Gladstone with respect to the alums, except in the case of cæsium and rubidium, in both of which, especially the former, the observed values are lower than the theoretical. The mean ray adopted for this calculation is, however, the arithmetical mean of the three indices observed for each of the lines of the spectrum, and has, therefore, no real physical significance. A glance at the tables of observations will show at once what a wide scope for error there is in arriving at a mean value by this process.

Analogy between refraction and dispersion and magnetic rotation. Gladstone and Perkin have recently observed an analogy between the magnetic rotation and the refraction and dispersion of light. They have tested this in the case of organic compounds containing nitrogen (*C. J.* 55, 750), with the result that they have found a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance. These three properties are really comparable with one another, for in each case the observed value is divided by the density of the substance, and it is determined, not for equal weights, but for an equal number of molecules. It has been found that each property is determined in the first instance by the atomic composition of the substance, so that it may be laid down as a primary law that the molecular magnetic rotation, like the molecular refraction or dispersion, of a compound is the sum of the molecular magnetic rotation, refraction, or dispersion of its constituents. The values are, however, subject to large modifications dependent upon differences in the structures of the compounds. Thus a change of valency is attended by a marked change of value in these optical properties, and they are apparently affected by some circumstances which are not as yet recognised in structural formulæ.

The following values have been deduced by Perkin for the molecular magnetic rotations of certain elements in the paraffin group of carbon compounds; and against them are placed the recognised values for their molecular refraction and dispersion:—

	Molecular magnetic rotation	R_A	R_{H-A}
CH_2 . .	1·023	7·6	0·34
C . . .	0·515	5·0	0·26
H . . .	0·254	1·3	0·04
O, alcoholic .	0·194	2·8	0·10
O, aldehydic .	0·261	3·4	0·18
Cl . .	1·733	9·9	0·50
Br . .	3·562	15·3	1·22
I . . .	7·757	24·5	2·62
N, in amines	0·717	5·1	0·38

These figures show a certain analogy; and when modifications are introduced by changes in the mode of combination, the change that occurs in the one property is noticeable also in the other two, and that in the same direction, though not necessarily to the same extent. Thus there are in all cases two different values for oxygen in alcohol and aldehydes, and a very great increase of the values in the case of unsaturated carbon compounds. The values also of CH_2 in the first and second members of homologous series (such as the alcohols, paraffinoid acids, &c.) are different from its value in the higher members of the same series, and always in the same direction.

P. also applied the same inquiry to solutions of HCl, HBr, and HI, which when dissolved in water were known to give higher values for refraction and dispersion than the normal. The same was found to be the case in the magnetic rotations. When HCl was dissolved in isoamyloxide, however, all three values were found closely approximating to the normal, as will be seen in the following table:—

Hydrochloric acid	Molecular magnetic rotation	R_A	R_{H-A}
In water . .	4·412	14·45	1·12
„ isoamyloxide .	2·238	11·36	0·51
By calculation for free acid . .	2·187	11·20	0·54

It is, therefore, laid down as generally, if not always, true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The investigation seems to indicate another close relationship between electro-magnetism and the velocity of light. G. G.

OPTICAL METHODS.—Section 2: SPECTROSCOPIC METHODS.

Historical notes.—Spectrum analysis is an optical method of making a diagnosis of the chemical composition, and in certain cases the chemical constitution, of either (*a*) a self-luminous body, or (*b*) an absorbing medium, whether self-luminous or not. Newton first discovered that light could be analysed when passed through a prism, and, in 1752, Thomas Melvill made an optical analysis of alcohol flames coloured with salt and with nitre. Wollaston, in 1802, observed with the prism certain obscure bands in the solar light which had traversed a narrow slit in his window shutter. Fraunhofer, in 1814–15, was the first to employ a very narrow and accurately-formed aperture with a prism, telescope, and divided circles, and he not only observed the dark lines in the solar spectrum, but measured their indices of refraction or refrangibilities. He examined, subsequently, the spectra of the stars, of electric light, and of the exterior envelope of the flame of a wax candle. The latter spectrum he discovered to consist of homogeneous yellow light, composed of two distinct rays very close together, and coincident with the two dark lines in the solar light which he had termed D. Brewster noted the presence of this yellow light in the combustion of many substances, but it was Fox Talbot who, in 1826, clearly proved that the source of this light was sodium. He likewise connected a red ray with the presence of potassium and an orange ray with strontium, and concluded that *a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect.* Herschel had previously described the spectra of a few of the metals and of boracic acid. In 1834 Fox Talbot described the strontia and lithia spectra, and stated that optical analysis could distinguish the most minute portions of these two substances with as much, if not greater, certainty than was afforded by any other known method.

Wheatstone, nearly at the same time, published some experiments similar to those of Fox Talbot, and Swan first estimated the amount of sodium which can produce the D lines. At the Manchester meeting of the British Association in 1842, Brewster read a paper *On Luminous Lines in Certain Flames corresponding to the defective Lines in the Sun's Light.* He discovered the dark lines of absorption in nitrogen peroxide gas when white light is directed through it, and he observed and mapped a number of atmospheric lines in the solar spectrum. In 1849 Foucault obtained a reversal of the D lines in the electric arc. Stokes, about 1850, gave in his lectures the true explanation of the coincidence of sodium lines with the dark lines D. Ångström in 1853 stated that an incandescent gas emits luminous rays of the same refrangibility as those which it absorbs, and Balfour Stewart, 1858–9, based the following statement on experimental data: *The radiating power of a body for any ray is equal to its absorbing power for the same ray.*

In 1859, Kirchhoff and Bunsen gave a great impetus to spectrum analysis by publishing their researches on the constitution of the sun, and also by designing an extremely simple spectroscope and describing its use. Chemists were further made aware of the new power placed in their hands by Bunsen's discovery of two new metals, rubidium and cæsium, in 1860, by the discovery of thallium by Crookes and by Lamy in 1862, of indium by Reich and Richter in 1863, and of gallium by Lecocq de Boisbaudran in 1875.

Fundamental laws. Spectrum analysis primarily depends on the following two laws:— 1. Every *solid* and *liquid* when heated begins by emitting rays of longest wave-length, which are the result of comparatively slow vibrations, but as the temperature rises the vibrations become more rapid, and shorter waves are emitted, so that at the highest temperatures the sum of the radiations is white light, consisting of waves of all possible lengths, the effect of which is a continuous spectrum. A mass of iron gradually raised to its melting-point would be an example of this. 2. Every *substance vapourised* by heat emits rays of definite wave-lengths, and these rays are characteristic of each substance, because it alone can emit them. In other words, every substance vapourised by heat has its own definite periods of vibration, by which it can be absolutely identified, because no other substance can vibrate in the same manner and with the same periods. All flame and spark spectra furnish examples. From this second law it follows that the spectrum of an element is a constant of very great importance. The determinations of the spectra and of the atomic weights present similar difficulties, which arise from the necessity for obtaining the elements or their compounds in the highest possible degree of purity, and also in many cases from the complexity of the spectra, and the careful observations which are necessary in identifying and measuring the wave-lengths of the rays.

Determinations of the *absolute wave lengths* of the bright lines in any spectrum are now usually made either with a plane or a concave diffraction grating ruled on speculum metal. When a sufficient number of accurately-measured lines is known for any region of the spectrum, determinations of the wave-lengths of lines in new spectra may be made by observing with a prism-spectroscope, and by the use of an interpolation curve the wave-lengths corresponding to the positions of the lines measured may be found. From time to time the curve will require verifying and correcting.

There are two classes of spectra, *emission* and *absorption* spectra.

Emission spectra consist of: (1) *Continuous spectra* and (2) *Interrupted spectra.* 1. *Continuous spectra* are characteristic of most incandescent solids, liquids, and gases at great pressures, or of a cloud consisting of solid glowing particles. 2. *Interrupted spectra* consist of: (*a*) Bands of light or 'fluted band' spectra, characteristic of certain vapours, especially the vapours of compound substances rendered glowing at comparatively low temperatures; (*b*) bright line spectra, characteristic chiefly of transparent vapours at high temperatures or at low pressures; (*c*) reversed line spectra, which are dark lines seen on a brilliantly-illuminated ground. When a bright line spectrum is observed in front of a more brilliant continuous spectrum, the lines appear dark on a bright ground of colour, instead of bright and coloured on a dark ground, and they are then said to be reversed.

Absorption spectra. When rays capable of giving a continuous spectrum are made to traverse (*a*) transparent solids, (*b*) transparent liquids, (*c*) transparent gases at ordinary temperatures, it is frequently observed that a definite band of rays is absorbed at either end of the spectrum. This is called *a continuous absorption.* Quite as frequently a band of rays is cut out of the middle of the spectrum; this is called a *selective absorption*, and the region of the rays absorbed is said to be occupied by an absorption band.

The production of emission spectra. Emission spectra may be produced in the following ways (*a*) By flames of low temperature, *e.g.* by a spirit lamp or Bunsen burner, acting on solids, or the spray of solutions. The flame may be fed with chlorine, bromine, or iodine, or with hydrochloric acid when salts of the halogens are examined. (*b*) By flames of high temperature: blow-pipe, and oxyhydrogen flame. (*c*) By sparks in vacuum tubes containing residual gases or vapours. (*d*) By sparks of low tension acting on solids or solutions. (*e*) By sparks of high tension. (*f*) By solids in the electric arc. (*g*) By electric discharge on solids *in vacuo*; these are phosphorescence spectra.

As a rule, *line spectra* are the spectra of elements, *band spectra* are the spectra of compounds.

Salts of the alkali metals in the Bunsen flame emit line spectra characteristic of the metals, while the alkaline earth salts emit lines and bands which are characteristic of the metallic oxides. On the other hand, the burning of hydrogen and of hydrogen compounds causes the emission of more than 160 lines in the ultra-violet region, which can only be assigned to the vapour of water at a high temperature. Carbon is an element which emits bands in the coloured region, in hydrocarbon flames. A list of compounds which emit characteristic banded flame-spectra is given on p. 246. Erbia and erbium phosphate emit luminous bands when the solid substances are heated in a Bunsen or blow-pipe flame. Discharges in vacuum tubes sometimes emit a continuous spectrum; oxygen does so at the lowest temperature at which it is luminous. Most gases emit a banded spectrum with low tension sparks at ordinary pressures; the spectrum alters with diminution of pressure until finally nothing but a line spectrum is visible—for example, this is the case with air in the ultra-violet region. Sparks of low tension from solids, such as metallic electrodes, and from solutions, emit lines chiefly in the visible region, while those of high tension are generally richest in radiations of high refrangibility, chiefly in the ultra-violet region.

Low-tension sparks may be produced in two ways from solutions, first by wires of platinum moistened by the liquid, secondly by pieces of charcoal giving the flaming spark used by Bunsen. Many elements have been shown to emit a few bands or lines in the infra-red. The difference in action of high- and low- tension sparks is chiefly, if not entirely, due to temperature; the highest temperatures cause the emission of rays of the highest refrangibility. Solid elements, with few exceptions, yield spectra in the electric arc. The lines exhibited by some of the metals are exceedingly numerous. Reversed line spectra are common in the sun, and afford evidence of the presence of metals whose bright line spectra are coincident therewith. The number of bright lines seen reversed in the sun's spectrum indicates the strength of the evidence of the existence in the sun of certain elements.

As to the distribution of known kinds of matter in space, the following list shows the elements observed in the sun with the numbers of their reversed lines seen in the solar spectrum: Fe 730, Ti 230, Ca 94, Mn 85, Ni 102, Co 91, Cr 71, Ba 26, Na 11, Mg 17, Cu 7, H 5, Pd 5, V 4, Mo 4, Sr 4, Pb 3, U 3, Al 18, Ce 2, Cd 2, Be 2, Sn 1.

Methods of spectrum analysis. For efficient work with the spectroscope an instrument is to be preferred which admits plenty of light, has a rigid collimator, and immovable prism. Compound prisms of Grubb's and of Thollon's construction are among the best. The arc should be divided on the vertical edge of the prism-table or on an edge inclined at an angle of 45°. A vernier travelling over the arc and a mounted lens, for convenience in reading the scale and vernier, should be fitted near the telescope. A beautiful instrument made by the *Société Génevoise pour la Construction des Instruments de Physique* has a circle completely divided, and fittings for investigating ultra-violet spectra, either by photography or with a fluorescent eye-piece of Soret's design. It is provided with two verniers, and an automatic arrangement admitting of the prism being placed at the minimum angle of deviation for each ray under examination. This is necessary in order to secure the best definition. The instrument, of whatever form, should be capable of dividing and measuring the lines D^1 and D^2 of sodium, the first, second, and third lines of the yellow band; and in the carbon spectrum the first, second, third, and fourth lines of the green band, and the first, second, and third lines of the blue band, which are seen in the green inner cone of a powerful Bunsen burner. An instrument with a photographic scale, if it is sufficiently delicate, which is seldom the case, is of great use. One of these, constructed by Duboscq, was employed by Lecocq de Boisbaudran. A lens of short focus should be used to concentrate the light, from whatever source, upon the slit of the instrument. A test tube about 12 mm. diam., supported vertically, if filled with water and placed close to the slit of the instrument, answers this purpose. The telescope should be capable of easy movement without vibration, and be supported for two-thirds of its length from the object glass; neither clamping nor the use of the focussing screw should be capable of displacing its position. The rays should pass straight down the collimator and completely fill the lens. Before commencing any serious work, the capabilities of the instrument and its use for obtaining measurements should be carefully studied.

Supports of platinum wire fused into glass tubes are used for examining concentrated solutions and fused beads of salts in ordinary flames. Bunsen burners with steatite tops are particularly useful. Blow-pipe flames with a vertical direction, urged by bellows worked by the foot, are useful for examining the alkaline earths. Hydrogen gas from a constant generator made of lead and of large size is better than coal-gas for all flame spectra. Whether coal-gas or hydrogen be used, it is advantageous in examining salts of the alkaline earths, particularly chlorides, to pass the gas through a litre of strongest hydrochloric acid into a Bunsen burner, which is made of hard glass tube tipped with platinum. The flame is thus supplied with hydrochloric acid, and the chlorides are volatilised apparently without decomposition, so that they emit rays of great brilliancy which yield simple line spectra. For high temperatures a very small gas blowpipe may be supplied with oxygen. In this case the supports of platinum would be fused, and it has therefore been found convenient to use a wire of iridium, twisted into a loop, the compound being placed in the loop. In this manner manganese dioxide yields the bands of the dioxide, the spectrum of which is observed in the Bessemer flame. Calcium fluoride and copper oxide readily yield characteristic spectra. The alkaline earths yield very brilliant spectra, which are due to the metallic oxide in each case. When volatile substances, such as salts of lithium and the other alkalis, are under observation, it frequently happens that a difficulty in measuring their lines occurs owing to the evanescent appearance of their spectra; more lasting spectra may be produced by converting the volatile salts into silicates or borates by heating in a platinum spoon, or even in a porcelain crucible, with crystals of boracic acid. Beads of the borates will continue to illumine a flame for a lengthened period; with lithium and thallium, measurements have been made for as long as twenty minutes without renewing the material. Should the alkalis be accompanied by lime, strontia, or baryta, the spectra of these earths are suppressed, but towards the end of the observation sometimes the green colour of boric oxide appears. Sparks, both of low and high tension, may be used with Delachanel and Mermet's fulgurator. This instrument has the advantage of using very little solution, and losing none. Some solutions, such as salts of yttria, do not yield their characteristic spectrum to low-tension sparks, and it is necessary to strengthen the current by interposing a Leyden jar in the circuit, or, what is better, a pane of glass coated on either side with 930 square centims. of tinfoil. The spark should be 3 to 6 mm. in length. The lines of platinum, hydrogen, sodium, and a few of chlorine are visible, but these are known and are measurable. When the solution becomes contaminated with platinum, it may be removed and purified to be used over again if necessary. For such work it is best to use a coil which can yield sparks 170–180 mm. long in air.

For observations on ultra-violet spectra the arrangements described by Soret and by Cornu consist of an optical train of quartz and a prism of 60°, which is composed of two halves each of 30°; one of the two lenses and one half of the prism are cut from a right-handed crystal, the other corresponding parts from a left-handed crystal, so that the double refraction of one is corrected by that of the other. One half of the prism may be fixed on the collimator close to the lens, the other in front of the object-glass. For ordinary observations a fluorescent eye-piece is necessary, but generally photography is more convenient. Cornu has used lenses achromatised with colourless fluorspar, but this is not necessary, because the peculiarity of the camera employed by Hartley enables whole spectra to be accurately focussed on one plate if only one prism of 60 degrees be used. The camera back is sloped at an angle of about 22° to the normal, which brings one end of the plate nearest to the rays of shortest wave-length, and the locus of the foci of all the rays, from the least to the most refrangible, lies upon the plate. There is thus a saving of time in the observation of complicated spectra, with the additional advantage that angular measurements are abolished and linear measurements substituted. Moreover, an increased dispersion and separation of the rays is obtained. This arrangement is most suitable for use with two half-prisms of quartz of 30°. Six hundred lines in the spectrum of iron have thus been photographed with such excellent definition that a magnifying power of 25 diameters was used in their measurement. A quartz lens 75 mm. in diameter and of 75 mm. focus is placed in front of the slit. The camera back is so constructed that by a rack and pinion motion a succession of twelve or fifteen spectra may be taken on one plate. The lenses, which are not achromatised, are of 425 mm. focus for yellow light, and 50 mm. in diameter, the prisms being of corresponding dimensions.

Sparks of high tension obtained in the manner already described are necessary. They may be passed between metallic electrodes 3 to 6 mm. apart.

For photographing spectra yielded by solutions electrodes of graphite are used, or wicks of fine wire drawn from pure gold. The solution is placed in a small J tube; in the shorter limb the electrode is placed, and a platinum wire passes down the longer limb to make connection with the coil. By means of a pipette the tube is easily charged. The graphite electrodes are cut from good sound pieces of Ceylon or Siberian graphite, and are chisel-shaped, with grooves scored along them with the point of a pin. The opposite electrode may be of graphite or of any suitable metal. In order that the strongest discharges may pass from below upwards the lower should be the negative electrode. The admirable work of Lecocq de Boisbaudran on flame and spark spectra (*Spectres Lumineux*, 1874) not only gives the practical details, but maps of prismatic spectra, and the same applied to a scale of wave-lengths, as well as a complete description of the spectra and a description of each line. The publication proves to be all that a guide to the use of the spectroscope should be, but it deals only with the visible region. In photographing spark spectra the trouble of making drawings is unnecessary, since the photographs themselves are better than any reproduction; all that is required is a description and a map of the principal lines on the scale of wave-lengths. In photographing the spectra of solutions by means of graphite electrodes it is, of course, necessary to ascertain that the material does not yield any of the numerous lines in the spectrum of iron, generally speaking four lines of magnesium with wave-lengths 2801·1 to 2789·6 are visible. Although photography has been applied almost exclusively to the ultra-violet rays and to the infra-red, there is no reason why it should not be used for visible rays, since gelatin plates stained with cyanine, eosine, erythrosine, and some other dyes, render the plates sensitive to the orange, red, and yellow rays. Cyanine is a dye which is sensitive to most of the spectrum as far as the rays of very long wave-lengths.

On the sensitiveness of emission spectra. The following table gives the sensitiveness of the emission spectra of various elements in fractions of a milligram. It will be observed that radiations in different regions, and excited by different means, greatly vary in emissive power even with the same element.

Visible flame spectra.

	Mgr.		
Ba	$\frac{1}{2,000}$	Kirchhoff a. Bunsen	
Ca	$\frac{1}{50,000}$	"	"
Cs	$\frac{1}{25,000}$	"	"
Cu	$\frac{1}{285}$	Simmler	
In	$\frac{1}{2,000}$	Cappel	
Li	$\frac{1}{600,000}$	Kirchhoff a. Bunsen	
Mn	$\frac{1}{83}$	Simmler	
K	$\frac{1}{3,000}$	Kirchhoff a. Bunsen	
Rb	$\frac{1}{7,000}$	"	"
Na	$\frac{1}{14,000,000}$	"	"
Sr	$\frac{1}{30,000}$	"	"
Tl	$\frac{1}{50,000}$	Lamy	

Visible spark spectra (Cappel).

	Mgr.		Mgr.
Ba	$\frac{1}{900,000}$	Li	$\frac{1}{40,000,000}$
Bi	$\frac{1}{70,000}$	Mg	$\frac{1}{500,000}$
Cd	$\frac{1}{18,000}$	Mn	$\frac{1}{200,000}$
Ca	$\frac{1}{10,000,000}$	Hg	$\frac{1}{10,000}$
Cr	$\frac{1}{4,000,000}$	Ni	$\frac{1}{600}$
Cs	$\frac{1}{4,000}$	K	$\frac{1}{400}$
Cu	$\frac{1}{20,000}$	Rb	$\frac{1}{1,000}$
Co	$\frac{1}{15,000}$	Sr	$\frac{1}{100,000,000}$
Au	$\frac{1}{4,000}$	Tl	$\frac{1}{80,000,000}$
In	$\frac{1}{90,000}$	Sn	$\frac{1}{17,000}$
Fe	$\frac{1}{26,000}$	Zn	$\frac{1}{600,000}$
Pb	$\frac{1}{20,000}$		

Photographed ultra-violet spark spectra (Hartley).

	Mgr.
Mg	$\frac{1}{100,000,000}$

On ultra-violet spectra. The conditions necessary in photographing ultra-violet spectra, are: 1st, a sensitive salt exerting an equality of action throughout the whole range of the spectrum; 2nd, a perfectly diactinic vehicle to hold the salt; 3rd, a process of development which will not exert a preferential action on any portion of the spectrum. These conditions are fulfilled by the use of silver bromide emulsion, the gelatin being of the purest description, and the image being developed by pyrogallol, hydroquinol, or hydroxylamine hydrochloride and caustic soda. The new developer eikonogen is suitable. Ferrous oxalate, as usually employed, is not to be recommended, because strong lines become developed much more strongly than weak lines. The exposure varies slightly with the sensitive nature of the plates, the width of the slit, the conducting power of the electrodes, the emissive power of the rays to be observed, and lastly with the excellence of the developer. Having once ascertained by comparative exposures how to obtain the best effect, there is very seldom any necessity for altering the exposure.

The following facts have been established regarding ultra-violet spark spectra: 1. When carbon or metallic electrodes, which emit short lines, are moistened or partially immersed in water, the short lines are lengthened. 2. The impurities in a metal, or the minute constituents of an alloy, generally appear as spectra composed of short lines. When both electrodes are of the same material, the impurities in minute proportion *appear at the negative pole only*, but when the proportion of the impurity or alloy is increased, the long lines are seen as short lines at both poles; a further increase in proportion brings them out as long lines. 3. Of the non-metallic elements, boron, carbon, and silicon exhibit line spectra. The line spectra of the elements are seen in spectra of borates and silicates, and in boracic and hydrofluosilicic acids. 4. The spectra of carbon and silicon may nearly always be detected in photographs taken from electrodes of metallic iron. 5. Insoluble compounds which are not volatile, such as ferrous sulphide, ferric oxide, and ferrous phosphate, do not yield spark spectra. Insoluble, though somewhat volatile, compounds, such as thallium chloride, yield a feeble spectrum of metallic lines. 6. With the exception of boron and silicon, the non metallic constituents of a salt do not affect the spark spectra of solutions. 7. The spectrum of a metallic chloride, nitrate, or sulphate yields spectral lines identical in number and position with the principal lines of the metal itself. Some of the short lines become long lines, but whether the spectra are produced by metallic electrodes or solutions their character is identical. 8. The effect of diluting solutions of metallic salts is first to weaken and attenuate the metallic lines, then, with a more extensive dilution, to shorten them, the length of the longest and strongest lines generally decreasing until they finally disappear. There are two lines in the spectrum of copper which disappear by attenuation only, and a similar pair of lines in the spectrum of silver behaves in like manner. Both pairs of lines have been observed as short lines in alloys containing very small quantities of these metals. 9. Accidental differences in the passage of the spark, or in the time of exposure of the photographic plate, when the normal period varies from half-a-minute to five minutes, do not cause sensible variations in spectra obtained from the same substances, under any ordinary circumstances. 10. Spectra of metallic electrodes and of solutions are liable to contain the lines of calcium, with wave-lengths

2967·3 and 3933, also occasionally those with wave-lengths 3736·5 and 3705·3. These calcium lines are due to dust when the electrodes are dry, and to impurity in the acids when solutions are prepared therewith and examined. 11. Five modified spectra have been observed in photographs taken from graphite electrodes, which apparently belong to no other element but carbon. The first and second were produced under identical circumstances, and were taken from dry points in air. The first contains 20 lines, the second only 12. The third was taken from wet electrodes in air, and consists of 20 lines, some of which are lengthened. The fourth was taken from dry electrodes in oxygen, and consists of 17 lines, some being much lengthened. The fifth was taken from dry electrodes in carbon dioxide, and consists of 18 lines, all much lengthened and strengthened (*T.* pt. i. 1884).

The examination of metals and alloys. When a metal is to be examined it may be filed, or hammered into electrodes of a convenient shape, and held between screw clips or between the points of cheap drawing pens. According to circumstances, both electrodes need not be of the same metal, but one may be of gold, platinum, or a tin-cadmium or lead-cadmium alloy containing in either case 20 p.c. of cadmium. Such an alloy gives convenient reference lines. If it be required to bring out the lines of the constituent of an alloy present in the metal in minute proportion, or present as an impurity in the metal, it is best to partially immerse the lower electrode in water contained in a small glass J tube, as if a solution were being photographed. Under these circumstances the short lines become much lengthened and consequently more prominent. The best form for electrodes is flat with curved edges, or even somewhat rounded discs, such as blow-pipe globules flattened.

The identification of lines in photographed spectra. When the spectrum of an alloy, metallic precipitate, or solution has been photographed, it is seldom easy to determine what substances are present or absent, partly on account of the complexity of the spectra and partly from the absence of colour. It is necessary in such cases to have recourse to one or both of the following methods of identification. (*a*) *Method of identifying the elements by lines photographed from a known specimen.* A series of photographs taken from metallic electrodes and from solutions should always be kept for reference. A substance may then be readily identified even when the wave-lengths of its lines are unknown, by superposing one photograph on the other, film to film, since there are but very few cases of actual coincidences of lines of similar character belonging to different elements. If this examination does not account for all the lines, it is necessary to proceed according to the next method. (*b*) *Method of identifying lines when comparison-spectra are not available.* By chemical processes of separation it is easy to ascertain what metals may be looked for. The wave-lengths of the unrecognised lines may then be ascertained by measurements and reference to an interpolation curve. The measurements need not be made with a micrometer unless great accuracy is required. It suffices generally to measure the spectra by means of an ivory scale with bevelled edges, the divisions on the scale being hundredths of an inch. With a strong magnifier we may read by judgment to tenths of a division or thousandths of an inch. The best form of magnifier is made like the compound eyepiece, of a microscope with cross hairs or fibres of cocoon silk in the field. The lens is placed very close to the surface of the scale and photograph, so that false readings caused by parallax are avoided. When all the lines in a photograph which have been recognised, or *vice versâ*, have been pricked off, the scale is very carefully adjusted so that it gives correct readings with lines of known wave-lengths at different parts of the spectrum, such for instance, with Nos. 9, 10, 11, 12, 17, and 25 of cadmium. In order to adjust the scale accurately, it is advisable to rule a line along the whole of the spectrum, which may be done when photographing by placing a wire at right angles to the slit, and one-third or one-fourth the length of the spark, above the lower electrode. The edge of the scale is applied to this line, and held in position by spring clips or screws. The scale numbers of the unrecognised lines are then read off, and by reference to the interpolation curve their oscillation-frequencies or their wave-lengths are obtained. From maps, or descriptions of spectra, accompanying a list of wave-lengths, the corresponding lines are selected and identified.

Descriptions of the spectra of the elements. Emission spectra. The spectra of non-metallic elements, particularly those which are gaseous, have been found to vary in character with the conditions under which they have been obtained. Thus N, O, C, Br, I, S, Se, Te, and P yield band spectra or line spectra, according to variations in temperature or pressure. The chlorides of B and Si likewise give line spectra due to B and Si; under certain conditions they emit spectra of their own. The fluted spectrum of carbon has given rise to great discussion. Swan, and later Ångström, attributed the bands to a hydrocarbon, so also did Morren, and Liveing a. Dewar, but they finally arrived at the conclusion first enunciated by Attfield, that the bands were caused by the element carbon. Van der Willingen, Plücker and Hittorf, Marshall Watts, Wüllner, Lockyer, and Fievez, have all adduced evidence of this. It appears, however, that a banded spectrum of cyanogen can be obtained which is distinct from that of carbon. Certain bands in the ultra-violet spark spectrum, which have been considered by Liveing and Dewar to be caused by cyanogen, have been observed by Hartley, and he is led to the conclusion that they are in reality carbon bands intensified by the presence of an atmosphere of nitrogen, but not cyanogen bands, for the reason that they cannot be obtained from various cyanogen compounds, such as soluble cyanides. They are always present when graphite electrodes are used in air, they are intensified when the electrodes are moistened, and they become particularly strong when concentrated solutions of chlorides, such as zinc chloride or calcium chloride, surround the electrodes; moreover, the strength of the bands increases with the strength of the solutions.

A review of the facts shows that large molecules give banded spectra, as is evident from the spectra of compounds, and various other considerations lead to the conclusion that the elements which give such are capable of existence in different molecular conditions, the most complex molecules emitting bands of rays, the simpler molecules emitting line spectra.

Hydrogen. When sparks are passed through hydrogen, four very well known lines appear. Huggins has observed the same in some stars, together with a remarkable series of lines in the ultra-violet, and it has been surmised that the whole series, visible and invisible, belong to the one element. Cornu has recently proved this to be the case. Fifteen lines in the visible and ultra-violet constitute the only true line spectrum of hydrogen.

The alkali metals, Li, Na, K, Rb, Cs. These metals are distinguished by the fact that most of their salts are decomposed in the flame, and the metal set free, or the metallic oxide formed from it, is sufficient to colour the flame intensely. The spectra are very simple, and all the principal lines are in the visible region. Their ultra-violet spark spectra are insignificant.

The alkaline earth metals, Ca, Sr, Ba. The spectra of these elements are obtainable by flames. When the chlorides are fused and heated in a flame supplied with hydrochloric acid, lines due to the metallic chlorides are visible. Without hydrochloric acid, the spectrum is at first a simple line spectrum, but subsequently bands, shown by Mitscherlich to be due to the oxides, take their place. Feeble sparks give line spectra with solutions of salts. In the ultra-violet, a series of well-marked groups of doublets and triplets is seen.

The magnesium group, Be, Mg, Zn, Cd. The element beryllium stands at the head of two families, that of the alkaline earths and the magnesium family. It occupies a position similar to that of lithium with regard to the alkali metals and the copper and silver family. Its spectrum is similar in many respects to that of lithium, being very simple and composed of isolated lines. There are two in the blue and five in the ultra-violet not visible in the flame, but obtainable by the action of condensed sparks. Magnesium and the compounds of the other metals of this group do not easily yield flame spectra, but give characteristic groups of lines when solutions are submitted to feeble or condensed sparks. In the ultra-violet these consist of well-marked groups of isolated lines, pairs, triplets, and groups of four and of five lines.

The aluminium elements, B, Al, Ga, In, Tl. Boron, which stands at the head of this group, gives a flame-spectrum only of its oxide, but the boron compounds, such as borates, emit three lines in the ultra-violet due to this element. Aluminium gives no flame spectrum, but gallium, indium, and thallium emit rays in the violet and green. Sparks taken from solutions of indium and thallium yield characteristic spectra in the ultra-violet consisting of many isolated lines and pairs of lines.

The tin elements, C, Sn, Ge, Pb. Carbon presents a very simple spectrum when condensed sparks are used; most of the lines are in the ultra-violet. It is a remarkable fact that under the same conditions the number of lines sometimes varies, and no satisfactory reason for this can be assigned. Four spectra of graphite have been mapped from photographs described as follows: 1. Dry electrodes in air. 2. Wet electrodes in air. 3. Dry electrodes in oxygen. 4. Dry electrodes in carbon dioxide. The strength and length of the lines vary under certain circumstances; in 1 the lines are all short, in 2 some lines are lengthened, in 3 some lines are much lengthened, and in 4 all the lines are lengthened and strengthened.

The spark spectra of tin, germanium, and lead contain numerous lines which are not characterised by any evident special grouping. The ultra-violet spectrum of germanium has yet to be photographed.

The group of rare earths, Ce, La, Di, Sm, Yt, Sc, Er, Tr. These elements give no flame spectra, and but weak spectra with feeble sparks. Ce, Di, Yt, Sm, Sc, Tr yield very complicated spectra to powerful sparks, the spectrum of cerium in the ultra-violet being remarkable for the immense crowd of lines. Yttrium and scandium chlorides give spectra composed of bands which are very characteristic in the visible region. Didymium, samarium, erbium, and thallium will be dealt with under the head of *Absorption spectra*. Lanthanum gives a large number of lines in the visible region, but very few in the ultra-violet.

The nitrogen elements, N, P, As, Sb, Bi, V. Nitrogen gives a large number of lines under the action of condensed sparks. The ultra-violet portion of the spectrum has been photographed. Nothing of the same kind is known of phosphorus. Phosphorus in a current of hydrogen gives a beautiful banded flame spectrum, especially when the flame is cooled. This reaction is exceedingly sensitive. The spectra of arsenic, antimony, and bismuth in the ultra-violet are very well marked, and they each contain a large number of lines, some of which are nebulous, others are mere dots, and there is a characteristic background of continuous rays. Vanadium yields spark spectra, with a large number of lines.

The chromium elements, Te, Cr, Mn. The line spectrum of tellurium obtained from the element is very complex, and by far the greater number of lines are in the ultra-violet; the character of the spectrum resembles those of arsenic, antimony, and bismuth. The chromium and manganese spectra are very complex and similar to those of the iron group.

The iron, nickel, and cobalt group. These metals present very complicated spectra when condensed sparks are employed in the visible, and more particularly the ultra-violet, regions. The grouping of the lines in the different spectra is similar.

The palladium, gold, and platinum group. These elements present complicated spectra, though less so than the foregoing. The strong lines of gold are few in number. These metals do not excel in emissive power. Feeble sparks with them give feeble spectra. Iridium gives a spectrum only with condensed sparks, which in the ultra-violet consists of a great crowd of lines.

The spectra of many elements, such as tungsten and uranium, have yet to be examined

thoroughly. It may here be remarked that elements usually associated by their natural occurrence, or by classification according to their chemical properties, exhibit spectra with characters in common.

A very important paper by Mitscherlich (*A.* 121, 459) first drew attention to the fact that a number of compounds emit distinct spectra, for the most part band spectra. A list of such compounds here follows, most of the spectra of which were originally described by Mitscherlich. Diacon also (*Thèses de Physique et de Chemie*, Montpelier, 1864), using a flame the interior of which was fed with chlorine, obtained distinct spectra of chlorides, such as those of the alkaline earths, gold, lead, iron, cobalt, and nickel; *the alkalis gave no spectra* excepting where they became converted into oxides or metal, as in the mantle of the flame.

Compounds emitting distinct spectra (Mitscherlich). *'Venetian-blind' or degraded band spectra. Flame.* BaO; $BiCl_3$, $BiBr_3$, BiI_3; B_2O_3; $CuCl_2$, $CuBr_2$, Cu_2I_2, CuO; $AuCl_3$; Fe_2O_3; MgO; MnO_2; $PbCl_2$, PbO; $MgCl_2$.

Plain band spectra. BaF_2, $BaCl_2$, $BaBr_2$; BiI_3; CaF_2, CaO; CuF_2; SrO.

Line spectra, or lines with bands. $BaCl_2$, $BaBr_2$, BaI_2; $CaCl_2$, $CaBr_2$, CaI_2; SrF_2, $SrCl_2$, $SrBr_2$, SrI_2.

Other observers have discovered and described specific spectra emitted by the following compounds:—Al_2O_3; feeble sparks (Wüllner and others). NH_3; flame (Dibbits). CO; spark (Plücker and others). CN; flame (Fox Talbot, Draper, Dibbits, and others). Er_2O_3 and $ErPO_4$; flame (Bunsen a. Bahr). MgO and hydride of Mg; flame and spark (Liveing a. Dewar). PH_3; flame cooled (Christofle a. Beilstein). $SiCl_4$, $SiBr_4$, SiI_4; spark (Plücker, also Salet). H_2O; flame (Liveing a. Dewar; Huggins).

Harmonic relations between the lines of a spectrum. The self-luminous nature of a molecule is connected with the vibrations of those parts of the molecule which are called atoms. The number of vibrations is indicated by the inverse wave-lengths of the lines in the spectra. The spectrum of iron contains more than 1,200 distinct lines, and it follows, therefore, that the molecule or its atoms must simultaneously excite as many different vibrations. We are acquainted with similar relations in acoustics. For instance, it has been observed by Hipkins that the simplest vibration of a pianoforte string will cause it to emit its own proper note, and as many as twenty-four overtones or harmonics. Johnstone Stoney first discovered such harmonics in spectra. The visible spectrum of hydrogen contains the three lines Hα wave-length 6563·9, Hβ = 4862·1, Hδ = 4102·4, these are the 20th, 27th and 32nd overtones of a vibration, of which the wave-length = 0·013127714 mm. But the fourth line Hγ = 4341, and the lines in the ultra-violet do not fall in with this system. Soret has calculated the harmonics of the three groups of triplets in the magnesium spectrum to be the 20th, 27th, and 31st harmonics of the fundamental vibration. Similar groups occur in the cadmium spectrum, which are the 20th, 23rd, 27th, and 31st of a fundamental vibration. Schuster has observed several harmonics in the spectrum of strontium; also in the spectra of bismuth, calcium, thallium, and gold. According to Mascart, sodium has five series of doublets which are the 132nd, 138th, 143rd, 158th, and 163rd harmonics. One of the most remarkable spectra is the absorption caused by chromyl chloride. Johnstone Stoney and Emerson Reynolds have shown that under great dispersion and lime-light illumination it gives a series of harmonics which are similar to those of a violin string, and of which the order lies between 628 and 733. Liveing and Dewar have observed that many ultra-violet spectra contain lines which are harmonically related, not so simply related perhaps as the harmonics of a uniform stretched string, but like the overtones of a string which is not of uniform thickness, or is loaded at different points, similarly related in origin though not exact harmonics. Lithium, potassium, calcium, magnesium, and zinc are such elements. The alkali metals have each one series in the visible spectrum, and another in the ultra-violet. It may happen in other cases that two or more such series overlap, and it may be very difficult to distinguish and separate them. There is a remarkable fact to be noted with regard to ultra-violet spectra, namely, that similar groups of lines, evidently harmonically related, are alternately sharp and nebulous in character.

Huggins discovered that the four hydrogen lines in the solar spectrum are part of a much longer series of lines which occur in the spectra of white stars. Cornu discovered the whole series in the spectrum of pure hydrogen, and Balmer showed that the whole series of lines can be expressed by the following formula:

$N_{m-2} = k\left(1-\frac{4}{m^2}\right)$, in which k is a constant for the whole series, and by substituting the whole numbers 3, 4, 5, 6, &c., for m, we obtain values for N which are the oscillation-frequencies of the successive lines.

Relations between the spectra of different elements. Lecocq de Boisbaudran has observed such a relationship between the lines in the different spectra of the alkali metals and their atomic weights, that he has been able to calculate the atomic weight of gallium from its spectrum. It may be stated that the atoms of greater mass vibrate more slowly, and therefore emit rays of proportionally greater wave-lengths. Ciamician made an extended series of observations on the spectra of elements usually classed together on account of their chemical properties, and he described several of these spectra as being homologous, that is to say, similarly constituted. A. Grünwald observed mathematical relations between the spectrum of water vapour and the line spectra of H and O, which led him to predict the existence of many lines in the spectrum of water vapour which had not been photographed. By prolonged exposures, Liveing and Dewar obtained photographs of a number of lines approximating very closely to those calculated by Grünwald.

Hartley, in 1883, observed the law of homology in the visible and ultra-violet spectra of the magnesium, zinc, and cadmium group. Elements with properties in common exhibit spectra with similar groupings of lines, but the dispersion of the lines and the refrangibility of the strong lines in each group vary with the atomic weights of the elements. In each spectrum the differences between the oscillation-frequencies of the individual lines of each triplet is a constant quantity. The law also applies to the series of doublets. The differences between the oscillation-frequencies of individual rays in the series of triplets increases with the atomic weights of the elements to which the triplets belong. A survey of these facts led to the conclusion that as the molecules of these elements contain but one atom, the atoms have a complex constitution, and that those elements the spectra of which are homologous are composed of the same kind of matter in different states of condensation, the molecules having similar modes, but different rates, of vibration. The law of homology has been studied by J. R. Rydberg, who it appears recognised it independently in 1885. J. S. Ames, in 1890, proved the perfect homology, line for line, of the arc spectra of zinc and cadmium. Kayser and Runge have shown that the series of triplets referred to in the magnesium, zinc, and cadmium spectra are in reality three series of harmonic vibrations, a principal series and two subordinate series overlying each other. The magnesium series they place along with those belonging to the calcium, strontium, and barium family, but according to the periodic law, the magnesium spectrum might be expected also to stand at the head of the spectra of the family which includes zinc and cadmium. The series of lines in the alkali and alkaline earth metals do not fall in with Balmer's law for the hydrogen lines. Homology has been observed

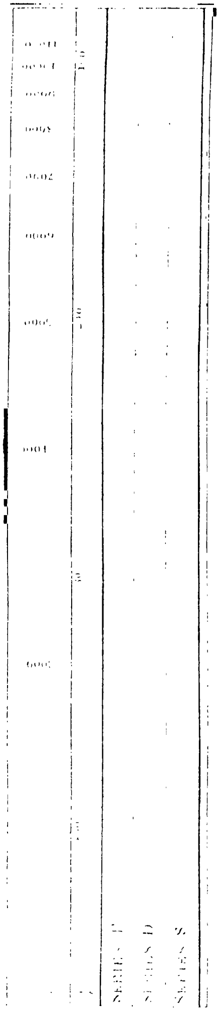


Fig. 1.

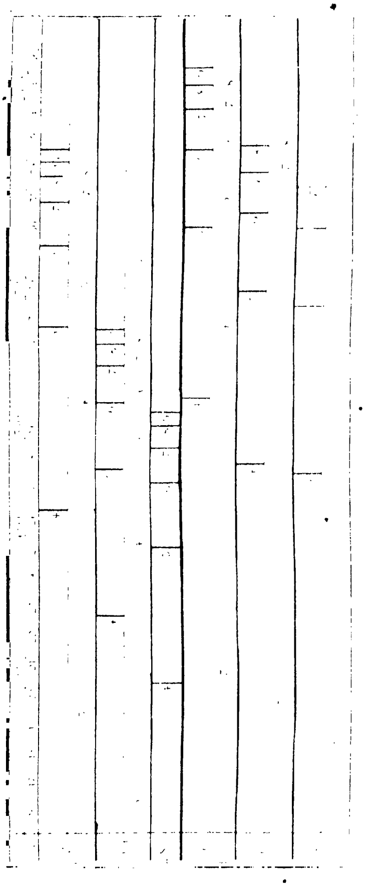


Fig. 2.

in the spectra of the following groups: lithium, sodium, potassium, rubidium, cæsium, also in aluminium, indium, thallium. Runge announces that doublets and triplets existing in the spectrum of an element can be arranged in series which show an appearance of great regularity, and are seemingly analogous to the overtones of a vibrating body (see figs. 1, 2, and 3). In fig. 1 the spectrum of sodium is shown with a scale of unequal parts, λ corresponding to wave-lengths, and a scale of equal parts $\frac{1}{\lambda}$ corresponding to oscillation-frequencies. The lines forming the entire spectrum are arranged in three series. Each line in the maps indicates a closely-placed pair of lines. Series P is the principal series, series D is the subordinate series of diffuse lines, series S the subordinate series of sharp lines. The three series are regular, the intervals between the lines decrease as the wave-lengths of the lines diminish from right to left. In fig. 2 we have similar maps, but the scales run the reverse way, from left to right. The principal and subordinate series of lines are shown in the spectra of Mg, Ca, Zn, Cd, and Hg. Corresponding lines in two different series of the same spectrum are numbered alike. The homology of the spectra is evidenced, and also variations following increase of atomic mass in elements of the same group. In fig. 3 the homology of the spectra of copper and silver is well shown. The difference of two consecutive oscillation-frequencies decreases as these values increase, and there seems to be a finite limit to the oscillation-frequencies of a series. If n represent whole numbers, the oscillation-frequencies of a series may, with great accuracy, be represented by the formula $A - Bn^{-2} - Cn^{-4}$, where A, B, C, are positive constants. B has nearly the same value for all the series of the different spectra. A is the limit towards which the oscillation-frequency tends when n increases. For elements that are chemically related the series are distinctly homologous, both in appearance of the lines and the values of A, B, C, and with increasing atomic weight they shift towards the less refrangible end of the spectrum. The spectra show relationships between the elements similar to those between their chemical properties.

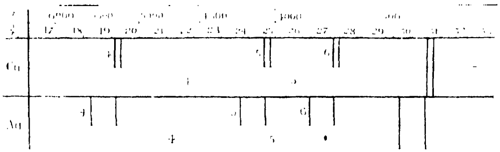


FIG. 3.

Quantitative analysis by the spectroscope. In 1862 W. A. Miller first attempted to apply the spectroscope to the quantitative estimation of the constituents of an alloy. Jansen, in 1870, proposed two methods of quantitative analysis. Champion, Pellet, and Grenier successfully applied a spectro-photometrical method to the estimation of alkalis. Lockyer and Roberts-Austen determined the composition of some homogeneous alloys of gold and silver, also of lead and cadmium, by comparison of their spectra with check pieces of known composition. Sir J. G. Alleyne estimated phosphorus in iron and steel, and Ballman attempted the estimation of lithium by the spectroscope. Liveing and Dewar made observations on a spectroscopic method of estimating sodium by measuring the width of the sodium lines. Hartley determined the different spectra emitted by solutions of different strengths, and found these constant when the ultra-violet lines were photographed. Accordingly, by comparison, the metals may be determined in solutions made from determinate weights of material, diluted to a definite volume. Quantitative determinations of the basic constituents of limestones, of copper in pyrites cinder, and of lead, silver, and copper in zinc blende, have been made with quantities of matter so small that no other method could have dealt with them. It will be seen later on, that absorption spectra are serviceable in quantitative analysis.

Spectra of the infra-red region and spectra of solids in vacuo. There are three methods of spectroscopy which have not yet been much employed. 1. The method of E. Becquerel for observing the infra-red rays. This is accomplished by the use of an eyepiece covered with Balmain's phosphorescent paint. When it is excited by exposure to a brilliant light, it glows, but as soon as any radiation of very low refrangibility falls upon it the phosphorescence is destroyed. 2. Abney observes the same rays by means of specially-prepared photographic plates, sensitive to exceedingly slow vibrations. Even the radiations from a kettle of boiling water can impress themselves permanently on his preparation of silver bromide. V. Schumann and also Waterhouse have used photographic plates prepared with cyanine, erythrosine, and other dyes for the same purpose with some success. 3. Crookes has made much use of the phosphorescent spectrum obtained by the action of an electric discharge in high vacua, and has made a most interesting series of observations on the rare earths by this means. Among other results he has proved the wide distribution of yttria, its occurrence in strontianite, coral, oyster shells, and limestones. He considers that there are several kinds of yttria with different phosphorescent spectra, but as they all give the same spectrum when excited by the spark in the usual manner, they must be considered as being derived from the same elementary yttrium.

Absorption spectra. **In dealing with absorption spectra, we may observe the effect on a continuous spectrum of (a) gases, (b) liquids, (c)** solids. When rays enter a transparent medium—either gaseous, liquid, or solid—they do not leave it in a condition identical with that in which they entered it. They may be either *partially absorbed* or *altered in refrangibility*. No known substance is capable of transmitting radiations of all known wave-lengths; those media which do not absorb appreciably any of the coloured rays, or any of the rays in the ultra-violet which are capable of being photographed, absorb a portion of the infra-red spectrum. It may be remarked that substances like air and water which in thin layers do not appear to absorb the rays in the visible spectrum, in thicker layers are seen to absorb the rays of a limited region. The A and B groups of lines in the solar spectrum have been shown to be due to oxygen in the atmosphere, while nine lines lying between the two D lines in the solar spectrum were observed, and proved by Josiah P. Cooke, in 1866, to be caused by water vapour in the atmosphere amounting to not more than 1·5 g. in 100 litres of air. With 0·18 g. only one line was visible, and with 0·55 g. two lines. The successful application by Piazzi Smyth of the spectroscope to weather forecasts is based upon such facts.

Many cases of absorption are known in the infra-red and in the ultra-violet, when no visible rays are absorbed. Colours may be either visible or invisible; since we must regard every substance which absorbs rays as coloured. The eye cannot always distinguish colour, because the most sensitive eye cannot observe the rays which are absorbed by its own aqueous humour, and are thus prevented from affecting the optic nerve. Hence the infra-red rays have no effect upon the retina, and most of the ultra-violet cannot affect it. The colour of a substance is determined by the combined effect of the rays which are not absorbed. Cobalt glass, which absorbs the yellow and green rays, transmits the red, blue, and violet, but as it transmits comparatively little of the red its colour appears blue. The purity of the light by which the substance is examined is of importance. Chromium solutions which are green by daylight are red by gaslight, because the yellow and red rays are predominant in gaslight, and as the red rays and the green are transmitted by pure white light, the dominant colour is red by light of less purity. There is but little importance to be attached to the general absorption of rays, but well-defined absorption bands afford evidence both of the composition and the constitution of substances.

The theory of absorption spectra. It is a well-known fact in acoustics that a vibrating musical instrument, a tuning-fork, or a stretched string, will communicate its vibrations to any similar instrument near to it which is capable of similar vibrations, and a sufficient number of strings or tuning-forks can entirely absorb the vibrations of a similar string or fork. In like manner when a molecule of a substance is capable of vibrating synchronously with a radiation, the rays received on the substance are absorbed by reason of the molecules being put in motion by the waves which strike them. The absorption is complete if the direction of vibration of the rays and of the molecule is the same, but the phase is opposite. A general absorption appears (in the ultra-violet at any rate) to be due to the vibration of the molecule, while selective absorption appears to be caused by the vibrations of atoms within the molecule. When a substance in solution absorbs all the rays of a certain region of the spectrum which fall upon it, it is because the molecules are vibrating synchronously with these rays, and the number of molecules present is sufficient to damp all the vibrations. When the rays traverse a smaller quantity of substance—as, for instance, when a solution is diluted—the number of molecules present is not sufficient to damp all the vibrations, and some rays pass through. If, however, certain atoms within the molecule are vibrating synchronously with certain rays, we shall have a selective absorption of these rays after the general absorption has been so weakened by dilution as to allow them to pass. It has been shown by Hartley that the vibrations of the atoms depend upon the rate of vibration of the molecule, or in other words, the rate of vibration of the molecule determines the rate of vibration of its parts. Four absorption bands in the three hydrocarbons benzene, naphthalene, and anthracene are evidence of this. The mean rate of vibration of the rays absorbed by naphthalene and anthracene is less than that of the rays absorbed by benzene, and the vibrations of the carbon atoms within the molecule are not independent of, but are a consequence of, the molecular vibrations; they must, in fact, be regarded as overtones or harmonics of the fundamental or molecular vibrations. When the rate of the fundamental vibration is reduced by an increase in the mass of the molecule, the rate of vibration of the carbon atoms is reduced in a similar ratio. Greater amplitude of vibration means a louder note, or in the case of luminous radiations a brighter light. Consequently the converse of this may be considered to hold good, that a greater intensity of absorption is caused by a greater amplitude of vibration in the molecules of the absorbing medium, the number of atoms or molecules remaining constant.

An examination of the three hydrocarbons benzene, naphthalene, and anthracene shows that the mean rate of vibration of the rays absorbed by benzene is greatest, naphthalene comes next, and anthracene is least; but the absorptive power is in the reverse order, that of anthracene being greatest. Hence we conclude that the amplitude of vibration is greater as the rate of vibration is slower (*C. J.* 1881). The approximate rates of vibrations of the three hydrocarbons are given as follows:—

	Mean wave-length of rays absorbed.	Molecular vibrations per second.	Molecular weights.
Benzene	2526	1,248 billions	78
Naphthalene	2687	1,177 „	128
Anthracene	3439	910 „	178

The various absorption spectra may be referred to in no better order than that of the refrangibility of the rays absorbed.

Infra-red absorption spectra. Abney and Festing have photographed rays extending down to λ 12000; the visible region ends about λ 7600. They studied the absorption spectra of water, hydrochloric acid, chloroform, carbon tetrachloride, cyanogen, and a number of hydrocarbons and their derivatives. The compounds containing hydrogen show the same group of lines, which, however, *do not appear in carbon compounds containing no hydrogen*; they do not all appear in some hydrogen compounds. The inference is that they belong to hydrogen. When oxygen is present as a part of hydroxyl it obliterates the rays between two of those lines which are due to hydrogen. When it forms part of the carbon nucleus of a compound, as it does in aldehyde, the spectrum is inclined to be linear, or the bands are bounded by well-defined lines. There appear to be characteristic bands which indicate the carbon nucleus of a series of substances. Certain radicles have a distinctive absorption lying near λ 7000 and others about λ 9000; thus in the three compounds C_6H_6, $C_6H_5.H_2N$, $C_6H_4(C_2H_5).H_2N$ we have the following coincident bands probably due to the benzene nucleus; the line λ 8670 is the principal one; λ 8670, λ 8670 to 8720, λ 8720 to 8860, a fourth band about λ 9300, a fifth about λ 10400–10660. In benzene and ethyl-aniline there occurs a band also at λ 10970 to 11050. If the line λ 8670 is associated with a band, it is almost certain to be caused by the benzene nucleus. Ethyl compounds are indicated by absorption at λ 7410, λ 8950 to 9030, 9040 to 9070, 9130 to 9180, 9270 to 9300·5, 9320 to 9420. The solar spectrum shows an absorption at λ 8660, and, with the exception of the line at 7410, the absorptions noted above have been observed to be coincident with bands or lines in the solar spectrum.

Visible and ultra-violet absorption spectra. The absorption spectra of the coloured region were long since carefully studied by Gladstone. These spectra pass gradually into the extreme violet and ultra-violet. In dealing with the subject it will be convenient first to consider the absorption caused by gases and vapours, elementary or compound, then the absorption by inorganic salts, and lastly the spectra of organic substances.

Elements which exhibit absorption spectra.

Gases and vapours.	Metals, the salts of which show banded spectra.
Br, Cl, I, O, ozone, K, Na.	Cr, Er, Sm, U, dysprosium, holmium, neodymium, prascodymium, thulium.

Compounds which exhibit absorption spectra.

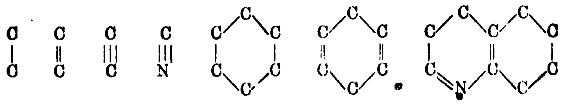
Gases and vapours.	Salts the acids of which show banded spectra.
ICl, IBr, NO_2, H_2O vapour, oxides of Cl.	Chromates } Ultra- Nitrates } violet. Nitrites (some); permanganates.

Organic suostances which exhibit absorption spectra. All benzenoid hydrocarbons and tertiary bases derived from the same. All haloid, hydroxyl, carboxyl, and amide, derivatives of benzenoid hydrocarbons. Cyanuric and uric acids, with colouring matters derived therefrom. Albumens and allied substances. Organic colouring matters of unknown constitution, such as chlorophyll and hæmoglobin. Many alkaloids and their derivatives, *e.g.*: Aconitine, pseudaconitine, japaconitine, morphine, narcotine, codeïne, papaverine, oxynarcotine, apomorphine hydrochloride, tetracetylmorphine, diacetylcodeïne, quinine, quinine sulphate, cinchonine sulphate, quinidine sulphate, cinchonidine sulphate, veratrine, piperine, brucine, strychnine.

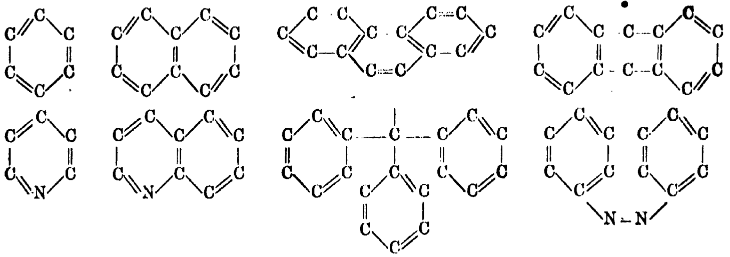
The relation of absorption spectra to the chemical constitution of carbon compounds. 1. Substances with a nucleus consisting of an open chain of carbon atoms transmit continuous spectra and are highly diactinic. Examples: the alcohols, acids, ethereal salts, haloid ethers, and the carbohydrates. 2. In homologous series the greater the number of carbon atoms the shorter the transmitted spectrum. 3. In substances with the same carbon nucleus that containing the most oxygen transmits the shortest spectrum, as, for instance, in acids the spectrum is shorter than in alcohols, and in dibasic shorter than in monobasic acids. 4. Substances with a closed chain nucleus when not more than two atoms of carbon are doubly linked transmit continuous spectra, but their absorptive power is much greater than that of open chain compounds; *e.g.* camphor, benzene hexachloride, and the terpenes, also hexahydropyridine. 5. The more closely the carbons in a closed chain are linked, the greater is the absorptive power of the molecule; *e.g.* the terpenes withstand dilution more strongly than benzene hexachloride, and camphor. 6. The carbon nuclei of benzenoid hydrocarbons possess strong absorptive power, and after great dilution exhibit absorption bands; *e.g.* four bands are seen in the spectrum transmitted by benzene when 1 part is diluted with 2,400 parts of alcohol, three bands in naphthalene with a dilution of 1 in 100,000 parts, one band in phenanthrene with 1 in 500,000 parts, and one band in anthracene with 1 in 5,000,000 parts of alcohol. 7. The introduction of radicles in place of hydrogen and of side-chains into the benzenoid nuclei diminishes the number of absorption bands, but increases their width and intensity. 8. The simple union of carbon to nitrogen does not cause selective absorption; *e.g.* in hydrocyanic acid and cyanides. 9. When a benzenoid nucleus contains an atom of nitrogen in place of an atom of carbon, the molecule exhibits absorption bands, and its absorptive power is generally not impaired, but is sometimes increased, *e.g.* picoline, pyridine, quinoline, and their derivatives. 10. Isomerides exhibit different spectra, *e.g.* the terpenes and isomeric benzene derivatives. 11. When the condensation of the carbon atoms in the quinoline nucleus is modified by the combination therewith of four atoms of hydrogen, the intensity of the absorption bands is reduced but is not destroyed. 12. Nitrogen combined with oxygen—as in nitroxyl, nitrites, and nitrates—exhibits absorption bands. 13. When several carbon atoms are united by oxygen and nitrogen atoms, the resulting compounds exhibit intense absorption bands, *e.g.* cyanuric acid, uric acid, and derivatives, including murexide. 14. Molecules of compounds—that is to say, molecules composed of dissimilar atoms—vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no visible relation to the chemical constituents of the molecule, whether these be atoms or groups of atoms. Hence it appears that a molecule is a distinct and individual particle which is not fully represented by our usual chemical formulæ.

since these only symbolise certain chemical reactions and fail to express any relation between physical and chemical properties. As certain molecular groupings are characterised by the absorption of rays of particular wave-lengths (absorption bands), it is evidently possible to draw conclusions as to the constitution of substances from their absorption spectra. Many of the foregoing statements may be usefully and clearly summarised by means of formulæ. These render evident how the optical properties of a compound are determined by the skeleton of carbon atoms.

Typical carbon nuclei, transmitting continuous spectra.

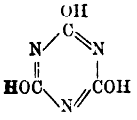


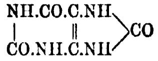
Typical carbon nuclei, exhibiting absorption bands.



Nuclei containing oxygen and nitrogen, exhibiting absorption bands. R representing any radicle.

NO_2 RNO_2 RNO,





NH.CO.C.NH
CO.NH.C.NH CO

On the cause of colour in organic compounds. According to O. Witt, the tinctorial character of aromatic compounds is conditional upon the simultaneous presence of a colour-producing group and a salt-forming group in the molecule. A group of atoms of the former kind he terms a *chromogen*, and of the latter a *chromophor*. He says: 'For instance, NO_2 is the chromophor of nitraniline and nitrophenol, but nitrobenzene is the chromogen of these bodies. The different nitrodiphenylamines are all acids and dye-stuffs, and their tinctorial power increases with the number of nitroxyls.' In this connexion it is of interest to study the relation of the hydrocarbons to the more complex compounds which are colouring matters derived from them.

If a source of light emits all luminous and invisible vibrations capable of being transmitted through 8 feet of air, a perfectly colourless substance will transmit these rays without impairing their intensity. A coloured substance is one which absorbs rays at either end of the spectrum, or selects rays of a definite wave-length from the middle of the spectrum. Every fluorescent substance is therefore coloured, and benzene, benzenoid hydrocarbons, phenols, and other derived compounds which exhibit selective absorption of the ultra-violet rays are coloured. The subtlety of the colour, however, is such that the eye cannot perceive it without the aid of photography or a fluorescent screen.

That which in the ordinary acceptation of the term is a coloured substance is merely one in which the absorption of rays extends into a region limited by the red and violet ends of the spectrum, or between wave-lengths 7000 and 4000. According to this view, the colour of a substance may be invisible to the unaided eye. As bands of selective absorption appear to be the effect of vibrations taking place within the molecules of a substance, and these are dependent upon the rate of vibration of the molecules themselves, they are called in general 'molecular vibrations.' If, then, it be desired to convert a substance such as benzene, the colour of which is invisible, into a compound with a visible colour, it is necessary to slacken its rate of vibration so that the molecule will absorb rays with oscillation-frequencies (inverse wave-lengths) occurring within the limits of visibility. That which is called a *chromogen* is an invisibly-coloured substance, and that termed a *chromophor* is an atom or group of atoms capable of so affecting the molecule as to reduce its rate of vibration, so that it absorbs rays within the limits of visibility. Under certain conditions of combination, nitrogen and oxygen are chromophors, hence also nitroxyl and hydroxyl; that is to say, they are themselves coloured either visibly or invisibly. When two benzene molecules are doubly linked by two nitrogen atoms, as in azobenzene, their mode of vibration is profoundly modified, and a brilliant colour as low down in the scale as the yellow rays is the result. A similar modification takes place when two atoms of oxygen replace two of hydrogen, as in quinone, which is of a golden-yellow colour. The effect of linking two or more benzene nuclei *by carbon atoms has been already dealt with*; the colours are not rendered visible, but the molecular vibrations are greatly reduced in rapidity, and the amplitude of the vibrations is much increased. That is to say, the absorption bands are transferred to less refrangible rays, and withstand a much larger amount of dilution. These modifications are both observed in the curve of benzene as modified in triphenylmethane. The vibrations of this radicle are reduced in rapidity in rosaniline hydrochloride, Hofmann's violet, iodine green, and other such derivatives in which the carbon nucleus remains intact.

There is a family likeness in the curves of azo-benzene, azo-naphthalene, chrysoïdine, and other derivatives of these substances, which is quite in accordance with these observations. In short, in a general way, the change of colour effected by any given series of reactions may be predicted from an inspection of the curve of molecular vibrations of any benzenoid hydrocarbon.

W. N. H.

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OPTICAL METHODS.—Section 3: ROTATION OF THE PLANE OF POLARISATION OF LIGHT.—When a ray of plane polarised light is passed through a plate of quartz cut at right angles to its optical axis, it is found that the plane of polarisation of the emergent ray is not coincident with that of the incident ray; the angle through which the plane has been rotated is called the *angle of rotation.* If the rotation takes place in the same direction as that in which the hands of a watch move when the face of the watch is looked at, the quartz is said to show *dextrorotatory power*; if the rotation is in the opposite direction, the quartz is said to show *lævorotatory power.* The symbol + is used to express dextrorotation, and the symbol − to express lævorotation. Substances which rotate the plane of polarisation of a ray of light passed through them are said to be *optically active.*

The *polarimeter* is an instrument wherein a ray of light can be polarised, the position of the plane determined, the ray passed through a determinate quantity of an optically active substance, and the position of the plane of the emergent ray determined.

The angle of rotation depends upon (1) the nature of the active substance, (2) the thickness of the layer of the substance through which the light passes, (3) the wave-length of the light used, and in most cases (4) the temperature.

The composition of the substance examined must then be known; the length of the column of liquid used if the substance be liquid, or the thickness of the layer if the substance be a solid, must be measured; the temperature must be noted—observations ought to be made at a common temperature; and monochromatic light should be employed.

Suppose we are dealing with a liquid carbon compound. Let l = length of column of liquid in decimetres, d = sp.gr. of liquid (referred to water), and α = angle of rotation of the plane of polarisation of light of stated wave-length; then $[\alpha] = \frac{\alpha}{l.d}$.

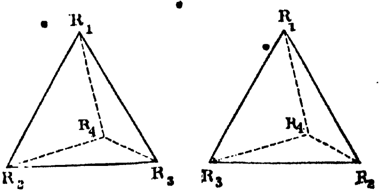
The value of $[\alpha]$ is usually called the *specific rotatory power* of the substance. It is customary to indicate the light employed by placing a letter to express the wave-length below the bracket; thus $[\alpha]_D$ means spec. rot. power for light of wave-length D. The spec. rot. power of a liquid as thus defined is the angle through which the plane of polarisation of a ray of light of stated wave-length is rotated by passing through a column one decimetre long of the liquid containing one g. of the substance in 1 c.c.

If a solid compound is to be examined, it must be dissolved in an optically inactive solvent. In this case l = length of column of solution in decimetres, d = sp. gr. of solution, p = g. of optically active substance in 100 g. of solution; then, assuming that the solvent is without influence on the rotatory power of the dissolved substance, $[\alpha] = \frac{100\alpha}{l.p.d}$. The question as to the effect of an inactive solvent on the rotatory power of an active substance in solution will be examined later (p. 257).

Connections between optical activity and constitution. Landolt (*Handbook of the Polariscope*, English trans.) has divided substances which rotate the plane of polarisation of a ray of light into three classes: (1) those which are active only when in the form of crystals; (2) those which are active only when liquid or in solution; (3) those which are active both as crystals and also in solution or in the liquid state. The only substance at present known to belong to the third class is strychnine sulphate. The liquid crystals examined by Lehmann (*Z. P. C.* 4, 462; 5, 427) probably belong to the first class.

The optical activity of carbon compounds. All compounds which exhibit optical activity unconnected with crystalline form—in other words, all compounds which are optically active when liquid or in solution—are compounds of carbon. Le Bel (*Bl.* [2] 22, 337) was the first (1874) to trace a definite connection between the optical activity and the constitution of carbon compounds. He was followed by van't Hoff (*Bl.* [2] 23, 295 [1875]). The subject has been much advanced by van't Hoff in his pamphlet, *La Chimie dans l'Espace*, and more especially by a small book published in 1887, *Dix Années dans l'Histoire d'une Théorie* (translated into English by Marsh, and published in 1891, entitled *Chemistry in Space*).

The hypothesis of Le Bel and van't Hoff connects optical activity with the presence of one or more *asymmetric* atoms of carbon in the molecule of the active compound. An *asymmetric* atom of carbon is one which is in direct combination with four different atoms or radicles, these atoms or radicles being arranged so that any three are similarly situated with regard to the fourth. The conception of the asymmetric atom carries with it the conception of the arrangement in space of the parts of the molecule. The asymmetric atom of carbon is supposed by van't Hoff to be placed in the centre of a regular tetrahedron, and a different radicle is supposed to be held by the carbon atom at each summit of the tetrahedron. Two forms of this arrangement may exist, and these forms are geometrically different. Neither is superposable on the other. They bear to one another the relation of an object to its image, or of the right hand to the left, as shown in the figure.



This arrangement corresponds to the *enantiomorphous* (non-superposable) form of crystals. Ammonium malate, for instance, crystallises in two non-superposable forms, which differ in exactly the same way as the molecules of two geometrical isomerides, each containing an asymmetric carbon atom and both having the composition $CR_1R_2R_3R_4$, are supposed to differ. If one of the isomerides $CR_1R_2R_3R_4$ rotates the plane of polarisation to the right, the other rotates to the left. If this hypothesis is to be accepted, every compound of carbon which is optically active must contain at least one asymmetric carbon atom. So far as investigation has gone, this deduction from the hypothesis has been confirmed (*v.* van't Hoff, *Dix Années &c.*, 31; Landolt, *Handbook*, 25 *et seq.*). Further, it has been found that compounds which do not themselves contain asymmetric carbon atoms are inactive, although they are derived from optically active compounds.

There is no doubt that compounds exist which contain asymmetric carbon atoms but do not affect the plane of polarisation of a ray of light. At first sight this fact might be supposed to be irreconcileable with the hypothesis; but the recognition of the existence of inactive compounds containing asymmetric carbon atoms has led to a most ingenious and interesting development of the hypothesis.

Some inactive compounds containing asymmetric carbon atoms can be separated each into two optically active isomerides, one of which is dextrorotatory and the other is lævorotatory. Some inactive compounds which contain asymmetric carbon atoms cannot be separated into active isomerides. Racemic acid, which can be resolved into dextrorotatory and lævorotatory tartaric acid, is an example of the first of these classes, called *inactive resolvable compounds*;

mesotartaric acid, which cannot be resolved into active isomerides, is an example of the second class, called *inactive non-resolvable compounds.*

Inactive resolvable compounds are said, in the language of van't Hoff's hypothesis, to be *inactive by external compensation*; inactive non-resolvable compounds are said to be *inactive by internal compensation.*

To understand these expressions consider the formulæ $(\mathrm{R}_3\mathrm{R}_2\mathrm{R}_1)C.C(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)$ and $(\mathrm{R}_2\mathrm{R}_3\mathrm{R}_1)C.C(\mathrm{R}_1\mathrm{R}_3\mathrm{R}_2)$; an italicised C represents an asymmetrical atom of carbon. Each formula contains two asymmetric carbon atoms, and both carbon atoms in either formula are united to the same radicles; in the first formula each C is united to the radicles R_1, R_2, R_3, and $\mathrm{C}(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)$; in the second formula each C is united to the radicles R_1, R_3, R_2, and $\mathrm{C}(\mathrm{R}_1\mathrm{R}_3\mathrm{R}_2)$. The structure represented by one of these formulæ is the reflected image of that represented by the other: hence if one of these geometrically isomeric compounds is dextrorotatory, the other will be lævorotatory, and both will rotate the plane of polarisation to the same degree. But if a compound were formed by the combination of equal numbers of molecules of these two geometrical isomerides, that compound would be inactive, for the tendency to right-handed rotation of one part of the compound molecule would be exactly neutralised by the equal tendency to left-handed rotation of the other part. Moreover, if the inactive compound were split into two compounds, one consisting of molecules of the form represented by the first of the above formulæ, and the other of molecules of the form represented by the second formula, then each of these compounds would be optically active, and the compounds would be active in opposite directions. The hypothetical inactive compound $\begin{array}{l}(\mathrm{R}_3\mathrm{R}_2\mathrm{R}_1)C.C(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)\\(\mathrm{R}_2\mathrm{R}_3\mathrm{R}_1)C.C(\mathrm{R}_1\mathrm{R}_3\mathrm{R}_2)\end{array}$ would be said to be *inactive by external compensation.*

Racemic acid, which is optically inactive, can be resolved into dextrorotatory and lævorotatory tartaric acids. Both tartaric acids have the formula $\mathrm{C}_2\mathrm{H}_2(\mathrm{OH})_2(\mathrm{CO}_2\mathrm{H})_2$; the hypothesis we are considering represents one of these acids as $(\mathrm{H.OH.HOOC})C.C(\mathrm{COOH.OH.H})$; and the other acid as $(\mathrm{H.COOH.OH})C.C(\mathrm{OH.COOH.H})$; and the hypothesis represents racemic acid as made up of an equal number of molecules of the two active acids, and therefore as a substance which is inactive by external compensation.

But suppose the molecule of a compound contained two asymmetric carbon atoms, both united to the same radicles but having one half of the molecule the reflected image of the other, then the tendency to right-handed rotation belonging to one part of this molecule would be neutralised by the tendency to left-handed rotation belonging to the other part of the molecule; the molecule as a whole would be incapable of rotating the plane of polarised light, and the compound would be *inactive by internal compensation*. The general formula of such an inactive compound is $(\mathrm{R}_2\mathrm{R}_3\mathrm{R}_1)C.C(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)$.

A compound of this type cannot be resolved into active isomerides, because a resolution into parts is only possible by splitting the molecule, removing one of the radicles, and so destroying the asymmetry of one, or both, of the atoms of carbon. Mesotartaric acid, which is non-resolvable, probably belongs to this class of compounds; it may have the formula

$$(\mathrm{H.COOH.OH})C.C(\mathrm{COOH.OH.H}).$$

The hypothesis therefore provides for the existence of two classes of optically inactive compounds, both containing asymmetric carbon atoms; the members of one class are resolvable into active isomerides, the members of the other class cannot be so resolved.

Those compounds which contain in their molecules more than one asymmetric carbon atom, each of which atoms is united to the same radicles, whether these radicles are arranged in space in exactly the same way, relatively to each carbon atom, or not, are called by van't Hoff *symmetrical compounds*; and the term *unsymmetrical compounds* is used to designate those which contain more than one asymmetric carbon atom each of which is united to different radicles. The typical formulæ for symmetrical compounds containing two asymmetric carbon atoms are
$(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)C.C(\mathrm{R}_3\mathrm{R}_2\mathrm{R}_1)$, $(\mathrm{R}_1\mathrm{R}_3\mathrm{R}_2)C.C(\mathrm{R}_3\mathrm{R}_2\mathrm{R}_1)$, &c.

The typical formula for an unsymmetrical compound containing two asymmetric carbon atoms is $(\mathrm{R}_1\mathrm{R}_2\mathrm{R}_3)C.C(\mathrm{R}_4\mathrm{R}_5\mathrm{R}_6)$.

Unsymmetrical compounds may be either active or inactive; if inactive, they must be inactive by external compensation, and therefore they must be resolvable into pairs of active isomerides. Symmetrical compounds may be active or inactive; if inactive, they may be inactive by external, or by internal, compensation, and therefore they may be either resolvable or not resolvable.

An unsymmetrical compound containing *n* asymmetric carbon atoms may exist in 2^n isomeric forms, which will always be grouped in pairs, one being dextrorotatory and the other lævorotatory. A symmetrical compound containing *n* asymmetric carbon atoms may exhibit $\frac{1}{2}2^n$ active isomeric forms, grouped in pairs of opposite rotatory power, and may also exist in $\frac{1}{2}2^{\frac{n}{2}}$ non-resolvable inactive modifications (van't Hoff; *Dix Années* &c., 54-5).

There are three general methods for separating inactive resolvable bodies into their dextrorotatory and lævorotatory isomerides.

In the first method advantage is taken of the differences between the actions of certain minute organisms on the two active isomerides. The second method proceeds by treating the inactive compound with an active body with which one of the isomeric constituents of the inactive compound combines more readily than the other. The third method consists in separating the inactive body into two active isomerides by crystallisation at a definite temperature (van't Hoff, *l.c.* 63-69).

Racemic acid, which is an inactive compound, can be resolved into equal quantities of right- and left-handed tartaric acid by each of the three methods. When *penicillium* is allowed to act on a dilute solution of ammonium racemate, lævorotatory ammonium tartrate is found in the solution after a time, the dextrorotatory tartrate having been destroyed by the action of the organism. When a quantity of active cinchonine sufficient to neutralise half of a determinate quantity of racemic acid is added to a solution of the racemic acid, crystals of lævorotatory cinchonine tartrate are obtained, and dextrorotatory tartaric acid remains in solution. When a solution of racemic acid is neutralised by soda, and another equal quantity is neutralised by ammonia, and the solutions are mixed, and evaporated at a temperature slightly below 28°, crystals of two forms are obtained; one set of crystals is dextrorotatory, and the other is lævorotatory, sodium-ammonium tartrate. Van't Hoff (*l.c.* 69) has shown that sodium-ammonium racemate is changed to a mixture of the active isomeric tartrates by heating the dry salt with water, in the ratio $\mathrm{NaNH_4.H_4C_4O_6.H_2O:3H_2O}$ (the salt crystallises with $\mathrm{H_2O}$), to a little under 27°, and that the reverse change is effected by heating the mixed tartrates to a little above 27°. The changes may be represented thus—

$$\mathrm{2(NaNH_4.H_4C_4O_6.4H_2O) \rightleftarrows 2(NaNH_4.H_4C_4O_6.H_2O) + 6H_2O.}$$

The racemate crystallises with $\mathrm{H_2O}$, and the tartrates with $\mathrm{4H_2O}$. Slight variations of temperature above or below 27° determine the direction in which the change shall occur.

The change of inactive sodium-ammonium racemate to a mixture of the active tartrates, and *vice versâ*, is very similar to some changes which occur among inorganic compounds; for instance, when a mixture of $\mathrm{MgSO_4.7H_2O}$ and $\mathrm{Na_2SO_4.10H_2O}$ is heated to a little above 21°, it is changed to the double sulphate $\mathrm{MgNa_2(SO_4)_2.4H_2O}$, and water, and this double sulphate is resolved into the two single sulphates at a little under 21°; these changes may be represented thus:—

$$\mathrm{MgSO_4.7H_2O + Na_2SO_4.10H_2O \rightarrow MgNa_2(SO_4)_2.4H_2O + 13H_2O.}$$

Van't Hoff calls the temperature at which such a chemico-physical change as this occurs the *transition-point* of the system (*v. Z. P. C.* 1, 165, 227).

Extension of the hypothesis of van't Hoff and Le Bel. The hypothesis of van't Hoff and Le Bel connects the power of rotating the plane of polarisation of a ray of light primarily with the configuration of the parts of molecules, but it points to the formation of molecular aggregates, without change of molecular structure, as a cause of the disappearance of optical activity. Although optical activity is primarily dependent on the arrangement of the parts of certain molecules, and although we cannot assign a definite part of the total rotatory power of a molecule to each atom, or to each group of atoms which together form the molecule, nevertheless a consideration of the constitution of optically active compounds shows that the amount of the activity of any compound is dependent on the greater or less differences between the four radicles which are in direct union with the asymmetric carbon atom or atoms in the molecule of that compound. The greater the differences between the radicles the greater will be the asymmetry of the molecule, and, therefore, the greater will be the rotatory power. An attempt has been made by P. A. Guye (*C. R.* 110, 714) to connect the degree of asymmetry of the molecule of an optically active compound with the mass of each radicle, and the distance of its centre of gravity from the centre of figure of the tetrahedron. When the molecule is asymmetric, the centre of gravity will not be situated on any one of the six planes of symmetry of the tetrahedron. So long as the substitution of one radicle by another does not move the centre of gravity of the molecule to the other side of one of the planes of symmetry of the tetrahedron, Guye supposes that the rotatory power is increased or diminished, but is not changed in sign, by such substitution; but that a change of sign of the rotatory power accompanies a substitution which results in moving the centre of gravity of the molecule from one side to the other side of one of the planes of symmetry of the tetrahedron. Guye gives about fifty cases to which he has applied his hypothesis successfully. The derivatives of tartaric acid afford the most complete example.

Replacement of the acidic hydrogen of tartaric acid by alcoholic radicles is accompanied by increase of rotatory power, and the greater the molecular weight of the replacing alkyl the greater is the increase of rotatory power; thus—

Methyl tartrate	$[\alpha]_D =$	$+2{\cdot}14$
Ethyl	„	$7{\cdot}66$
Propyl	„	$12{\cdot}44$
Isobutyl	„	$19{\cdot}87$

Replacement of the hydroxylic hydrogen of the acid by benzoyl moves the centre of gravity to the other side of the plane of symmetry which is situated between the COOH and OH groups; this replacement is accompanied by a change of sign of the rotatory power. But if the H of the COOH group is now replaced by one alkyl group, the centre of gravity is moved back towards the plane of symmetry already mentioned, and the rotatory power is diminished. Thus—

Dibenzoyl	tartaric acid	$[\alpha]_D =$	$-117{\cdot}7$
Methyl salt of		„	$88{\cdot}8$
Ethyl	„	„	$60{\cdot}0$
Isobutyl	„	„	$42{\cdot}0$

If acetyl is used in place of benzoyl the rotatory power changes its sign, but the value of the lævorotation of diacetyl tartaric acid is less than that of dibenzoyl tartaric acid; the replacement of acidic hydrogen in the diacetyl acid by alkyl radicles decreases the rotatory power, and, as the alkyl radicles of large molecular weight exert a greater effect than the acetyl group, and an effect in the opposite direction, the rotatory power again changes its sign. Thus—

Diacetyl	tartaric acid	$[\alpha]_D =$	$-23{\cdot}1$
Methyl salt of		„	$14{\cdot}3$
Ethyl	„	„	$+1{\cdot}0$
Propyl	„	„	$6{\cdot}5$
Isobutyl	„	„	$10{\cdot}3$

Crum Brown (*Pr. E.* 17, 181) has tried to connect the greater or less rotatory powers of different active compounds with differences between the constitutions of the substituting radicles. Crum Brown admits the influence of the masses of the radicles, but he tries to show that their constitution must also be taken into account. If two methyl groups are introduced into dextrorotatory tartaric acid, the salt thus obtained is still dextrorotatory; in this change two CO.OH radicles have been changed into two radicles CO.O.CH_3. If now this dimethyl tartrate is treated with acetyl chloride, a strongly lævorotatory dimethyl diacetyl-tartrate is obtained; in this change the CO.O.CH_3 groups remain, and two OH groups have been changed to two groups O.CO.CH_3. In the first change, the introduction of the group CO.O.CH_3 for H altered the rotatory power but did not change its sign, in the second change the introduction of the group O.CO.CH_3 changed the sign of the rotatory power; therefore, Crum Brown argues, the effect of the radicle O.CO.CH_3 on the rotatory power is greater than the effect of the isomeric radicle CO.O.CH_3. As the masses of these two radicles are the same, it is evident that the constitution of the substituting radicle affects the rotatory power of the compound.

The specific rotatory powers of compounds often change more or less with small changes in certain physical conditions. Some active bodies become inactive by heating, and at another temperature the change is sometimes reversed. The values of the rotatory powers of active bodies dissolved in inactive solvents are dependent on the nature and the quantity of the solvent used (*v. post*, p. 257); the rotatory power of a solution sometimes changes on keeping until a constant value is attained (*v.* Landolt's *Handbook of the Polariscope*, 62). This readiness to change shown by the rotatory powers of carbon compounds finds some explanation in van't Hoff's hypothesis, and especially in the development of it made by Wislicenus. According to Wislicenus (*Kön. Sächsischen Ges. der Wiss.* 14, 1) the arrangement of the four radicles attached to an asymmetric carbon atom is conditioned chiefly by the affinities of these radicles for one another in the sense that those radicles which have the greatest mutual affinity will tend to get as near as possible to one another; but besides those configurations which are conditioned by the affinities of the radicles, and which will be comparatively stable, other configurations will probably exist conditioned by the temperature and by the collisions of other molecules—for instance, the molecules of the solvent—and these arrangements will be relatively unstable. These unstable forms may be optically active, as they are only geometrically different from the stable forms, but their rotatory powers will probably differ from those of the stable forms. This way of looking at the question of optical activity enables us to connect the fact that active compounds easily undergo changes in the values of their rotatory powers with the conception which the hypothesis of van't Hoff and Le Bel furnishes of the cause of optical activity.

Molecular rotatory power. The notion of molecular rotation, as the product of the specific rotation into the molecular weight of a substance, was introduced by Wilhelmy (*P.* 81, 527). Krecke (*J. pr.* [2] 5, 12) proposed to define *molecular rotatory power* as $[m] = \frac{m}{100} \times \frac{\alpha}{l.d}$, where m = molecular weight of compound, and α, l, and d have the same meaning as before (p. 253); m is divided by 100 to obviate the use of inconveniently large numbers.

Krecke endeavoured to generalise the relations between the values of $[m]$ for certain compounds and bodies derived from, or closely connected with, these compounds. Some years before Krecke's attempt, Mulder (*Z.* 1868. 58) put forward a statement to the effect that optically active compounds contain certain active radicles, which may be transferred to other active atomic aggregations, and the rotatory powers of the new bodies bear a simple relation to those of the original radicles. Krecke, on the basis of further experimental results, modified and extended Mulder's statement. Krecke announced two generalisations:

(i.) 'When an optically active body forms a compound with an inactive body, or when it is altered by the action of chemical reagents, either the molecular rotatory power of the body is unchanged, or the molecular rotatory power of the new substance is a simple multiple of that of the parent substance.'

'(ii.) 'The molecular rotatory powers of isomerides are multiples of one and the same value.'

Most of Krecke's values were obtained from measurements of substances in solution, and, as we shall see in another paragraph, the results of such measurements are trustworthy only in a few cases. Landolt (*B.* 6, 1073) made a careful examination of the rotatory powers of tartrates in solution; he came to the conclusion that the value of $[m]$ for tartrates containing a single atom of a monovalent metal is double the value of $[m]$ for free tartaric acid, and that $[m]$ for tartrates containing two atoms of a monovalent metal is three times $[m]$ for the free acid. In this case, Krecke's first statement was confirmed.

In 1885, Oudemans (*v. P. B.* 9, 635) arrived at the conclusion that the compounds of active bases with inactive acids, and also the compounds of active acids with inactive bases, follow the simple law that 'the molecular rotatory power of a salt, in fairly dilute solution, is independent of the nature of the inactive part of the salt.' This result has been confirmed by the measurements of camphorates and tartrates made by Landolt, of salts of cholic acid by Hoppe-Seyler, of malates by Schneider (*A.* 207, 286), and of camphorates by Hartmann (*B.* 21, 221).

This result indicates that the rotatory powers of salts in solution are not affected, to anything like the extent that the rotatory powers of liquid compounds are affected, by the nature of the radicles which compose them. The rotatory power of a salt in solution approaches to being an additive property, whereas the rotatory power of a liquid compound is a constitutive property (*cf.* Ostwald, *Lehrbuch*, 1, 499 [2nd ed.]).

Optical activities of bodies in solution. The specific rotatory power of an active substance in an inactive solvent has been defined (p. 253) as $[\alpha] = \frac{100\alpha}{l.p.d.}$, where l = length of column of solution in decimetres, d = spec. grav. of the solution, and p = g. of active substance in 100 g. of the solution. This formula is expressed in more general terms as $[\alpha] = \frac{n.\alpha}{l.g.d.}$, where n = g. of solution containing g g. of the substance; in this case, 1 c.c. of the solution weighs d g. and contains $\frac{g.d.}{n}$ g. of the active substance.

This formula assumes that the rotatory power of the dissolved active substance is not affected by the inactive solvent. In 1838 Biot (*A. Ch.* [3] 36, 257; *cf.* 59, 206) found that the rotatory power of tartaric acid in aqueous solution increased with increasing dilution; that solutions, of equal concentration, of the same active substance in different inactive solvents had different rotatory powers; and that the same inactive solvent raised the rotatory powers of some active substances, and decreased the rotatory powers of others. Results similar to those of Biot were obtained by Oudemans (*A.* 166, 65; 182, 33), Hoorweg (*Maanblad voor Natuurwet,* 3, 12 [1873]), and Hesse (*A.* 176, 89, 189).

Landolt (*A.* 189, 241; *B.* 21, 191; *Handbook of the Polariscope*, 80-94) made many observations on the effect of inactive solvents on the rotatory powers of active substances; he came to the conclusion that the specific rotatory powers of such solutions are expressed by equations of the following forms: $[a] = A + Bq$, or $[a] = A + Bq + Cq^2$, or $[a] = A + \frac{Bq}{C+q}$, where A, B, and C are constants, and q is weight of active substance in 100 pts. of the solution. Which formula must be employed is discovered from the results of several observations made with solutions of different concentrations in different solvents. In some cases the observed values of $[a]$ for liquid compounds agree with the values calculated from series of observations of a for solutions of the same compounds. Thus Landolt got the following results:—

Active substance	$[a]_D$ observed	$[a]_D$ calculated from observations on solutions in					Max. diff.
		(1) EtOH	(2) MeOH	(3) H_2O	(4) C_6H_6	(5) AcOH	
Dextro-ethyl tartrate	8·31	8·27	8·42	8·09	—	—	−·22
Dextro-turpentine	14·15	14·87	—	—	—	—	+·72
Lævo-turpentine	37·01	36·97	—	—	36·97	36·89	−·12
Lævo-nicotine	161·55	160·83	—	161·29	—	—	−·72

It is not possible to determine with certainty whether the true values of $[a]$ for solid compounds can be determined from observations on solutions of such compounds. In some cases the values obtained seem to approach constancy when the solutions become very dilute; but according to Pribram (*B. B.* 1887. 505; *B.* 20, 1840), who used a very delicate method of measuring, $[a]$ does not certainly attain final constant values in aqueous solutions of tartaric acid, nicotin, and cane sugar, even with very great dilution. R. von Sonnenthal (*Z. P. C.* 9, 656) determined $[a]$ for dilute aqueous solutions of normal and acid tartrates of K, Na, Li, and NH_4; he found that $[a]$ decreased as dilution increased, but that when the solutions became very dilute (c. ·4 to ·2 p.c. salt in solution) $[a]$ began to increase as dilution still further increased. The conclusion come to by von Sonnenthal was, that a change in the state of the dissolved tartrates occurred when more water was added to the very dilute solutions; this change was supposed to be of the nature of dissociation. The dilution whereat the change occurred was found to depend on the nature of the metal of the tartrate, and on the solubility in water of the salt used; the greater the atomic weight of the metal, the greater was the concentration whereat the change began, and the greater was the difference from the normal state of the salt. Schneider (*A.* 207, 257) found that the rotation of an aqueous solution of malic acid was right-handed in concentrated solutions, left-handed in dilute solutions, and at 34 p.c. was equal to zero. These observations, and others of a similar character, seem to me to show that observations of the rotatory powers of solutions of solid compounds cannot be applied, at least not in all cases, to draw conclusions concerning the connections between the rotatory powers and the chemical constitutions of the compounds themselves. There is undoubtedly an action of some kind between the molecules of the active dissolved substance and the molecules of the inactive solvent. Molecular aggregates of the solid substance may be broken down by the solvent, or the solvent may form a series of unstable compounds with the dissolved substance, or the solvent may bring about changes in the configuration of the atoms which form the molecule of the dissolved body, or the dissolved compound may be electrolytically dissociated into ions by the solvent. Some of these actions may occur in certain cases, and others in other cases. The action of much water on active salts dissolved therein seems to consist in the electrolytic dissociation of the salts into their ions.

Magnetic rotatory power. Following observations made in 1871 by A. de la Rive (*A. Ch.* [4] 15, 57), Becquerel in 1877 (*A. Ch.* [4] 22, 5) made a number of measurements of the rotatory powers of liquid substances, and of salts in solution. The subject was taken up by Perkin in 1882, since which time a series of memoirs by this investigator has appeared (*C. J.* 45, 421; 49, 777; 51, 808; 53, 561; 55, 680; 59, 981; 61, 800). The methods employed in the measurements are based on the discovery which Faraday made in 1846 (*T.* 1846. 1), that most transparent bodies acquire the power of rotating the plane of polarisation of a ray of light when they are brought within the action of a magnet, or of an electric current which is made to pass round the body so that its plane is at right angles to the direction of the ray of light. Faraday showed that the amount of rotation is proportional to the strength of the current, or the intensity of the magnetic action, and to the length of the layer through which the light passes, and that it is dependent on the temperature and on the nature of the substance examined. Perkin has worked with liquid compounds and with solutions. The fluid to be examined was placed in a glass tube about 103 mm. long, and 9 mm. diameter, the ends of which were closed by circles of glass cemented on; the ends of the tube were let into the pole-pieces of a large electro-magnet. Sodium light was employed by Perkin. (For a description of the apparatus, and the various precautions and corrections, *v.* Perkin, *C. J.* 45, 421–445.) Perkin calculates his results so that the observed rotations of liquid compounds are referred to lengths of the liquids related to one another in the same proportion as the molecular weights of the gaseous compounds obtained by vapourising the liquids; the results when thus calculated represent the magnetic rotatory powers of quantities of the various compounds proportional to the weights of the gaseous molecules of these compounds.

The molecular rotation of water is taken as unity. If r is the rotation of unit-length of liquid, and r' is the rotation of the same length of water under the same conditions, then $\frac{r}{r'}$ is the specific rotation of the liquid; and sp. rot. $\times \frac{\mathrm{M}}{\mathrm{M}'.d}$ is the molecular rotation, where M = molecular weight of substance, M′ = molecular weight of water, and d = relative density of substance. The calculation may be expressed by one equation, thus: $(\text{Mol. R.}) = \frac{r.\mathrm{M}}{r'.\mathrm{M}'.d}$.

About 200 compounds have been examined by Perkin, the observation of r being repeated five to ten times for each compound, and the specific gravity of each being determined with great care.

Magnetic molecular rotatory powers of liquid carbon compounds. In strictly homologous normal series of carbon compounds, each increment of CH_2 produces a constant increase in molecular rotatory power, amounting to 1·023. But when the addition of CH_2 is accompanied by a change in the distribution of the atomic interactions the change of Mol. R. is not constant; the change from a normal paraffin, $CH_3.nCH_2.CH_3$, to the next higher isoparaffin, $CH(CH_3)_2.nCH_2.CH_3$, raises Mol. R. by 1·023 + ·105; in the change from a normal acid to the next higher iso- acid of the same series, CH_2 has a different value; and so on. When Cl is substituted for H in a hydrocarbon the mol. rotatory power increases, but each Cl atom has a different value from the others. So with the replacement of H in a hydrocarbon by OH; each OH group has its own value, the effect on Mol. R. of the second OH being less than that of the first. So again with the group NO_3; the second NO_3 does not increase Mol. R. so much as the first.

The molecular rotatory powers of various homologous series of carbon compounds may be expressed by the general formula

(Mol. R.) = $c + n1{\cdot}023$, where n = number of atoms of C in the molecule of any stated compound in the series, and c is a constant for each series. Perkin gives the following table (*C. J.* 45, 574):—

Mol. R. of members of homologous series.

Paraffins	C_nH_{2n+2}	·508 + n1·023
„ iso-	„	·621 „
Alcohols	$C_nH_{2n+2}O$	·699 „
„ iso- and sec.	„	·844 „
Oxides	„	·642 „
„ iso-	„	·932 „
Aldehydes	$C_nH_{2n}O$	·261 „
„ iso- and ketones	„	·375 „
Acids	$C_nH_{2n}O_2$	·393 „
„ iso-	„	·509 „
Formic ethereal salts (Et, and higher)	„	·495 „
Acetic „ „	„	·370 „
„ „ „ iso-	„	·485 „
Methyl salts	„	·273 „
Ethyl „ and higher salts	„	·337 „
„ „ iso-	„	·449 „
Succinic methyl salts	$C_nH_{2n-2}O_4$	·093 „
„ ethyl „	„	·196 „
„ „ „ iso-	„	·422 „
Chlorides	$C_nH_{2n+1}Cl$	1·988 „
„ iso- and sec.	„	2·068 „
Bromides	$C_nH_{2n+1}Br$	3·816 „
„ iso- and sec.	„	3·924 „
Iodides	$C_nH_{2n+1}I$	8·011 „
„ iso- and sec.	„	8·099 „
Ethyl salts, unsaturated	$C_nH_{2n-2}O_2$	1·451 „

These results indicate that the molecular rotatory power of a liquid carbon compound is not the sum of certain constant values belonging to each atom or atomic group, but that it depends, to some extent, on the arrangement of the atoms which form the molecule. This result is confirmed by the outcome of attempts to assign values to the atomic rotatory powers of oxygen and carbon. The following data are given as examples of such attempts.

The atomic rotatory power of hydrogen may be deduced thus:

1. Mol. R. C_nH_{2n+2} = Mol. R. $nCH_2 + H_2$; but Mol. R. $nCH_2 = n1{\cdot}023$.

The value thus deduced for At. R. of H = ·254.

2. Mol. R. C_nH_{2n+2} *minus* Mol. R. C_nH_{2n+1} = At. R. of H.

Thus, $\text{Mol. R. } C_3H_8 = 3{\cdot}577$

$$\text{Mol. R. } C_3H_7 = 3{\cdot}323 = \text{Mol. R. } \frac{C_6H_{14}}{2}$$

$$\text{At. R. of } H = \cdot 254$$

Now, At. R. of O = Mol. R. CH_2 *minus* At. R. of H × 2 = 1·023 − ·508 = ·515.

By applying similar methods to the data for compounds of O, the following results are obtained:

At. R. of O in alcoholic OH = ·194
" " carboxylic OH = ·137
" " " CO = ·261

The At. R. of Cl varies according to the series of compounds considered, and also as one or two atoms of H are replaced by one or two atoms of Cl, according as the H replaced is in one part of the molecule or in another part, and so on. Two values are obtained for At. R. of N, according as the atom of N is directly connected with 3 or 5 other atoms or groups. The general conclusion is that changes in the magnetic molecular rotatory powers of liquid carbon compounds are intimately connected with changes in molecular structure, so that any cause which alters this structure also alters the rotatory power.

In *C. J.* 61, 800, Perkin gives an elaborate study of the constitution of ethyl acetoacetate and allied compounds, which elucidates very clearly the connections between the constitution and the magnetic rotatory powers of carbon compounds.

Mol. R. of compounds in presence of water. Perkin has used determinations of Mol. R. of certain compounds before and after addition of water, to throw light on the question whether hydrates are formed by the action of water on these compounds (*C. J.* 49, 777; 51, 808; 55, 680). In all measurements of Mol. R. the molecular rotatory power of water is taken as unity; if therefore a compound is formed by the addition of water to another compound, the Mol. R. of the new compound might be expected to be nearly equal to that of the original compound, *plus* one unit for each molecule of water added; if the observed Mol. R. is distinctly less than that calculated in this way, the difference may be explained by supposing that the formation of the new compound has been accompanied by a rearrangement of the atoms of the reacting molecules.

The following are examples of the application of this method. In each case the compound and water were mixed in the ratio shown by the formula given, and the Mol. R. of the product was determined; the Mol. R. of the product was then calculated by adding one unit for each molecule H_2O to the observed Mol. R. of the original compound without water.

Compound and water	Mol. R. observed	Mol. R. calculated for	Diff.
$HCO_2H.H_2O$	2·666	$H.CO_2H + 1 = 2{\cdot}671$	− ·005
$CH_3CO_2H.H_2O$	3·554	$CH_3CO_2H + 1 = 3{\cdot}525$	+ ·029
$C_2H_5CO_2H.H_2O$	4·512	$C_2H_5CO_2H + 1 = 4{\cdot}462$	+ ·05
$H_2SO_4.H_2O$	3·188	$H_2SO_4 + 1 = 3{\cdot}315$	− ·127
$H_2SO_4.2H_2O$	4·113	$H_2SO_4 + 2 = 5{\cdot}188$	−1·075
$H_2SO_4.3H_2O$	5·064	$H_2SO_4 + 3 = 6{\cdot}188$	−1·124
$HNO_3.2{\cdot}67H_2O$	3·656	$HNO_3 + 2{\cdot}67 = 3{\cdot}85$	− ·194
$CCl_3.CHO.H_2O$	7·037	$CCl_3.CHO + 1 = 7{\cdot}591$	− ·554

Perkin thinks that when water is added to formic, acetic, and propionic acids in the ratio of equal molecules of water and acid, either a hydrate or a mixture is formed in each case; but that when H_2SO_4 and H_2O react in about the ratio $H_2SO_4{:}H_2O$ (or a little more H_2O than this), a rearrangement of atoms occurs with formation of a new compound of S, O, and H (perhaps $SO(OH)_4$); and that reactions of this nature, involving rearrangements of atoms, also occur between HNO_3 and H_2O, and $CCl_3.CHO$ and H_2O.

The following data are interpreted by Perkin to mean that a solution of NH_3 in water, or in alcohol, 'simply consists of the solvent and ammonia':

$$\text{Mol. R. } NH_3 + 2{\cdot}1H_2O = 3{\cdot}91$$
$$\text{"} \quad 2{\cdot}1H_2O = 2{\cdot}1$$
$$\text{"} \quad NH_3 \quad 1{\cdot}81$$
$$\text{Mol. R. } NH_3 + 2{\cdot}18C_2H_6O = 7{\cdot}886$$
$$\text{"} \quad 2{\cdot}18C_2H_6O = 6{\cdot}06$$
$$\overline{1{\cdot}826}$$

Mol. R. of acids and salts in aqueous solutions. Perkin (*C. J.* 55, 680; 59, 981) gives Mol. R. for HCl as 2·187. This is arrived at by finding values for At. R. of H and Cl from observations of Mol. R. of various chlorides of alcoholic radicles. By similar methods of calculation values for Mol. R. of HBr and HI were obtained. The three results are:

Mol. R. HCl = 2·187
" HBr = 4·016
" HI = 8·211

The value for HCl was confirmed by measuring Mol. R. of HCl dissolved in isoamyl oxide; the result was Mol. R. HCl = 2·24.

Values were then obtained for the three acids in aqueous solutions. The numbers increased as dilution increased; in any case they were much larger than the values obtained by the method stated above. The following table gives the minimum and maximum values for each acid:

Mol. R. in aqueous solutions.	Maximum.	Minimum.
HCl	4·419 (15·63 p.c. HCl)	4·045 (41·7 p.c. HCl)
HBr	8·519 (15·47 p.c. HBr)	7·669 (65·99 p.c. HBr)
HI	18·451 (31·77 p.c. HI)	17·769 (67·02 p.c. HI)

It is evident that the magnetic mol. rotatory powers of HCl, HBr, and HI in aqueous solutions are much greater than the values calculated from those obtained for the same three acids from observations made with compounds of them with C and H; in the case of HCl, the value of Mol. R. in aqueous solution is much greater than the value for the same compound in solution in isoamyl oxide. There must be an action of some kind between water and these three compounds.

It has been shown already that addition of water to H_2SO_4 results in a value for the Mol. R. of the acid different from that observed for the pure acid itself; but in this case addition of water reduces the Mol. R. of the acid. A similar reducing effect was noticed as accompanying the addition of water to HNO_3.

Perkin was unable to explain these results. Ostwald, however, has shown that they are in keeping with the electrolytic dissociation hypothesis (*C. J.* 59, 198). According to this hypothesis strong acids are dissociated in aqueous solutions into their ions. Aqueous solutions of HCl, HBr, and HI, contain the ions $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{Cl}}$, $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{Br}}$, and $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{I}}$, each with its electric charge. The observed rotatory powers of these solutions, *minus* the value for the water contained in them, therefore represent the rotatory powers of these ions, and not of the compounds themselves; and the rotatory powers of these ions are considerably greater than those of the non-dissociated compounds. An aqueous solution of H_2SO_4, or HNO_3, must also contain dissociated, electrically charged, ions—according to the hypothesis; but Perkin's observations (*ante*, p. 259) show that the rotatory powers of the ions of these acids are slightly smaller than those of the acids themselves.

Now, the hypothesis of electrolytic dissociation asserts that the metallic salts of acids are dissociated into electrically charged ions in dilute aqueous solutions; hence determinations of Mol. R. for aqueous solutions of metallic salts of HCl, HBr, HI, H_2SO_4, and HNO_3 ought to give results different from the values obtained for these salts themselves. But the values obtained for aqueous solutions of salts of HCl, HBr, and HI ought, on the whole, to be greater than the calculated values, whereas the values obtained for salts of H_2SO_4 and HNO_3 ought, generally, to be slightly smaller than the calculated values. This deduction is partly confirmed by Perkin's results.

The values of Mol. R. for NH_4Cl is calculated by Perkin as follows (*C. J.* 55, 743). The value for HCl is found from determinations of Mol. R. of alcoholic chlorides, which enable values to be found for H and Cl in combination; the value for NH_3 is taken as 1·818, which is the mean of the values found from observations on NH_3 in water and alcohol (*ante*, p. 259); the sum of the values for HCl and NH_3, with the subtraction of ·5, gives the calculated Mol. R. of NH_4Cl. The number ·5 is taken from the sum of the values for HCl and NH_3 because observation has shown that this is about the difference between the values for N^{III} and N^{V}, and in NH_3 the N atom is trivalent, while in NH_4Cl it is supposed to be pentavalent. The values for the other salts of NH_4 are calculated in a similar way. Perkin's results for Mol. R. of NH_4I, NH_4Br, and NH_4I show that practically the same values are obtained for solutions containing from c. 30 to c. 60 p.c. of the salts. The results with the six salts were as follows:

—	Calculated	Observed, in aqueous solutions	Differences
NH_4Cl	4·305	6·096	+ 1·791
NH_4Br	6·096	7·997	+ 1·901
NH_4I	8·149	9·896	+ 1·747
NH_4NO_3	2·298	2·320	+ ·022
NH_4HSO_4	3·433	3·455	+ ·022
$(NH_4)_2SO_4$	4·551	4·980	+ ·439

With regard to NH_4NO_3 and the two sulphates, it is to be observed that the calculated values are found by adding the values for the acid and the base (NH_3), then deducting ·5 for the change of N^{III} to N^{V}, and then deducting ·2 for the change from the free acid and base to the combination of these compounds; now, ·5 is merely an approximate value for the change from N^{III} to N^{V}, and ·2 is also merely a rough approximation for the value of the process of combination of acid and base. As the differences between the observed and calculated values for NH_4Cl, NH_4Br, and NH_4I are large, small errors in the method of calculating Mol. R. for these compounds do not materially affect the differences in question; but as the differences are small in the cases of the nitrate and sulphates, small errors in the method of calculating Mol. R. for these compounds do materially affect those differences. Moreover, the observations of Mol. R. of the nitrate and the sulphates of ammonium in aqueous solutions were made with a single solution in each case (59·7 p.c. NH_4NO_3, 66·6 p.c. NH_4HSO_4, and 40 p.c. $(NH_4)_2SO_4$); hence it is not certain that the numbers set down as the values of Mol. R. of these compounds in aqueous solutions are the true values.

Perkin has also (*C. J.* 59, 981) made measurements of the magnetic mol. rotatory powers of the ammonium salts of formic, acetic, and propionic acids in aqueous solutions, and compared the results with the values calculated. He gives the results as follows:

—	Observed, in aqueous solution	Calculated	Differences
Ammonium formate	3·363	3·489	− ·126
" acetate	4·247	4·343	− ·096
" propionate	5·259	5·280	− ·021

The interpretation which the electrolytic dissociation hypothesis gives of these results is that, as in their aqueous solutions the salts examined are dissociated into their ions, and as the observed results are smaller than the calculated values, therefore the magnetic mol. rotations of the ions of HCO_2H, CH_3CO_2H, and $C_2H_5CO_2H$ are slightly less than the rotations of the acids themselves (*v.* Ostwald, *Z. P. C.* 9, 513; *cf.* Ostwald, *C. J.* 59, 201).

But it seems to me that the numbers given by Perkin as the calculated values of Mol. R. for the three salts cannot be accepted as correct. For these values were found by adding the values of Mol. R. for the free acids to the value for free NH_3; no deduction was made for the change of rotation accompanying the combination of the acid and the base, and no deduction was made for the change of N^{III} to N^{V}. Either these values cannot be accepted as the true values, or the values calculated for the salts of NH_4 with the halogen acids, and with HNO_3 and H_2SO_4, are not correct (*ante*, p. 260). If the values of Mol. R. for the salts of formic acid &c. are calculated by the same method as was used in the cases of the other salts of ammonium, then the results of this investigation are as follows:

—	Observed in aqueous solution	Calculated	Differences
Ammonium formate	3·363	2·789	+·574
„ acetate	4·247	3·643	+·604
„ propionate	5·259	4·580	+·679

If these results are accepted, then the differences are much greater than those given by Perkin, and they are in the opposite direction.

Measurements of the Mol. R. of formic, acetic, and propionic acid in aqueous solution would enable the question to be settled as to the effect of water on these acids; at present it seems that the magnetic rotations of the ions of these acids would be found to be greater than the rotations of the acids themselves.

This conclusion is confirmed by combining the results obtained by Perkin (*C. J.* 59, 986) for Mol. R. of sodium salts of formic and other acids with the value calculated by him for sodium (*C. J. Proc.* 1890. 141). In the following table I have calculated the values for the salts as Perkin calculated the values for NH_4Cl, NH_4NO_3 &c., by deducting ·2 from the sum of Mol. R. of acid and At. R. of Na, and then further deducting ·254 for the loss of H:

	Observed in aqueous solution	Calculated	Differences
Sodium formate . .	2·347	1·775	+·572
„ acetate . .	3·281	2·629	+·652
„ propionate .	4·308	3·566	+·742
„ butyrate. .	5·332	4·576	+·756

In a more recent communication (*C. J.* 63, 57) Perkin gives the Mol. R.s of aqueous solutions of H_2SO_4, HNO_3, Na_2SO_4, and $LiNO_3$ of varying degrees of concentration. His results show that the Mol. R.s of these solutions do not vary with dilution in the same way as the electrical conductivities vary. The most dilute solution of H_2SO_4 examined by P. contained c. 9·2 p.c. H_2SO_4, and the most dilute solution of HNO_3 contained c. 22·5 p.c. HNO_3. Now it has been shown repeatedly, by Ostwald and others, that measurements of the conductivities of fairly conc. solutions of acids and salts cannot lead to just conclusions regarding the amount of electrolytic dissociation of the compounds in solution; hence it is not to be expected that the amount of dissociation of H_2SO_4 and HNO_3 should be calculable from the Mol. R.s of these compounds as deduced from observations on solutions so concentrated as those used by Perkin. What the observations of P. show is that the magnetic rotations of certain compounds diverge from the calculated results in all cases wherein electrolytic dissociation occurs. The laws which express the electric dissociation of compounds are to be deduced from the study of very dilute solutions, and as no measurements of magnetic rotations have yet been made for such solutions, it is not justifiable to draw detailed quantitative conclusions concerning the electrolytic dissociations of compounds from the measurements of the magnetic rotations of those compounds which P. has made.
M. M. P. M.

VIII. OSMOTIC PRESSURE, METHODS BASED ON; *v.* MOLECULAR WEIGHTS, vol. iii. p. 418; and ELECTRICAL METHODS, this vol. p. 185.

IX. PHOTOGRAPHIC METHODS; *v.* PHOTOGRAPHIC CHEMISTRY, this vol. p. 154.

X. SPECIFIC HEATS OF SOLIDS, METHODS BASED ON; *v.* ATOMIC AND MOLECULAR WEIGHTS, vol. i. p. 342.

XI. THERMAL METHODS. Determinations of the quantities of heat which are produced, or which disappear, in chemical reactions help to elucidate the nature of these reactions. There are two sides to every chemical operation; there is a change in the form or distribution of matter, and a change in the form or distribution of energy. Light is thrown on the second of these changes by thermo-chemical investigations, and the connections between the two parts of the complete occurrence, and the mutual dependence of both, are thus made clearer. Thermo-chemical methods rest on the principle of the conservation of energy. When a chemical reaction occurs, heat may be produced, electricity generated, mechanical work done by expansion, and sound or radiant heat may leave the system; the sum of these forms of energy, added to the energy remaining in the system at the close of the reaction, must equal the energy originally present in the system at the moment when the change began. As a large part of the energy set free during any chemical reaction usually takes the form of heat, it follows that measurements of the heat produced during the reaction must give information regarding the differences between the initial and final energies of the system. The primary aim of thermo-chemical measurements is to determine such energy-differences; the secondary aim is to connect these differences with the differences of composition, constitution, and properties which the reacting systems undergo.

The loss or gain of energy which accompanies the passage of a system from one defined state to another is independent of any intermediate states through which the system may pass. This generalisation was proved experimentally for several cases, so far as heat energy was concerned, by Hess in 1840 (*P.* 50, 385); the generalisation may be deduced from the principles of energy. On this statement rest the methods for determining the thermal values of chemical changes when these values cannot be observed directly.

Notation used in thermo-chemistry. Thomsen's notation is followed in this DICTIONARY; the formulæ of the reacting substances are taken to represent grams of these substances—thus HCl means 36·5 g. of hydrogen chloride; the formulæ are inclosed in a square bracket, and the figures representing the number of atoms of each element are placed above the symbols; the reacting substances are separated by a comma. The unit of heat is that quantity which raises the temperature of 1 g. of water at c. 18° through 1°. Ostwald, in his *Lehrbuch der Allgemeinen Chemie*, employs a unit almost exactly 100 times greater than this, viz. the quantity of heat given out by 1 g. of water in cooling from 100° to 0°. The symbol Aq means that a large quantity of water is present. Thus [H,Cl] = 22,000 means that 22,000 gram-units of heat are produced when 1 g. H combines with 35·5 g. Cl; [H,Cl,Aq] = 30,660 means that 30,660 gram-units of heat are produced when 1 g. of H combines with 35·5 g. of Cl in presence of a large quantity of water in which the HCl dissolves; [HCl,Aq] = 17,320 means that 17,320 gram-units of heat are produced when 36·5 g. of HCl dissolve in a large quantity of water; and [HClAq,KOHAq] = 13,750 means that the neutralisation of 36·5 g. HCl, dissolved in much water, by 56 g. KOH, dissolved in much water, the products of neutralisation being allowed to remain in solution, is accompanied by the production of 13,750 gram-units of heat. The symbol H_2O is used as in ordinary notation to represent 18 g. of water; thus $[As^2O^5,3H^2O] = 6,800$ means that 6,800 gram-units of heat are produced during the formation of 284 g. H_3AsO_4 by the combination of 230 g. As_2O_5 with 54 g. water; and $[As^2O^5.3H_2O,Aq] = -800$ means that 800 gram-units of heat disappear during the solution of 284 g. H_3AsO_4 in a large quantity of water. Thomsen's notation does not indicate the products of the reaction, the thermal value of which is set down; nor does it show the physical states of the reacting substances, or of the products of the reaction, except in the one case when the substances are dissolved in much water. Ostwald (*Lehrbuch*) uses the ordinary notation, and adds figures to express the quantities of heat which are produced or disappear in the reactions; he employs ordinary type for liquids, thick type for solids, and italics for gases. Thus, $H_2 + Cl_2 = 2HCl + 44,000$ means that 44,000 gram-units of heat are produced when 2 g. gaseous hydrogen combine with 2 × 35·5 g. gaseous chlorine to form 2 × 36·5 g. gaseous hydrogen chloride; $2H_2S + 2\mathbf{I}_2 = 4HI + 2\mathbf{S} - 34,000$ means that 34,000 gram-units of heat disappear when 2 × 34 g. gaseous hydrogen sulphide react with 2 × 254 g. solid iodine to form 4 × 128 g. gaseous hydrogen iodide and 2 × 32 g. solid sulphur; and $2\mathrm{H_2SAq} + 2\mathrm{I_2Aq} = 4\mathrm{HIAq} + 2\mathbf{S} + 34,000$ means that 34,000 gram-units of heat are produced when 2 × 34 g. hydrogen sulphide dissolved in much water react with 2 × 254 g. iodine dissolved in much water, to form a dilute aqueous solution of 4 × 128 g. hydrogen iodide, and 2 × 32 g. solid sulphur. Ostwald sometimes indicates the temperature by figures in brackets placed after the formulæ of the substances: thus, $\mathrm{H_2O}_{(0)} = \mathbf{H_2O}_{(0)} + 1440$ means that 1440 gram-units of heat are produced when 18 g. liquid water at 0° become 18 g. solid water at the same temperature.

Measurements of thermal values of chemical changes. The quantities of heat produced during chemical processes are measured by causing the processes to take place in vessels arranged so that the whole of the heat is used in raising the temperature of known masses of water, or of water and a solution the specific heat of which is known. When the process consists in a reaction between substances in aqueous solutions, the calorimeter employed usually consists of a vessel of platinum holding 500 to 1000 c.c. placed inside another vessel of silver, or thin sheet iron, with water between the two vessels. The reacting liquids are brought to the same temperature, and are then mixed in the platinum vessel, and the rise of temperature of the contents of this vessel is noted, any change in the temperature of the outside water being also measured. When the thermal value of a process of combustion is to be determined, the combustion is caused to proceed in a vessel, usually made of platinum, surrounded by a determinate quantity of water; if the products of combustion are gases, an apparatus is attached wherein these gases are absorbed, and thus the quantity of substance burnt is determined.[1]

To calculate the thermal value of a reaction, it is necessary to know the initial temperatures of the reacting bodies, the final temperatures of the products of reaction, the masses of the reacting substances, the specific heat of water, the specific heat of the liquid formed by the reaction if the reaction be one wherein a solution is produced, and the water-equivalent of the calorimeter. The water-equivalent of the calorimeter must be determined; it is equal to the number of unit-weights of water which would be raised to the same temperature as that to which the calorimeter and its accessories—thermometer, stirrer, &c.—are raised by the heat produced in the process. When dilute solutions of acids and alkalis, or similar compounds, react, the specific heat of the dilute salt-solutions produced may be taken as equal to the specific heat of the water they contain, without appreciable errors.

Let Q be the quantity of heat produced in a reaction between two solutions; let t be the initial temperature of one solution, t' the initial temperature of the other solution, and T the final temperature of the solution produced; further, let a be the calorimetric equivalent of one solution, *i.e.* mass × spec. heat, b the calorimetric equivalent of the other solution, and c the water-equivalent of the calorimeter; then

$$Q = (T - t)a + (T - t')(b + c).$$

In the cases of dilute aqueous solutions, a and b represent the masses of water in the solutions mixed. If a change occurs in the state of aggregation of some of the constituents of the reacting system, *e.g.* if liquid water is formed from gaseous hydrogen and oxygen, the quantity of heat which is produced or disappears in this change must be taken into account in the calculation of the thermal value of the reaction. If contraction or expansion occurs, without change of state, the thermal value of such contraction or expansion must be determined and allowed for.[2]

Heats of combustion, and of formation, of compounds. The heat of combustion of an element or compound is the thermal value of the reaction which takes place when that element or compound is completely oxidised to those masses of the product, or products, of oxidation which are represented by the formulæ of these products. Thus [H^2,O] = 68,360; [CO,O] = 67,960. In this DICTIONARY the quantities represented by formulæ are taken in grams.

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[1] For references to descriptions of calorimetrical apparatus *v. References*, p. 268.

[2] For methods of calculating Q at one temperature when it is known at another temperature, *v. TA.* 1, 60-78.

The heat of formation of a compound is the thermal value of the reaction whereby the formula-weight of the compound is produced from the formula-weights of its constituents. Thus, the heat of formation of H$_2$SO$_4$ varies according to the constituents from which it is produced; we have the following statements: [SO^3,H^{2}O] = 21,320; [SO^2,O,H^{2}O] = 53,480; [SO^2,O^2,H^2] = 121,840; [S,O^3,H^{2}O] = 124,560; [S,O^4,H^2] = 192,920.

It is often practicable to measure heats of combustion directly; but in very many cases it is necessary to determine heats of formation by indirect methods. These indirect methods rest on the principle, deduced from the laws of energy, that the total change of energy, and therefore the total thermal change, which accompanies the passage of any system from a definite initial composition to a definite final composition is independent of the intermediate states. Suppose that a system changes from a certain arrangement or configuration A to another configuration B, and that x units of heat are produced in this change. Suppose also that the same initial system then passes from the state A to a new state a, from that to b, from that to c, and, lastly, from that to B, and that there are x' units of heat produced in the first of those intermediate changes, x'' units produced in the second, and x''' units in the third; then $x - (x' + x'' + x''')$ gives the thermal value of the change from the state c to the state B. If then the thermal value of a chemical process, whether the formation of a compound, or other process, cannot be determined by direct measurement, it may be determined if the process can be made a portion of a series of changes, the total thermal value of which is measurable, and the thermal values of all the portions of which are measurable with the exception of the value of that portion which is sought.

For instance, formic acid, CH$_2$O$_2$, cannot be directly produced from C, H, and O, and, therefore, the heat of formation of this acid cannot be determined by direct measurement; but C and H can be burnt to CO$_2$ and H$_2$O, and CH$_2$O$_2$ can also be burnt to CO$_2$ and H$_2$O; hence we can acquire the data needed for calculating the value of [C,H^2,O^2]. The data are these: [C,O^2] = 96,960; [H^2,O] = 68,360; sum = 165,320; [CH^{2}O^2,O] = 65,900. Now, suppose that the first stage of the combustion of C and H$_2$ consists in the formation of CH$_2$O$_2$, and that this is then burnt to CO$_2$ and H$_2$O, we should have the statement: [C,O^2] + [H^2,O] = [C,H^2,O^2] + [CH^{2}O^2,O] = 165,320. But [CH^{2}O^2,O] = 65,900; and also [C,O^2] + [H^2,O] − [CH^{2}O^2,O] = [C,H^2,O^2]. Hence [C,H^2,O^2] = 165,320 − 65,900 = 99,420.

Another example will show the application of the principle to a more complicated case. It is required to find the heat of formation of gaseous hydrogen bromide from gaseous H and Br, *i.e.* the thermal value of the reaction H + Br = HBr. To begin with: let [H,Br,Aq] = x, and let [H,Br] = x'; direct measurement gives [HBr,Aq] = 19,900. ∴ x − 19,900 = x' = heat of formation of HBr. Hence it is necessary to determine x.

Now, the thermal values of the neutralisation of HClAq and HBrAq respectively by KOHAq are found to be the same, *i.e.* [KOHAq,HClAq] = [KOHAq,HBrAq]. If these reactions are analysed, the first is seen to consist in (1) the splitting of HClAq into H and Cl in presence of water; (2) the separation of KOHAq into K, O, and H in presence of water; (3) the combination of K and Cl, in presence of water, to form KClAq; (4) the combination of H, H, and O, in presence of water, to form water; and the second is similar to this, only putting Br in place of Cl. These reactions may be stated in thermo-chemical notation thus:

(1) [KOHAq,HClAq] = − [K,O,H,Aq] − [H,Cl,Aq] + [K,Cl,Aq] + [H,H,O,Aq];
(2) [KOHAq,HBrAq] = − [K,O,H,Aq] − [H,Br,Aq] + [K,Br,Aq] + [H,H,O,Aq].

The first and fourth terms on the right side are the same, and the total thermal values are the same. Are the values of the second and third terms the same? To answer this question we pass Cl into KBrAq, forming KClAq and BrAq, and measure the thermal disturbance; we then analyse the reaction, and see what information it has afforded. These are the results:

[KBrAq,Cl] = 11,500,
i.e. − [K,Br,Aq] + [K,Cl,Aq] + [Br,Aq] = 11,500.

Now, [Br,Aq] − 500, by direct measurement, ∴ − [K,Br,Aq] + [K,Cl,Aq] 11,000, *i.e.* to form KCl, in solution, from K and Cl produces 11,000 units of heat more than to form KBr, in solution, from K and Br.

Now, turning back to equations (1) and (2) above, and remembering that the thermal values of these are the same, it is evident that, since 11,000 more heat-units are produced in forming KClAq than in forming KBrAq, each from its elements, 11,000 more heat-units must disappear in splitting up HCl, in presence of water, into H and Cl, in presence of water, than in similarly separating HBr into H and Br in presence of water; and therefore, since the heat energy required to decompose a stated mass of a compound is equal to the heat energy that is produced when the same mass of that compound is formed, 11,000 more heat-units will be produced in the formation of HClAq from H, Cl, and Aq than in the formation of HBrAq from H, Br, and Aq; or, stated in thermo-chemical notation: [H,Cl,Aq] − 11,000 = [H,Br,Aq]. Now [H,Cl,Aq] = 39,300 by direct measurement,

∴ [H,Br,Aq] = 39,300 − 11,000 = 28,300.

At the beginning of this calculation we had [H,Br,Aq] − 19,900 = [H,Br]. We can now substitute the value of [H,Br,Aq], and write [H,Br] = 28,300 − 19,900 = 8,400. That is to say, 8,400 gram-units of heat are produced when 81 g. gaseous hydrogen bromide are formed from 1 g. gaseous hydrogen and 80 g. gaseous bromine.

Exothermic and endothermic reactions. Chemical changes which are accompanied by production of heat are sometimes classed together as exothermic reactions, and are distinguished from changes accompanied by disappearance of heat, which changes are called endothermic reactions. The terms endothermic and exothermic are sometimes useful. It should not be forgotten that most chemical reactions consist of portions which are exothermic and portions which are endothermic. Substances which are formed with the disappearance of heat are generally more readily decomposed by the application of outside forces than substances which are formed with the production of heat.

Interpretation of thermo-chemical measurements. Thermo-chemical measurements aim at determining the quantities of heat which are produced or disappear during definite and defined chemical changes. But every chemical change is inextricably bound up with more or less extensive physical changes; hence some portion of the thermal value of a chemical occurrence is always due to a process which is not, strictly speaking, chemical. A purely chemical change is a change in the distributions, configurations, and motions of atoms. But in only some cases are we able to form clear conceptions as to the configurations and motions of atoms; therefore, even if it were possible always to disentangle the purely chemical from the accompanying physical parts of a change, we should still very frequently be unable to connect the thermal values of purely chemical processes, in a clear and definite way, with measurable changes in the distributions, configurations, and motions of atoms.

The heats of formation of HCl, HBr, and HI are said to be 22,000, 8,440, and −6,050 gram-units respectively. But these thermal values are not strictly comparable, because the first represents the heat produced in forming gaseous HCl from gaseous H and Cl; the second represents the heat produced in forming gaseous HBr from gaseous H and liquid Br, and the third represents the heat which disappears when gaseous HI is formed from gaseous H and solid I. In other words, more heat is used in the second change than in the first, and still more in the third than in the second, in accomplishing subsidiary physical changes. Steam is decomposed by chlorine, with formation of hydrogen chloride and oxygen. All the reacting substances are gases. This change, which is stated in formulæ as $2H_2O + 2Cl_2 = 4HCl + O_2$, when analysed thermo-chemically, is found to consist of four parts, thus: $[2H^2O,2Cl^2]$

$$= -2[H,H,O] - 2[Cl,Cl] + [O,O] + 4[H,Cl].$$

We measure the thermal value of this complete change, but we cannot at present separate the portions of the change and assign to each its proper thermal equivalent; hence we cannot give a complete explanation of the thermo-chemical measurement we have made.

Notwithstanding these difficulties, attempts have been made to generalise from thermo-chemical measurements to statements of universal applicability. The most widely known of such attempts is that which finds expression in Berthelot's '*law of maximum work*.'[1] This so-called law asserts that '*Every chemical change accomplished without the addition of energy from without tends to the formation of that body, or system of bodies, the production of which is accompanied by the development of the maximum quantity of heat.*' In another place Berthelot states the law more rigidly, thus: '*Every chemical change which can be accomplished without the aid of a preliminary action, or the addition of energy from without the system, necessarily occurs if it is accompanied by disengagement of heat.*'

The same generalisation was stated by Thomsen (*v. Th.* 1, 12–16) some years before it was enunciated by Berthelot. Thomsen's statement took this form: '*Every simple or complex reaction of a purely chemical kind is accompanied by production of heat.*' None of these statements is strictly applicable to actually occurring chemical changes, because we never have to deal with reactions of a purely chemical kind, but with reactions that are partly chemical and partly physical—that is, with reactions which consist in part in changes in the arrangement and motions of atoms, and partly in changes in the arrangement and motions of molecules. A consideration of the way in which the so-called law is applied, especially by Berthelot and his school, shows that it is taken to mean that measurements of the thermal values of various possible chemical changes enable us to predict which of these will occur. Thus, suppose we start with a system $A + B + C$, and suppose that from this may be formed $AB + C$, $AC + B$, or ABC; suppose also that x thermal units are produced in the first of these changes, x' thermal units in the second, and x'' thermal units in the third; finally, suppose that $x'' > x' > x$; then the law of maximum work is taken as asserting that the reaction $A + B + C = ABC$ will occur, and will occur to the complete, or almost complete, exclusion of the two other possible reactions.

It is easy to show that many reactions are known to occur which would be impossible were this 'law' a true generalisation. But it is better to treat the law as a deduction from the principles of energy, and to show that it is not a warrantable deduction.

The statements made by Thomsen and Berthelot are true only when an arbitrary separation is made of chemical changes into two parts, and one of these parts is alone called chemical. Every chemical change, however simple, consists of at least two parts, the first of which is the necessary antecedent of the second; the 'law of maximum work' ignores this duality, or, it might be more accurate to say, the law assumes that the second part of a chemical process may occur without the first. A process of chemical change may be compared to the flight of a stone from, and its return to, the surface of the earth. During the first part of this process there is a continual transference of kinetic energy from the moving stone to the surrounding medium and during the second part there is a continual transference from the medium to the stone, until the stone comes to rest, when its energy becomes a part of the total energy of the system earth *plus* stone. If the final resting-place of the stone is nearer the centre of the earth than the spot from which it was projected in its upward flight, then the stone contains less energy, relatively to surrounding systems, at the close of the transaction than at the beginning. On the other hand, if the starting-point is nearer the earth's centre than the final point of rest, then the transaction has resulted in a gain of energy to the stone. In both cases the second part of the transaction, that which occurs between the turning-point and the coming to rest of the stone, is attended with loss of energy to the stone; but this second part does not represent the complete transaction. The 'law of maximum work,' if applicable at all, is applicable only to the second part. And, moreover, this law ignores the fact that the stone, or chemical system, does not leave its initial resting-place of its own accord; the law assumes that no work need be done, no energy need be expended, in the passage of the stone, or chemical system, from its original position to that whereat the energy-relations between it and surrounding systems come within the cognisance of the law.

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[1] *Mécanique Chimique*, i. xxix.

The 'law of maximum work' asserts a certain condition of equilibrium for a chemical system, for the law states that equilibrium results when that change has occurred which is attended with the maximum production of heat. But the true condition of equilibrium of a material system undergoing a reversible change is laid down in the statement that equilibrium results when the *entropy* of the system has attained the maximum value under the conditions which prevail.

Let Q = quantity of heat added to a body at constant temperature T, then $\frac{Q}{T}$ = gain of entropy to the body; let Q_1 = quantity of heat lost by a body at constant temperature T_1, then $\frac{Q_1}{T_1}$ = loss of entropy to the body. All chemical and physical changes which occur spontaneously increase the entropy of the system. This statement holds good for non-reversible changes; and as no actually occurring change is completely reversible, the statement holds for all changes.

Suppose that one of two bodies is hotter than the other and loses heat to the colder body; the hotter body at temperature T_1 loses heat Q, therefore its entropy is diminished by $\frac{Q}{T_1}$; the colder body at temperature T_2 gains heat Q, therefore its entropy is increased by $\frac{Q}{T_2}$; but as $T_1 > T_2$, it follows that $\frac{Q}{T_1} < \frac{Q}{T_2}$; in other words, the entropy of the system is increased by the passage of heat from the hotter to the colder body.

Now, a system is in equilibrium when its entropy has attained the maximum value possible under the conditions. But, inasmuch as entropy is measured by a quantity of heat divided by a temperature, it is only at the absolute zero of temperature that $dS = dQ$ (S = entropy, Q = quantity of heat); hence it is only at the absolute zero that thermal changes directly measure changes of entropy. When a chemical change is accompanied by the production of much heat, and the change occurs at a low temperature, the thermal change will roughly measure the change of entropy; therefore, if such a change be possible, it will occur. But if the quantity of heat produced in a chemical process is small, the change of entropy may be conditioned, to a large extent, by changes other than the thermal change. Indeed, in some cases, heat may disappear from the system, and yet the total change of entropy may be positive; in such cases, chemical change will occur with the disappearance of heat, because the decrease in the entropy of the system caused by the loss of heat will be more than balanced by the increase in the entropy caused by the changes of state which the system undergoes.

The general conception of chemical change which is given by applying the law of entropy is that of a system attaining equilibrium as the result of processes taking place in opposite directions. According to van't Hoff (*Dynamique Chimique*, 153), the directions of chemical processes which result in equilibrium vary with variations of temperature in such a way that the lower the temperature the more is equilibrium established with the production of heat, but the changes can take place wholly in one direction only at the absolute zero. The 'law of maximum work' would then hold good for the limiting case that the change should occur at −273°. As the temperatures at which most chemical changes occur are not very high, many chemical processes are accompanied by production of heat.

The 'law of maximum work' is not, then, a law of nature. But it is true that most chemical processes which occur without the expenditure of much energy from without, and which take place at moderate temperatures, are accompanied by the disengagement of heat. If it is known that a certain chemical change would be attended by the disappearance of much heat, we may conclude that this change will be difficult to accomplish; that it will be brought about only by the expenditure of a considerable quantity of energy, and that the most successful way of accomplishing the change will be to make it one part of a series of changes the sum of which is attended with the disengagement of heat.

Applications of thermo-chemical methods. The applications of thermo-chemical methods are many and varied. A few of the more important will be briefly dealt with here.

Neutralisation of acids and bases. In 1842 Hess stated the principle of the *thermo-neutrality* of salts in solutions (*P.* 52, 79). He said that when aqueous solutions of two normal salts are mixed the thermal disturbance is *nil*; in other words, that the thermal value of the reactions consisting in the exchange of the acids and bases is equal to zero. Hess supposed that the heats of neutralisation of acids were independent of the nature of the bases used. Andrews (*P.* 54, 208; 59, 428) thought that the heats of neutralisation were dependent only on the bases, and were independent of the nature of the acid employed. Favre a. Silbermann (*A. Ch.* [3] 34, 357; 36, 1; 37, 406) put the law of thermo-neutrality in its proper form by showing that the differences between the heats of neutralisation of any two bases by any acid have a constant value, and the differences between the heats of neutralisation of two acids by any base are constant. Let the composition of various salts be represented by the scheme:

$A+B$	$A'+B$	$A''+B$	$A'''+B$
$A+B'$	$A'+B'$	$A''+B'$	$A'''+B'$
$A+B''$	$A'+B''$	$A''+B''$	$A'''+B''$
$A+B'''$	$A'+B'''$	$A''+B'''$	$A'''+B'''$

And let $f(A+B)$, $f(A'+B)$, &c., represent the quantities of heat produced by the union of the acid A with the base B, the acid A′ with the base

B, &c. Then the law of thermo-neutrality asserts that

$$f(A+B)+f(A'+B')-f(A+B')-f(A'+B)=0$$
or $$f(A+B)-f(A+B')=f(A'+B)-f(A'+B')$$
and $$f(A+B)-f(A'+B)=f(A+B')-f(A'+B')$$

Exceptions have been found to this law, but these exceptions have all proved to be connected with some abnormality in the behaviour of the salts formed. The law may be stated by saying that, in the normal formation of a salt, in solution, by the reaction between an acid and a base, the acid contributes a definite portion of the total heat of neutralisation, independently of the nature of the base, and the base contributes a definite portion of the total heat of neutralisation, independently of the nature of the acid. If the statement is correct, then the heat of neutralisation of an acid, in solution, must be independent of the nature of the base, and the heat of neutralisation of a base, in solution, must be independent of the nature of the acid, unless there be some divergence from the normal condition of affairs. By the *heat of neutralisation* of an acid is meant the quantity of heat produced when an equivalent weight of the acid reacts with an equivalent weight of a base, both being in *dilute* aqueous solution. If A′ represents a formula-weight of a monobasic acid, A″ a formula-weight of a dibasic, and A‴ a formula-weight of a tribasic, acid; and if B represents a formula-weight of a mono-acid base; then the heats of neutralisation of these three acids are the thermal values of the reactions, [A′Aq,BAq] ; [$\frac{1}{2}$A″Aq,BAq] ; and [$\frac{1}{3}$A‴Aq,BAq]. Sometimes it is more convenient to take the thermal values of the reactions [A″Aq,2BAq] and [A‴Aq,3BAq] to represent the heats of neutralisation of the dibasic and tribasic acids respectively.

The following table, taken chiefly from Thomsen's results, shows that the heats of neutralisation of the strong acids are practically independent of the base, provided the base used is strong; the numbers all refer to reactions between dilute solutions of the acids and bases:—

Acid	NaOH	KOH	LiOH	TlOH	$\frac{1}{2}BaO_2H_2$	$\frac{1}{2}CaO_2H_2$	$\frac{1}{2}SrO_2H_2$	$\frac{1}{2}Pt(NH_3)_4(OH)_2$	$S(C_2H_5)_3OH$	$N(CH_3)_4OH$
HCl	13,300	13,300	13,300	13,300	13,300	13,300	13,300	13,600	13,700	13,600
HBr	13,300	13,300	—	—	—	—	—	—	—	—
HI	13,300	13,300	—	—	—	—	—	—	—	—
HNO_3	13,500	13,500	—	13,500	14,000	13,900	—	—	—	—
$HClO_3$	13,600	13,600	—	—	14,000	—	—	—	—	—
$HBrO_3$	13,600	13,600	—	—	—	—	—	—	—	—
HIO_3	13,600	13,600	—	—	—	—	—	—	—	—
$HClO_4$	14,000	14,000	—	—	—	—	—	—	—	—
$\frac{1}{2}H_2S_2O_6$	13,500	—	—	—	13,800	—	—	—	—	—
$\frac{1}{2}H_2PtCl_6$	13,600	—	—	—	—	—	—	—	—	—
$H.C_6H_5.SO_3$	13,500	—	—	—	13,600	—	—	—	—	—

If concentrated solutions are employed, the heats of neutralisation, even of the strong acids, show considerable differences with different bases. If the salt which is formed by neutralising an acid by a base is allowed to precipitate, then the apparent heat of neutralisation as thus determined is not the true heat of neutralisation (*v. Th.* 1, 440). The following numbers represent the heats of neutralisation of two strong acids by weak bases; these numbers differ from one another, and also from the values given in the preceding tables in which strong acids and strong bases only were included:

Acid	NH_3	NMe_3	NH_2OH
HCl	12,200	8,700	9,200
HNO_3	12,300		

When weak acids neutralise strong bases, the thermal values differ from those obtained for strong acids; and when weak acids neutralise weak bases the reactions have different values from any of the preceding cases. The following numbers illustrate this:

Acid	NaOH (strong bases)	$\frac{1}{2}BaO_2H_2$ (strong bases)	NH_3 weak base
Weak { CO_2Aq	10,100	10,900	8,400
Weak { H_2S	7,700	7,800	6,200

The electrolytic dissociation hypothesis gives an explanation of the facts concerning the thermo-chemical reactions between acids and bases. According to this hypothesis, a dilute aqueous solution of a salt contains the ions of the salt each with its electric charge; the salt is dissociated into its ions; when two dilute salt solutions are mixed, the ions remain as they were, there is no change, and therefore heat is neither produced nor consumed. The law of thermo-neutrality holds. The hypothesis looks on a dilute aqueous solution of a strong acid, or a strong base, as containing the ions of the acid or the ions of the base; when the solutions of the strong acid and strong base are mixed, a salt is not formed in the solution, because in dilute solutions salts are wholly dissociated, but water is formed by the union of the ion H of the acid with the ion OH of the base. Thus, the composition of dilute solutions of HCl and NaOH, before and after mixing, are represented by the hypothesis as follows:

$$\underbrace{\overset{+}{Na}+\overset{-}{OH}+\overset{+}{H}+\overset{-}{Cl}}_{\text{before mixing}} \text{ and } \underbrace{\overset{+}{Na}+\overset{-}{Cl}+HOH.}_{\text{after mixing}}$$

Or, generally, if M represent the positive ion of a strong base, and A the negative ion of a strong acid; we have the composition of the dilute aqueous solutions, before and after mixing, represented by the two schemes:

$$\underbrace{\overset{+}{M}+\overset{-}{OH}+\overset{+}{H}+\overset{-}{A}}_{\text{before mixing}} \text{ and } \underbrace{\overset{+}{M}+\overset{-}{A}+HOH}_{\text{after mixing}}$$

Hence, as the only process wherein heat can be produced consists in all cases in the union of H with OH, the quantity of heat produced is always the same.

The hypothesis asserts that HOH is produced because water is a non-dissociable, or nearly a non-dissociable, compound; pure water is, approximately, a non-electrolyte.

But when a weak acid is mixed, in dilute aqueous solution, with a strong base, or when dilute solutions of a weak acid and a weak base are mixed, the processes are more complex; for, according to the hypothesis, only a portion of the weak acid is dissociated into ions, and only a portion of the base is dissociated if the base is weak. In such cases the state of matters, before and after mixing, would be represented thus (supposing both acid and base to be weak)—

$$\underbrace{HA + \overset{+}{H} + \overset{-}{A} + MOH + \overset{+}{M} + \overset{-}{OH}}_{\text{before mixing}}$$

$$\text{and}\quad \underbrace{HA + MOH + \overset{+}{M} + \overset{-}{A} + HOH}_{\text{after mixing}} \quad . \quad .$$

But the process does not necessarily stop here; there is a striving towards the formation of the comparatively non-electrolytic compound HOH, therefore more of the acid and more of the base become dissociated, so that we have, as a final condition, less or more of the acid *HA*, and less or more of the base *MOH*, *remaining in the* solution. The dissociation of the acid and the base, when these are mixed, is accompanied by a thermal change; and as the degree to which this dissociation proceeds depends on the nature of the acid and the base, the values of the heats of neutralisation of weak acids and weak bases differ one from another (*cf.* ELECTRICAL METHODS, p. 189 in this vol.).

If this treatment of the heats of neutralisation of acids and bases is accepted, it is evident that the thermal values of the neutralisations of acids by a base do not necessarily measure the affinities of these acids for that base. If the acids were all equally dissociated in solution, they would all be equally strong—or their affinities would be equal—and their heats of neutralisation would be equal. The statement Q = about 13,500 + A + B expresses the heat of neutralisation of any acid by any base in dilute aqueous solution. A represents the heat of dissociation of the acid, and B is the heat of dissociation of the base, into their ions; A and B may be positive or negative at any specified temperature. Under the conditions of the experiment only a portion of the acid, or of the base, may be dissociated; therefore the observed heat of neutralisation cannot measure the affinity of the acid for the base. But at the same time, it is evident that there is a connection between the heats of neutralisation and the affinities of acids and bases. On the one hand, measurements of the thermal values of the reactions between acids and bases enable conclusions to be drawn as to the distribution of two acids between one base, or two bases between one acid, and such measurements therefore lead to determinations of the affinities of acids and bases (*v. infra*); on the other hand, although the affinity of an acid for a base probably consists in a striving towards electrical equilibrium among the ions, yet, as electrical and thermal phenomena are closely connected, measurements of the heats of dissociation of acids and bases, in aqueous solutions, must help us to understand the relative affinities of acids and bases, to classify acids and bases in accordance with their affinities, and to connect the affinities of these substances with their constitution (*cf.* ELECTRICAL METHODS, especially pp. 208 and 209).

Monobasic and polybasic acids. When an equivalent of a monobasic acid is added to an equivalent of a base, both in dilute solutions, a certain quantity of heat is produced, and there is no further thermal disturbance on adding more of the acid to the neutral solution; but heat is either produced or disappears when a polybasic acid is added to a solution of the same acid which has been neutralised by an equivalent quantity of a base. This behaviour enables a thermo-chemical distinction to be drawn between monobasic and polybasic acids (*cf.* ACIDS, BASICITY OF, vol. i. p. 51).

Distribution of an acid between two bases. Thomsen found the following data:

$$[H^2SO^4Aq, 2NaOHAq] = 31{,}380;$$
$$[2HNO^3Aq, 2NaOHAq] = 27{,}230;$$
$$[Na^2SO^4Aq, 2HNO_3Aq] = -3{,}500.$$

Now, supposing that the reaction of equivalent quantities of Na_2SO_4 and HNO_3, in dilute solution, produced $NaNO_3$ and H_2SO_4, and these *compounds only, this reaction would be attended* by the disappearance of 31,380 − 27,230 = 4,150 thermal units; but as only 3,500 thermal units disappear in the reaction, it is evident that some change has occurred wherein heat has been produced, or that the whole of the Na_2SO_4 has not been changed to $NaNO_3$ by the reaction of the equivalent quantity of HNO_3. If we suppose that the discrepancy in the quantity of heat consumed is due to the partial decomposition of the Na_2SO_4 by the HNO_3; in other words, if we suppose that when equivalent quantities of Na_2SO_4 and HNO_3 react in solution, some of the base remains united with the H_2SO_4 and some goes into combination with the HNO_3, and that no other reaction occurs, it is easy to calculate the distribution of the base between the two acids. For it is evident that, on this supposition, $\frac{3500}{4150} = {\cdot}845$ of the quantity of Na_2SO_4 present has been decomposed. Thomsen found that H_2SO_4 reacts with Na_2SO_4 to form $NaHSO_4$, with disappearance of heat. He also found that this reaction is expressed thermo-chemically by the statement $[nH^2SO^4Aq, Na^2SO^4Aq]$

$$= 31{,}380 - \frac{n}{n + {\cdot}8}\, 3{,}300.$$

These data give a means for calculating the distribution of the base between the two acids. The complete reaction between equivalent quantities of Na_2SO_4 and HNO_3 will consist of three parts: (1) the decomposition of *a* equivalents of Na_2SO_4, attended with the disappearance of *a* . 31,380 thermal units; (2) the formation of *a* equivalents of $NaNO_3$, attended with the production of *a* . 27,230 units of heat; (3) the reaction of *a* equivalents of H_2SO_4 with $1-a$ equivalents of Na_2SO_4, attended with the disappearance of

$$1-a\,\frac{\dfrac{a}{1-a}}{\dfrac{a}{1-a}+{\cdot}8}\,3{,}300 \text{ units of heat.}$$

The complete thermo-chemical change may be stated thus:

$$[Na^2SO^4Aq, 2HNO^3Aq] = -3{,}500$$

$$= a(27{,}230 - 31{,}380) - (1-a)\,\frac{\dfrac{a}{1-a}}{\dfrac{a}{1-a} + \cdot 8}\,3{,}300.$$

Thomsen found that if a is taken as ⅔, the number −3550 is obtained, which is almost identical with the observed value. Hence Thomsen concluded that ⅔ of the base, NaOH, went to the nitric acid, and ⅓ to the sulphuric acid; or, that the affinity of nitric acid for soda (Thomsen used the term *avidity*) is twice as great as the affinity of sulphuric acid for the same base.

The relative affinities of various acids for different bases have been measured by Thomsen by this method (*v.* Affinity, vol. i. pp. 74–75).

Allotropy and isomerism. The generally accepted views regarding the allotropy of elements and the isomerism of compounds would lead us to expect that the formation of one allotropic form of an element from another form, or the formation of one isomeride from another, should be accompanied by changes of energy, and, therefore, probably by the production or disappearance of heat. This expectation is confirmed by thermo-chemical measurements. The following tables present some typical data:—

Combustion of allotropic forms of sulphur, phosphorus, and carbon.

$[S,O^2]$	to form	gaseous SO_2
71,220	for	S crystallised from CS_2
71,720	„	rhombic S
72,300	„	native opaque S

$[P^2,O^5]$	to form	solid P_2O_5
369,900	for	ordinary P
362,800	„	red P

$[C,O^2]$	to form	gaseous CO_2
96,900	for	amorphous C
93,200	„	diamond

Combustion of isomeric carbon compounds.

$[C^6H^6,O^{15}]$	to form	$6CO_2 + 3H_2O$
787,900	for	benzene
883,200	„	dipropargyl

$[C^2H^6O,O^6]$	to form	$2CO_2 + 3H_2O$
330,400	for	ethylic alcohol
344,200	„	methylic ether

$[C^3H^6O,O^8]$	to form	$3CO_2 + 3H_2O$
442,600	for	allyl alcohol
424,000	„	acetone
420,000	„	propaldehyde

These values, and many more might be given, show that the quantity of heat produced in the change from the combination of a certain number of atoms to certain other combinations of these atoms is dependent, in part, on the arrangement of the atoms in the initial combination. Isomeric molecules differ in the arrangements of their parts; and they also differ in the quantities of energy which are associated with the different atomic arrangements.

The attempts which have been made, chiefly by Thomsen (*v. Th.* vol. iv.), to connect in a definite way the thermal values of the combustion and formation of carbon compounds with the constitutions of these compounds have not led, as yet, to any very satisfactory results (*v.* also Armstrong's criticism of some of Thomsen's conclusions; *P. M.* Feb. 1887. 73).

Dissociation.—This very important branch of the subject is fully discussed in the article Dissociation in vol. ii. pp. 385–410.

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M. M. P. M.

XII. VAPOUR-PRESSURES OF SOLUTIONS, METHODS BASED ON, *v.* Molecular weights, vol. iii. p. 420; Electrical methods, this vol. p. 185; and Solutions, this vol.

XIII. VISCOSITY OF LIQUIDS. A perfect fluid, if such existed, would offer no resistance to a change of shape, and if its parts were set in motion relatively to each other by the action of any forces, the work done would be exactly equal to the kinetic energy produced. Moreover, this energy of motion would continue unchanged in amount if the fluid were then left to itself, and would not die away by being converted into heat as is the case with every known fluid. The property which causes this subsidence of relative motion is called viscosity. In consequence of the existence of viscosity a continual expenditure of energy is required to maintain the parts of a fluid in a state of steady motion relatively to each other, just as the existence of friction makes it necessary to apply a constant force to a body to keep it moving uniformly over another. From this resemblance in the two cases the viscosity of a substance is often called its internal friction.

Imagine a layer of a liquid one cm. thick, contained between two flat plates, one of which is at rest and the other is moving parallel to the first. The liquid in contact with the plate which is at rest is at rest also, and the successive layers have velocities which increase uniformly as we go towards the moving plate, so that the liquid is being sheared, and this requires a continual supply of work; which is proportional to the area and velocity of the moving plate. If this velocity is one cm. per second, the coefficient of viscosity is defined as the tangential force which must be applied per sq. cm. to the moving plate to maintain the motion, or if the relative velocity of the two surfaces is v, and their distance apart is l, the tangential force T per unit area required to maintain the motion is given by $\mathrm{T} = \eta \frac{v}{l}$ where η is the coefficient of viscosity.

From this definition it can be proved that if a circular plate or other solid of revolution be set vibrating about its axis of figure in a liquid, the amplitudes of successive vibrations will bear a constant ratio to each other, and the experimental verification of this is the best proof we have of the proportionality of the viscous forces to the relative velocity of the parts of the fluid.

The coefficient of viscosity is regarded by Maxwell (*P. M.* [4] 35, 133) as being the product of two factors, a coefficient of elasticity and a time of relaxation. If between the parallel plates spoken of above we have an elastic solid without viscosity, instead of a liquid, the result of moving one of the plates parallel to the other will be to distort the solid, and give rise to a force or stress tending to restore it to its original shape, and this force will be proportional to the amount of distortion and to the coefficient of rigidity of the body. Now, if the body is a viscous substance like pitch, the stress will soon die away, even though the surfaces be held in the new position, the molecules rearranging themselves so that this position becomes one of equilibrium. The time required for this to take place is what Maxwell called the time of relaxation. For solids it may be very large, extending to several hours or even days, but for ordinary liquids it is a small fraction of a second, while for a gas, such as air, Maxwell estimated it at the fifty thousand millionth of a second. The rate at which this internal stress is disappearing at any moment is proportional to the strain at that moment. If the upper surface is moved uniformly, relatively to the lower one, the strain will never disappear entirely, for, although the rearrangement of the molecules is continually going on andthe substance is tending towards its equilibrium state, the strain is being continually set up again by the relative motion of the two surfaces we are considering, and the body will soon get into a steady state in which the rate whereat the strain is being produced is equal to the rate whereat it is dying away. The stress produced by this constant strain is the tangential force required to maintain the motion, and Maxwell proved that this stress is proportional to the coefficient of rigidity of the substance and to the time of relaxation.

For the determination of coefficients of viscosity, Coulomb and others allowed some solid of revolution, such as a circular plate or a sphere immersed in the fluid, to vibrate about its axis of figure, and observed the ratios of the amplitudes of consecutive vibrations, from which the coefficient can be calculated. O. E. Meyer (*W.* 43, 1) modified the method by hanging a flat cylindrical box by a bifilar suspension, filling it with liquid, and observing the rate at which the vibrations died away. This method has been used by Mützel (*W.* 43, 15), and is capable of considerable accuracy. For absolute measurements it has some advantages in the fact that the lengths to be measured are not very small; but in most cases only relative values are required, and for obtaining these the transpiration method described below is preferable, as it is more readily applied, requires a smaller quantity of material, and lends itself better to accurate adjustment of temperature.

In the common form of the experiment the liquid is caused to flow through a capillary tube in consequence of a constant difference of pressure, P, between the ends, and the time, t, is observed which is required for a volume, v, to flow through the tube; then the coefficient of viscosity, η, is given by the equation $\eta = \frac{\pi}{8} \frac{\mathrm{P}r^4 t}{lv}$, where r is the radius and l is the length of the tube. Hence the coefficients for two liquids will be in the ratio of the times required for the outflow of the same volume with the same difference of pressure. If the liquid flows through the tube in consequence of its own weight, P will be proportional to its specific gravity, and the coefficients of viscosity will be proportional to the product of specific gravity and time of flow.

The formula given above assumes that the work done by the pressure is entirely converted into heat inside the tube, or, in other words, that the liquid flows out without any appreciable kinetic energy. If the tube is very long and narrow this may be taken to be the case, but generally a small correction has to be applied for the energy of the issuing fluid. The form of this correction is doubtful. Hagenbach (*P.* 109, 385) has given a formula which has been largely used, but Wilberforce (*P. M.* 1891. 407) has pointed out an error in his assumptions which makes the correction probably too small.

The coefficient of viscosity falls off very rapidly with rise of temperature, the average rate of fall for water between 0° and 10° being nearly 3 p.c. per degree, which shows the necessity for very accurate adjustment of the temperature during an experiment.

Using Maxwell's conception of the nature of viscosity, and making certain assumptions as to the way in which the rigidity and the time of relaxation vary with the temperature, Graetz (*W.* 24, 25) deduced the formula $\eta = \mathrm{A} \frac{t_0 - t}{t - t_1}$, where t_1 is some low temperature at which η is infinite, and t_0 is the critical temperature. The formula expresses the facts very well over a moderate range, but, as we might as reasonably assume the connection between η and t as between the time of relaxation and t, it can only be regarded as empirical.

Extensive observations of the viscosity-coefficients of organic liquids have been made by Graham (*T.* 1861), Rellstab (*Inaug. Diss.* Bonn, 1868), Guerout (*C. R.* 81, 1025; 83, 1291), Pribram a. Handl (*Sitz. W.* 1878 and 1879), and Gartenmeister (*Z. P. C.* 6, 524); but few laws have been observed beyond qualitative relations applicable to small classes of compounds. In general the viscosity increases with the molecular weight, but formic acid is an exception, as it is more viscous than acetic acid. Isomeric esters have nearly the same viscosities, that with the higher alcohol radicle having the greater. Normal compounds are generally more viscous than the corresponding iso- compounds, but the propyl halogen compounds, and a few others, form exceptions. At high temperatures these differences are less marked than at lower ones, rise of temperature tending to efface the distinction between normal and iso- compounds. Pribram a. Handl endeavoured to find the conditions of temperature under which the results are comparable by determining the coefficients of viscosity of a number of liquids at various temperatures up to 50°. Taking the series PrCl, EtBr, PrBr, EtI, and PrI, they plotted the curve connecting viscosity with molecular weight, and found that while at the lower temperatures it was distinctly curved it got gradually flatter with rise of temperature, till at 50° it was almost a straight line, showing that at this temperature the increase of viscosity is proportional to the increase of molecular weight, whether this be due to the introduction of CH_2 or of a halogen.

Though sulphuric acid is much more viscous than water, the first effect of adding water to it is, as Graham showed, to increase its viscosity, and this continues till 18 p.c. of water has been added, when a maximum is reached, and further addition of water causes a rapid diminution of viscosity. The mixture with maximum viscosity corresponds to the proportions given by the formula $H_2SO_4.H_2O$, and there is a maximum in the electrical resistance near the same point. Similar relations are shown by nitric and acetic acids. For mixtures of alcohol and water Graham showed that the particular proportion of the constituents which gives the greatest contraction has maximum viscosity, and Traube (*B.* 19, 871) showed further that aqueous solutions of most alcohols and acids of the fatty series have maxima which occur at different concentrations according to temperature.

Arrhenius (*Z. P. C.* 1, 285) has investigated the relation between the concentration of a solution and its viscosity; he finds that for indifferent substances the exponential formula $\eta = A^{1-x}B^x$ expresses the results, where η is the viscosity, x the proportion by volume of the dissolved substance, and $1-x$ that of the solvent, so that A is the viscosity of the pure solvent, and B is a constant for the dissolved substance which is independent of the concentration up to about 10 p.c. As the solvent is usually water, and its viscosity is taken as the unit in comparative measurements, the formula can be written in the form $\eta = B^x$. In every case investigated by Arrhenius B proved to be greater than unity, showing that the viscosity of water is increased by the addition of a small quantity of an indifferent substance. The same is generally true of salts, but not quite invariably so. A viscous fluid like glycerin has less effect than ether has; there seems, in fact, to be no relation between the value of B and the viscosity of the dissolved substance alone.

The latest and most comprehensive determinations of the viscosities of salt solutions are by Reyher (*Z. P. C.* 2, 744), Wagner (*Z. P. C.* 5, 31), and Lauenstein (*Z. P. C.* 9, 417). The formula of Arrhenius in the form $\eta = A^x$, where x is now the number of gram-molecules in a litre of solution, or A is the viscosity of a normal solution, is found to hold moderately well, but for many salts of acids of the aromatic series it shows divergences if the strengths of the solutions are greater than half normal.

Wagner worked with sulphates, nitrates, and chlorides of metals, and found that the viscosities of solutions of equivalent quantities of the various salts are additive quantities, the part which the base or the acid contributes being approximately constant. A further relation is shown by tabulating the viscosities of normal solutions of the chlorides arranged according to the periodic law, when the coefficients are found to diminish in any group as the molecular weight increases. From this arrangement it would seem that copper and manganese should be put in the eighth group, for their coefficients are almost exactly equal to those of nickel and cobalt.

Reyher determined the viscosities of a number of acids and their sodium salts, and found they could be divided into two classes. The strong mineral acids have viscosities about 3 p.c. less than those of the sodium salts, while the weaker mineral acids and organic acids have coefficients from 20 to 30 p.c. less.

Lauenstein has found the viscosity-coefficients of solutions of the sodium salts of many organic acids. In the fatty series he found that substitution of CH_3 for H increases the viscosity, while the replacement of H by COOH or OH diminishes it. The change from succinic to maleic acid diminishes the viscosity, but if we remove two more atoms of hydrogen, giving acetylene dicarboxylic acid, we get a large increase.

In the aromatic series the results are less regular. Introduction of a carboxyl group into the ring still diminishes the viscosity, and this diminution is greater in the para- position than in the meta-, and greater in the meta- than in the ortho-; thus the viscosity diminishes regularly in the series shown by the formulæ at the top of p. 271.

According to the usual theory, the electricity which constitutes the current in an electrolyte is carried by charged ions, and it might be expected that the conductivity would be greater the more easily these ions were able to move along under the influence of the electromotive force—that is to say, the less the frictional resistance they had to overcome. On this account Wiedemann thought there would prove to be a connection between the viscosities and conductivities of solutions. Some experiments which he made seemed to point to the conductivity being inversely proportional to the viscosity, but though this was found at a later time to hold only in a few special cases, it has been shown that there is

$$C_6H_5.COONa,\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\COONa\end{smallmatrix}1{:}2,\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\COONa\end{smallmatrix}1{:}3,\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\COONa\end{smallmatrix}1{:}4.$$

With other replacing groups we have the following series, each being arranged in order of diminishing viscosity: —

$$1{:}2\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\NO_2\end{smallmatrix},\ 1{:}3\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\NO_2\end{smallmatrix},\ C_6H_5COONa,\ 1{:}4\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\NO_2\end{smallmatrix}$$

$$1{:}4\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\OH\end{smallmatrix},\ C_6H_5COONa,\ 1{:}3\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\OH\end{smallmatrix},\ 1{:}2\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\OH\end{smallmatrix}.$$

$$1{:}2\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\CH_3\end{smallmatrix},\ 1{:}4\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\OH\end{smallmatrix},\ C_6H_5.COONa,\ 1{:}3\ C_6H_4\Big\langle\begin{smallmatrix}COONa\\OH\end{smallmatrix}.$$

undoubtedly a close connection between the two properties.

This connection is shown very clearly by the work of Grotrian (*P.* 157, 130, 237; 160, 238), who determined the proportional rate of change with temperature of the viscosity and conductivity of salt solutions for various concentrations — that is, he calculated from his observations the values of $\frac{1}{f}\frac{df}{dt}$ and $\frac{1}{k}\frac{dk}{dt}$, where f is the coefficient of viscosity and k is the electrical conductivity, and found that though not equal they always vary in the same way with the concentration. If curves be drawn with the values of these coefficients at a fixed temperature for ordinates, and the concentrations for abscissæ, W. N. Shaw (*Camb. Phil. Proc.* 7, 21) has shown that the two curves run almost exactly parallel, any peculiarities in the shape of one being repeated in the other.

That the conductivity is not dependent on the viscosity alone is shown by the fact that if we add to an electrolyte such quantities of different non-conductors, as alcohol, sugar, glycerin, &c., as increase the viscosity by the same amount, the conductivity will generally be affected differently by the different substances. Arrhenius (*Z. P. C.* 9, 495) has investigated this effect at some length. He finds that the conductivity can be expressed by the equation: $l=l_0\left(1-\frac{\alpha}{2}x\right)^2$, where l_0 is the conductivity of the electrolyte alone, and l that which it has when x p.c. of the water is replaced by a non-conductor. Thus α may be taken as defining the change in the conductivity. The change in the viscosity of the electrolyte on the addition of 1 p.c. of non-conductor is the same as the change would be with water alone, and is hence equal to $A-1$, where A is the constant of the formula $\mu=A^x$.

On tabulating the values of 1000α and $1000\,(A-1)$ for a number of different salt solutions and non-conductors, it appears that the equation, $1000\,\alpha=c+1000\,c'(A-1)$ holds as a first approximation, and the electrolytes fall into four classes, for the members of any one of which the constants c and c' are the same. These classes are:

(1) Solutions of strong acids and bases;
(2) Solutions of salts of the type KCl;
(3) „ „ „ K_2SO_4;
(4) „ „ „ $BaCl_2$.

Arrhenius considers the relation not to be exact, but thinks it should include a term depending on the degree of dissociation, which can be neglected only in the cases of the more completely dissociated salts. J. W. C.

XIV. VOLUME-CHANGES, METHODS BASED ON, *v.* VOLUMES, SPECIFIC; this vol.

PHYSODIN $C_{10}H_{10}O_7$. [125°]. Extracted by ether from the dried lichen *Parmelia physodes* (or *Ceratophylla*) and crystallised from alcohol (Gerding, *N. Br. Arch.* 87, 1). Mass of minute prisms, insol. water. Forms a yellow solution in KOHAq.

PHYSOSTIGMINE *v.* ESERINE.

PHYTO-ALBUMOSES *v.* PROTEÏDS.

PHYTOLACCIC ACID. Occurs as K salt in the Poke Berry, the fruit of *Phytolacca decandra* (Terreil, *C. R.* 91, 856; *cf.* Claesson, *Ph.* [3] 10, 566). Extracted by dilute alcohol. Yellowish-brown resin.

PHYTOSTERIN *v.* vol. ii. p. 149.

PHYTO-VITELLIN *v.* PROTEÏDS.

PIAZTHIOLE $C_6H_4\Big\langle\begin{smallmatrix}N\\N\end{smallmatrix}\Big\rangle S$. [44°]. (206°). Formed by heating *o*-phenylene-diamine with aqueous SO_2 at 190° (Hinsberg, *B.* 22, 2899). Colourless crystals, sl. sol. hot water. Feeble base. Reduced by tin and HCl to *o*-phenylene-diamine.

Reference.—METHYL-PIAZTHIOLE.

PICENE $C_{22}H_{14}$. [345° cor.]. (520°). V.D. 9·8 (obs.). Occurs in the highest boiling portions of brown-coal tar (Burg, *B.* 13, 1884), and in the residues of Californian petroleum (Graebe a. Walter, *B.* 14, 175). Appears also to be formed by the action of ethylene bromide and $AlCl_3$ on naphthalene (Lespeau, *Bl.* [3] 6, 238). White plates with blue fluorescence, insol. alcohol and ether, sol. boiling solvent naphtha (150°–170°). On oxidation with CrO_3 it yields picoquinone $C_{22}H_{12}O_2$, which crystallises from HOAc as a dark orange-red powder, sublimes in red needles, and forms a green solution in pure H_2SO_4.

Di-bromo-picene $C_{12}H_{12}Br_2$. [206°]. Needles. (from xylene), insol. alcohol.

Picene hydrides $C_{22}H_{34}$ (over 360°) and $C_{22}H_{38}$ [175°] (over 360°) are got by heating picene with HIAq and red P at 250° (Liebermann a. Spiegel, *B.* 22, 781). $C_{22}H_{34}$ is liquid.

PICHURIN OIL contains the glyceryl ether of lauric acid (Sthamer, *A.* 53, 390).

PICOLINE *v.* METHYL-PYRIDINE.

PICOLINIC ACID *v.* PYRIDINE CARBOXYLIC ACID.

Dipicolinic acid *v.* PYRIDINE DICARBOXYLIC ACID.

DIPICOLYL *v.* DI-METHYL-DIPYRIDYL.

PICRACONITINE *v.* ACONITE ALKALOIDS.

PICRAMIC ACID *v.* DI-NITRO-AMIDO-PHENOL.

PICRAMIDE *v.* TRI-NITRO-ANILINE.

PICRASMIN $C_{35}H_{46}O_{10}$. [204°]. A bitter substance which, together with $C_{36}H_{48}O_{10}$ [209°–

212°], may be extracted by dilute alcohol from *Picræna excelsa* (Massute, *Ar. Ph.* [3] 28, 147; *C. J.* 58, 791). HClAq converts it into picrasmic acid $C_{31}H_{40}O_{6}(CO_2H)_2$, while fuming HIAq displaces three methyls.

PICRIC ACID *v.* Tri-nitro-phenol.

PICRO-ACONITINE *v.* Aconite alkaloids.

PICROCROCIN $C_{38}H_{66}O_{17}$. [75°]. Obtained by extracting saffron with ether (Kayser, *B.* 17, 2233). Colourless prisms. V. sol. water and alcohol, sl. sol. ether. Bitter taste. By heating with baryta-water or with dilute acids it is split up into crocose and the ethereal-oil of saffron $C_{10}H_{16}$.

PICROERYTHRIN *v.* Erythrite.

PICROLICHENIN $C_{12}H_{20}O_6$. [100°] (A.). S.G. 1·176. Extracted by alcohol from the lichen *Variolaria amara* (Alms, *A.* 1, 61; Vogel, *J.* 1857, 515). Trimetric octahedra, sl. sol. hot water, v. sol. alcohol and ether. Tastes very bitter. Its alkaline solutions turn red in air.

PICROROCCELLIN $C_{27}H_{39}N_3O_5$. [194°]. Occurs in a variety of the lichen *Roccella fuciformis* (Stenhouse a. Groves, *A.* 185, 14). Prisms, insol. water, m. sol. boiling alcohol, sl. sol. ether. Yields benzoic acid when oxidised by chromic acid mixture. Converted by boiling with HOAc and HCl into xanthoroccellin $C_{21}H_{18}N_2O_2$, which crystallises from alcohol in yellow needles [183°]. Boiling dilute (1½ p.c.) NaOHAq converts picroroccellin into $C_{21}H_{23}N_2O_3$ crystallising from alcohol in prisms [154°].

PICROSCLEROTIN. Occurs in ergot of rye (Dragendorff, *C. C.* 1878, 125, 141; Blumberg, *Ph.* [3] 9, 23, 66, 147). Dissolved in acids and is reppd. by ammonia. It is an active poison with bitter taste. *V.* Ergotinine.

PICROTOXIN $C_{30}H_{34}O_{13}$ (P. a. O.; S.); $C_{15}H_{16}O_6$ (B. a. K.). Occurs in Cocculus Indicus, the seeds of *Menispermum cocculus* (Boullay, *A. Ch.* [1] 30, 209; Casaseca, *A. Ch.* [2] 30, 307; Oppermann, *Mag. Pharm.* 35, 233; Pelletier a. Couerbe, *A. Ch.* [2] 54, 181; Liebig, *A.* 10, 203; Regnault, *A. Ch.* [2] 68, 160; Barth, *J. pr.* [1] 91, 155; Paterno a. Oglialoro, *G.* 6, 521; 7, 193). It is accompanied by anamirtin and picrotin (Barth a. Kretschy, *M.* 1, 99, 2,796).

Preparation.—1. The grains are exhausted with boiling alcohol, the extract evaporated, and the residue boiled with water. The aqueous solution is ppd. by lead acetate and the filtrate, freed from lead by H_2S, evaporated. The residue is crystallised from benzene and water successively (B. a. K.).—2. The powdered seeds are boiled with water, the filtrate treated with lead acetate and H_2S successively, and evaporated to crystallisation. The product is recrystallised from water and alcohol successively (Schmidt, *A.* 222, 313).

Properties.—Colourless needles, v. sl. sol. cold water, sl. sol. ether and chloroform, v. sol. alcohol. Very poisonous and very bitter. Sol. alkalis. Reduces Fehling's solution and ammoniacal $AgNO_3$.

Reactions.—1. When boiled with benzene for some time it is split up into picrotin and picrotoxinin (Schmidt). Probably the picrotoxin employed was a mixture of these two bodies.—2. HCl passed into an ethereal solution forms picrotoxide.—3. Cold AcCl also forms picrotoxide, but on boiling it yields a crystalline acetyl derivative [185°].—4. NaOAc and Ac_2O form $C_{19}H_{22}O_9$ [227°].

Picrotoxinin $C_{15}H_{16}O_6$ aq. [201°]. S. ·14 at 15°; S. (benzene) ·34 at 21°. Obtained from picrotoxin by treatment with benzene, $CHCl_3$, HCl, or AcCl. It constitutes about 30 p.c. of crude picrotoxin (Barth a. Kretschy). Colourless needles or plates. Very bitter and very poisonous. V. sol. hot water. Colours H_2SO_4 orange-red. Mixed with dry KNO_3 (3 pts.), moistened with H_2SO_4, and saturated with conc. NaOHAq it gives a red colour (Langley, *Am. S.* [2] 34, 109). After heating with milk of magnesia, the cold filtrate is coloured red by $FeCl_3$, the colour being destroyed by HCl. Bromine forms $C_{15}H_{15}BrO_6$ [250°-255°]. BzCl gives a crystalline compound (not the benzoyl derivative) [238°].

Picrotoxide $(C_{15}H_{16}O_6)x$. [above 310°]. Formed by the action of AcCl on picrotoxin, and by passing HCl into its ethereal solution (P. a. O.). Crystalline, insol. ordinary solvents. According to Schmidt, picrotoxide obtained by means of AcCl crystallises in needles [225°], sl. sol. cold water and alcohol.

Picrotin $C_{25}H_{30}O_{12}$. [c. 247°]. S. ·16 at 17°; S. (benzene) ·023 at 22° (Schmidt). Constitutes 60 p.c. of crude picrotoxin (B. a. K.). Crystallises with 2½ aq, 3½ aq, and 4½ aq. It is very bitter, but not poisonous. Reduces hot Fehling's solution and ammoniacal $AgNO_3$. H_2SO_4 forms a yellow solution. BzCl forms a benzoyl derivative [245°] (S.).

Anamirtin $C_{19}H_{24}O_{10}$. Constitutes 2 p.c. of crude picrotoxin (Barth a. Kretschy, *M.* 1, 131). Short needles (from water), v. sl. sol. benzene. Neither bitter nor poisonous. Turns brown at 260° and black at 280° without melting.

Cocculin $C_{19}H_{26}O_{10}$. Occurs in small quantity in Cocculus Indicus (Löwenhardt, *A.* 222, 353). Slender needles, sl. sol. hot water, nearly insol. alcohol and ether. Does not give Langley's reaction. Is perhaps identical with anamirtin.

PICRYL. The radicle tri-nitro-phenyl.

PICRYL CHLORIDE *v.* Chloro-tri-nitro-benzene.

PIGMENTS, ANIMAL.

Bile pigments. Bile contains bilirubin, bilifuscin, biliprasin, and probably also biliverdin, which is a product of oxidation of bilirubin. Nitric acid changes the colour of the bile pigments through green, blue, and red to yellow (Gmelin). These colours may be observed by adding nitric acid to a dilute solution of the bile pigments in aqueous alkali, or by gently pouring H_2SO_4 into a solution of the pigments mixed with $NaNO_3$ (Fleischl, *Fr.* 15, 502). The changes in the absorption spectra produced by nitric acid have been studied by Jaffé (*Z.* [2] 5, 666). An alcoholic solution of bromine also produces a play of colours with bile pigments (Capranica, *G.* 11, 430). The absorption spectra of the bile pigments have been studied by Heynsius a. Campbell (*Pf.* 4, 497) and McMunn (*Pr.* 35, 388). Bilirubin, hæmoglobin, and chlorophyll all absorb the violet end of the spectrum, giving an abrupt edge: biliverdin transmits more green; biliprasin, bilifuscin, and bilihumin absorb up to between D and E. The colouring matters of bile are probably got by reduction of hæmatine,

itself formed by the action of bile acids on hæmoglobin (McMunn, *Pr.* 31, 206). According to Latschenberger (*M.* 9, 52), hæmoglobin yields simultaneously melanin and bile pigments. All the colouring matters of bile, including hæmatine, urobilin (in bile), and bilirubin, are oxidised to choletelin, which body apparently passes into blood serum, and is then excreted by the kidneys. The absorption bands of bile are due to choletelin and urobilin.

Bilirubin $C_{32}H_{36}N_4O_6$ (Städeler, *A.* 132, 323; Maly, *A.* 181, 106), or $C_{16}H_{18}N_2O_3$ by Raoult's method (Nencki a. Rotschy, *M.* 10, 568). S. (chloroform) ·17 (Thudichum, *Z.* [2] 4, 554). Ox gall stones are often largely composed of the lime compound of bilirubin (Maly, *A.* 175, 76).

Preparation.—Brown human gall stones are powdered and extracted with ether; the residue is boiled with water, and treated with dilute HCl. The mass is washed, dried, and extracted with chloroform; the chloroform is distilled off, and the residue treated with absolute alcohol. It is then treated with ether and alcohol repeatedly, again dissolved in chloroform, and precipitated by absolute alcohol (Burdon-Sanderson).

Properties.—Orange powder, insol. water, nearly insol. ether, v. sl. sol. alcohol, sol. benzene and chloroform. The colour of the skin in jaundice is probably due to bilirubin. Bilirubin dissolves in alkalis, forming an orange solution, which gradually absorbs oxygen from the air, and then gives a green pp. of biliverdin on adding an acid. An alkaline solution of bilirubin mixed with an equal bulk of alcohol gives, on adding HNO_3 containing nitrous acid, a green colour changing through blue to red. Sodium-amalgam forms hydrobilirubin. Bromine-vapour yields various brominated products (Thudichum, *C. J.* 28, 389; 30, 27). Br in chloroform gives $C_{32}H_{33}Br_3N_4O_6$, a dark bluish-green powder, forming a dark-blue solution in alcohol or ether (Maly, *A.* 181, 106). Chlorine passed into a solution of bilirubin in $CHCl_3$ forms several chlorinated bodies (Thudichum). A solution of *p*-diazobenzene sulphonic acid added to a solution of bilirubin in chloroform mixed with alcohol gives a red colour changing to blue on adding conc. HClAq, and turned red again on adding an alkali (difference from other bile-pigments) (Ehrlich, *Fr.* 23, 275).—$CaC_{32}H_{34}N_4O_6$. Occurs in gall stones. Obtained also by ppg. an ammoniacal solution by $CaCl_2$, as brown flakes drying to a lustrous dark-green mass, which yields a dark-blue powder.

Hydrobilirubin $C_{32}H_{40}N_4O_7$. Obtained by reducing bilirubin in alkaline solution with sodium-amalgam (Maly, *A.* 163, 77). According to McMunn it is not, as had been stated, identical with the urobilin which is found in normal urine, in the urine of febrile patients (Jaffé, *Virchow's Archiv*, 47; Disqué, *H.* 2, 271), and in excrement (Vaulair a. Masius, *Centralbl. f. d. Med. Wissensch.* 1871, No. 24). A similar substance is formed by reducing hæmoglobin, hæmatine, or hæmatoporphyrin in alcoholic solution with tin and HCl (Hoppe-Seyler, *B.* 7, 1065; Le Nobel, *C. C.* 1887, 538; McMunn, *Proc. Physiol. Soc.* 1888, 1), and by the action of H_2SO_4 on a solution of albumen in HOAc (Michailoff, *J. R.* 16, 269). Reddish-brown powder with green lustre, sl. sol. water, v. sol. alcohol, m. sol. ether. Its alkaline solutions are brown, its solution in chloroform is yellowish-red. The alcoholic solution shows an absorption-band near F. Does not give Gmelin's reaction with HNO_3. May be reduced by sodium-amalgam or by tin and HCl to a colourless product, which in acid solutions is reoxidised by air to hydrobilirubin.

Choletelin $C_{16}H_{18}N_2O_6$. Occurs in normal urine, and is obtained by passing nitrous vapours into a solution of bilirubin in alcohol (Heynsius a. Campbell; McMunn, *J. Th.* 1881, 213). Brown amorphous powder, sol. alkalis and alkaline carbonates, alcohol, ether, and chloroform. Ammoniacal $AgNO_3$ ppts. reddish-brown $C_{16}H_{16}Ag_2N_2O_6$. Does not give Gmelin's reaction. Its absorption spectrum contains a broad band from *b* to F.

Biliverdin $C_{32}H_{36}N_4O_8$. Formed by oxidation of a solution of bilirubin by air or by PbO_2. Dark-green powder, insol. water and chloroform, sl. sol. ether, v. sol. alcohol, CS_2, and benzene. Its solutions are green. Its alcoholic solution gives dark-green pps. with baryta-water, ammoniacal $CaCl_2$, and $AgNO_3$. Ag_2O added to its alcoholic solution ppts. bilipurpin, sol. NH_3Aq and reppd. by HCl as a purple powder. Prolonged treatment with Ag_2O converts bilipurpin into yellow biliflavin. HNO_3 added to an alcoholic solution of biliverdin gives a bluish-violet, red, and, finally, yellow colour (Thudichum).

Bilifuscin $C_{16}H_{20}N_2O_4$. Prepared by washing gall stones with ether, hot water, and chloroform, adding dilute HClAq, and extracting with hot chloroform. The extract is evaporated and the bilifuscin dissolved in alcohol, which leaves bilirubin undissolved (Brücke, *J. pr.* 77, 72; Städeler, *A.* 132, 325). Almost black mass, which yields a dark-brown powder. Forms a brown solution in alcohol and alkalis, nearly insol. water, ether, and chloroform. Gives Gmelin's colour-reaction. Ppd. by ammoniacal $CaCl_2$. Simony (*Sitz. W.* [3] 73, 181) obtained from the bile of a corpse a bilifuscin which did not give Gmelin's reaction, and which formed an olive-brown solution in alcohol, HOAc, and alkalis.

Biliprasin $C_{16}H_{22}N_2O_6$. Extracted by alcohol from the residue of gall stones from which bilirubin and bilifuscin have been removed by chloroform (Städeler). Nearly black mass, yielding a greenish-black powder, insol. water, ether, and chloroform, v. e. sol. alcohol, forming a green solution which, unlike one of biliverdin, is turned brown by ammonia. Gives Gmelin's reaction.

Bilihumin. Left after extracting biliprasin with alcohol (S.). Black powder, m. sol. warm NaOHAq. Exhibits Gmelin's reaction.

Bilicyanin. A product of partial oxidation of bilirubin and other bile pigments (Maly, *Sitz. W.* [2] 59, 597). Prepared by adding an alcoholic solution of Br to a solution of bilirubin in chloroform. Occurs in gall stones. Its alcoholic solution is blue, but turned dingy green by alkalis, the blue colour being restored by acids. Bile also contains a blue substance strongly resembling indigo, forming a yellowish solution in alkalis (Ritter, *Bl.* [2] 13, 212; Andouard, *Bl.* [2] 31, 139).

Urinary Pigments. Urine usually contains urobilin (*v. supra*). After urine, containing urobilin, has been mixed with its own bulk of

HClAq and heated to boiling, and then allowed to cool, the urobilin may be extracted by ether and recognised by its absorption band (Grimbert, *J. Ph.* [5] 18, 481). According to McMunn (*Proc. Physiol. Soc.* 1888, 5), there are two kinds of urobilin, one in normal urine and the other in pathological urine, and neither is identical with hydrobilirubin. Normal urobilin is identical with a pigment got from acid hæmatin by successive treatment with H_2O_2 and sodium-amalgam. By the action of oxidising agents indigo-blue and indirubin can be obtained from urine (*v.* Indigo). Pigments can also be obtained by boiling urine with HClAq.

Uromelanin. Prepared by evaporating urine to one-sixth of its bulk at 60°, adding 10 p.c. HCl, and, after two days, removing uric acid by filtration. The filtrate is then boiled for 18 hours, and the ppd. pigment washed with water, alcohol, and ether, dissolved in NaOKAq, and reppd. by H_2SO_4 (Udranski, *H.* 11, 537; 12, 33; *cf.* Plosz, *H.* 8, 89). Brownish-black plates, insol. cold water, ether, and chloroform, sl. sol. alcohol and HClAq, v. sol. isoamyl alcohol and alkalis. Not decomposed at 115°. Potash-fusion yields NH_3, formic, acetic, butyric, and protocatechuic acids and pyrocatechin. Urine contains ·03 p.c. of this substance, which appears to be a humous body formed by decomposition of the reducing substance of normal urine.

Urofuscohæmatin $C_{31}H_{51}N_4O_{13}$ (?) and **ururubrohæmatin** $C_{31}H_{18}N_4FeO_{18}$ (?) were obtained by Baumstark (*B.* 7, 1170) from the urine of a patient suffering from Lepra. Urofuscohæmatin is a black pitchy substance, insol. water, alcohol, ether, chloroform, acids, and NaClAq, sol. alkalis, alkaline carbonates, and alkaline phosphates, forming brown solutions. Ururubrohæmatin is a light blue-black mass, which differs from urofuscohæmatin in not being ppd. when HCl is added to its solution in NaOHAq.

Black pigment in *Melanuria*, *v.* vol. iii. p. 199.

Uroroseïn. An unstable substance which can sometimes be extracted from acidified pathological urine by isoamyl alcohol, to which it imparts a rose colour. The solution shows an absorption band in the green (Nencki a. Sieber, *J. pr.* [2] 26, 333). A similar substance (urorubin) was extracted by ether from urine that had been boiled 15 minutes with 7 p.c. HCl, exposed to air (Plosz, *H.* 8, 85). It was left on evaporation as a dark cherry-red mass. Apparently the same pigment, or rather its leuco- compound, occurs in urine of dogs after administration of skatole (Mester, *H.* 12, 130). The pigment itself is then got by adding HCl to an alcoholic, ethereal, or aqueous extract of the evaporated urine.

OTHER PIGMENTS.

Blood pigments *v.* Hæmoglobin.

Muscle pigments *v.* Muscle.

Eye pigment *v.* Melanin. A purple pigment occurs in the retina of animals. It is insol. ordinary solvents, but dissolves in bile, and in an aqueous solution of the bile acids. It loses its colour in daylight, but recovers it in the dark (Boll, *J. Th.* 1877, 313; Kühne, *J. Th.* 1877, 313; 1878, 279; Ayres, *J. Th.* 1879, 259).

Yellow pigment of animals *v.* Luteïn.

Tetronerythrin. A red pigment extracted by chloroform from the red spot in the eye of the blackcock and red grouse (Wurm, *J.* 1872, 842; 1875, 885; Merejkowski, *J. Th.* 1881, 371). H_2SO_4 gives a blue colour changing to black.

Pyocyanin. Occurs in blue pus (Fordos, *J.* 1860, 596; Lücke, *J.* 1863, 658; Gessard, *J. Th.* 1882, 55). It is formed, together with other pigments, by *Bacillus pyocyanicus* in peptonised gelatin (Babès, *C. R. Soc. Biol.* [9] 1, 438). Blue trimetric prisms or needles (from $CHCl_3$) which become green on keeping, v. sol. chloroform, alcohol, and water. Turned red by acids, but becomes blue again on adding alkalis. It shows two absorption bands, one being in the ultra-violet.

Pigments of Purpura lapillus. The pigments are furnished by a yellowish-white fascia which extends along the rectum (Letellier, *C. R.* 109, 82). This contains two green substances, apple-green monoclinic crystals turned dark blue by light, and dull-green trimetric crystals turned violet or crimson by light. The green substances are sol. ether and chloroform, but become insoluble on exposure to light. The change to purple (punicin) is accompanied by absorption of oxygen (Schunck, *B.* 12, 1359).

Pigments of sea-anemones. *Actinia mesembryanthemum* contains a pigment allied to hæmo-chromogen and hæmato-porphyrin, and to hæmatine. It also contains biliverdin. *Actinia cereus*, *Bunodes ballii*, and *Sagartia bellis* contain a green pigment resembling chloro-fucin, but not identical with any animal or plant chlorophyll (McMunn, *Pr.* 38, 85).

PIGMENTS, VEGETABLE, *v.* Chlorophyll, Alkanet, Beth-a-barra colour, Bixin, Brazileïn, Chica, Coleïn, Curcumin, Dragon's blood, Hæmatoxylin, Lithospermum erythrorhizon, Litmus, Luteic acid, Palmellin, and Santalin.

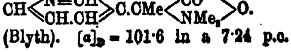
Anthocyanin. The blue pigment of flowers is sol. water and alcohol, insol. ether. It is free from N, and is turned red by acids and green by alkalis (Fremy a. Cloez, *J. Ph.* [3] 25, 249; Filhol, *C. R.* 39, 194; 50, 345, 1132; Schönn, *Fr.* 9, 328).

Anthoxanthin. Yellow flowers contain anthoxanthin, which is insol. water, and **anthoxantheïn**, which is sol. water. Both are sol. alcohol and ether. The petals of *Rosa gallica* contain a pigment sol. alcohol, insol. ether, which forms amorphous $Pb_2C_{21}H_{30}O_{30}$ (?) (H. Senier, *Ph.* [3] 7, 650). The colouring matter of the berries of *Phytolacca decandra* has been examined by Hilger and Bischoff, *L. V.* 23, 456; *B. C.* 1879, 875).

PILIGANINE. A very poisonous alkaloid occurring in piligan, a Brazilian lycopod (Adrian, *C. R.* 102, 1322). Soft mass, with alkaline reaction, fuming with HCl. Sol. water, alcohol, and chloroform, sl. sol. ether. Emeto-cathartic in action. Its hydrochloride forms minute deliquescent crystals.

PILOCARPENE $C_{10}H_{16}$. (178°). $S.G.^{15}$ ·852. V.D. 4·0. $[\alpha]_D = 1{\cdot}21$. Obtained by steam distillation from jaborandi leaves (Hardy, *Bl.* [2] 24, 498). Fragrant oil. Dextrorotatory. Yields $C_{10}H_{16}2HCl$ [49·5°].

PILOCARPINE $C_{11}H_{16}N_2O_2$ *i.e.*



$$CH{<}\begin{matrix}N{=}CH\\CH.CH\end{matrix}{>}C.CMe{<}\begin{matrix}CO\\NMe_2\end{matrix}{>}O.$$

[159°] (Blyth). $[\alpha]_D = 101{\cdot}6$ in a 7·24 p.c. solution.

Occurs in the leaves and bark of jaborandi (*Pilocarpus*) (Gerrard, *Ph.* [3] 5, 865, 965; Hardy, *Bl.* [2] 24, 497; Kingzett, *C. J.* 30, 367; Harnack a. Meyer, *A.* 204, 67). Prepared synthetically from α-oxy-α-pyridyl-propionic acid $CH_3.C(OH)(C_5H_4N).CO_2H$ by treatment with phosphorus tribromide and heating the resulting $CH_3.CBr(C_5H_4N)CO_2H$ with NMe_3 at 150°. In this way pilocarpidine $C_{10}H_{14}N_2O_2$ is formed, and this is converted into pilocarpine by heating with MeI and MeOH, and oxidising the product with aqueous $KMnO_4$ (Hardy a. Calmels, *C. R.* 105, 68; *Bl.* [2] 48, 233).

Preparation.—Jaborandi leaves are digested with 1 p.c. HClAq, the extract treated with $Pb(OAc)_2$, filtered, and the filtrate ppd. by phosphomolybdic acid. The pp. is decomposed by baryta-water at 100° (Pöhl, *Bl.* [2] 34, 340).

Properties.—Crystalline; begins to sublime at 153°; at 160°–170° the sublimate consists of yellow drops (Blyth). Dextrorotatory. Pilocarpine may be estimated by means of the aurochloride (Christensen, *Ph.* [3] 12, 400). Poisonous, being diaphoretic. Forms resinous compounds with potash, NaOH, and baryta; these compounds are v. sol. water, v. sl. sol. alcohol, and are decomposed by acids, even by CO_2. They may be considered to be salts of pilocarpic acid $C_{11}H_{18}N_2O_3$.

Reactions.—1. Fuming HNO_3 (300 pts.) converts it into pilocarpidine nitrate (Chastaing, *C. R.* 94, 968).—2. *Boiling with water* for twelve hours splits it up into trimethylamine and oxy-pyridyl-propionic acid (Hardy a. Calmels, *C. R.* 102, 1562).—3. Boiling HClAq forms MeOH and pilocarpidine.—4. $KMnO_4$ forms NMe_3, oxy-pyridyl-malonic acid, and finally pyridine (β)-carboxylic acid.—5. *Bromine* added to a chloroform solution forms $C_{11}H_{15}N_2O_2Br_5$, crystallising in minute prisms, converted by moist Ag_2O into di-bromo-pilocarpine $C_{11}H_{14}Br_2N_2O_2$ (Chastaing, *C. R.* 97, 1435). Chlorine forms $C_{11}H_{13}N_2O_2Cl_5$, which is amorphous, and slowly forms crystalline $C_{11}H_{15}N_2O_2Cl_3$.—6. Yields NMe_3 when distilled with potash (Harnack a. Meyer; *cf.* Chastaing, *C. R.* 94, 223).—7. The barium compound on distillation yields jabonine $C_9H_{14}N_2$, an oil with fœtid odour, yielding the amorphous salts $B'AuCl_3$, $B'HAuCl_4$, B'_2PtCl_4, and $B'_2H_2PtCl_6$.

Salts.—$B'HCl$: needles, v. sol. alcohol.—$B'HNO_3$: trimetric lamellæ.—$B'_2H_2PtCl_6$: golden tablets (from hot water).—$B'PtCl_4$: crystals.—$B'HAuCl_4$: minute needles.—$B'AuCl_3$ [88°]: slender needles.—$B'2AuCl_3$: small needles.—$B'HAu_2Cl_7$: minute needles.—$B'AgNO_3$: minute radiating needles.—$B'2AgNO_3$: needles.—$B'CrN_2H_7(SCN)_4$: red silky needles, sol. alcohol (Christensen, *J. pr.* [2] 45, 368).—$B'_2CuO_2H_2$: green powder, ppd. by adding $CuCl_2$ to a solution of pilocarpine in baryta-water.—$B'AgOH$: curdy pp.—$B'Me_2PtCl_6$: crystals.—$B'EtI$. [c. 30°].—$B'EtBr$. [c. 60°]. Very hygroscopic (Chastaing, *C. R.* 101, 507).

Pilocarpidine $C_{10}H_{14}N_2O_2$ *i.e.* $NMe_2.CMe(C_5H_4N).CO_2H$. Occurs in jaborandi leaves (Harnack, *A.* 238, 230). Formed by the action of HClAq or fuming HNO_3 on pilocarpine, by heating dry pilocarpine for twenty-four hours at 120°, by boiling pilocarpine or its baryta compound with water for forty eight hours, and by heating the baryta compound for thirty minutes at 150°. Prepared synthetically by heating $CH_3.CBr(C_5H_4N).CO_2H$ with trimethylamine at 150° (H. a. C.). Very deliquescent, m. sol. water, v. sol. alcohol. Acts physiologically like pilocarpine, but not so strongly. Its alkaline salts are gummy, sol. water, insol. alcohol, and decomposed by CO_2.—$B'HCl$: radiating needles, v. soluble in water.—$B'HAuCl_4$ aq. Rectangular prisms.—$B'AuCl_3$. [145°]. Yellow plates.—$B'_2H_2PtCl_6$ aq: small red prisms.—$B'MeI$.—$B'MeAuCl_4$ [153°]. Prismatic needles. Changes when fused into MeCl and $B'AuCl_3$.

PIMARIC ACID $C_{20}H_{30}O_2$. [211°]. $[\alpha]_D = 72\cdot5$ in a 3·8 p.c. (saturated) alcoholic solution at 15°. Occurs in galipot, the hardened resin of *Pinus maritima* (Laurent, *A. Ch.* [2] 72, 384; [3] 22, 459; Sievert, *Z. f. d. g. Naturwiss.* 14, 311; Maly, *A.* 129, 94; 132, 253; Strecker a. Duvernoy, *A.* 148, 143; 150, 131; Cailliot, *Bl.* [2] 21, 387; Bruylants, *B.* 11, 447; Haller, *B.* 18, 2165; Vesterberg, *B.* 18, 3331; 19, 2167; 20, 3248).

Preparation.—Finely-divided galipot is stirred with half its weight of dilute (70 p.c.) alcohol, left for some days, and squeezed in a cloth. The press-cake is treated several times in this way, finally with 80 p.c. alcohol. The residue is dissolved in somewhat more than the calculated quantity of hot dilute (3 p.c.) NaOHAq. The mixture of Na salts that separates after some days is recrystallised from water, decomposed by HCl, and the free acids crystallised from alcohol or HOAc. (β)-Pimaric acid remains in the mother-liquor.

Properties.—Rectangular plates, insol. water, v. sl. sol. alcohol, ether, and HOAc, m. sol. hot ligroïn, m. sol. hot NaOHAq, sl. sol. NH_3Aq. On shaking the ethereal solution with a drop of ammonia the NH_4 salt separates in slender needles. Not reduced by sodium-amalgam. May be distilled *in vacuo*. Dextrorotatory. HIAq (S.G. 1·96) forms $C_{20}H_{34}$ (320°–330° uncor.). By distillation of the (crude) Ca salt Bruylants obtained ethylene, propylene, amylene, acetone, methyl ethyl ketone, di-ethyl ketone, toluene, xylene, ethyl-toluene, terebene, and diterebene.

Salts.—All the salts are insol. ether. KA' (dried at 100°). Soapy mass of pliant needles.—NaA' 5aq. Slender needles (from 80 p.c. alcohol), sl. sol. cold water.—CaA'_2 aq: needles.—BaA'_2 9aq: pliant needles.—CuA'_2.—PbA'_2.—AgA': amorphous pp., becoming crystalline.

Ethers.—MeA'. [69°].—EtA. [52°].

Chloride $C_{20}H_{29}OCl$. [66°]. Got by adding PCl_5 to a solution of the acid in CS_2. Small prisms, v. e. sol. ether and CS_2.

(β)-Pimaric acid $C_{20}H_{30}O_2$. [140°–150°]. S. 9·26 in 98 p.c. alcohol at 15°. $[\alpha]_D = -272°$ in a 3·17 p.c. alcoholic solution. Obtained as above (Vesterberg, *B.* 20, 3248). Trimetric prisms; *a*:*b*:*c* = ·810:1:·614, insol. water, v. sol. NH_3Aq. Lævorotatory.—NaA': m. sol. ether.—PbA'_2: needles, insol. alcohol and ether. Haller (*B.* 18, 2165) obtained an inactive pimaric acid [c. 149°], which was perhaps a mixture of the dextro- and lævo- varieties.

PIMELIC ACID $C_7H_{12}O_4$ *i.e.* $CO_2H.CHPr.CH_2.CO_2H$. *Isopropyl-succinic acid.* Mol. w. 160. [114°]. *Electrical conductivity*: Walden, *B.* 24, 2037. Formed by fusing camphoric acid with potash (Hlasiwitz a. Grabowski, *A.* 145, 205; Kachler, *A.* 169, 168). Formed also by heating either of the following isopentane tricarboxylic acids: $(CO_2H)_2CPr.CH_2.CO_2H$ or $CO_2H.CHPr.CH(CO_2H)_2$ (Waltz, *B.* 15, 609; *A.* 214, 60; Hjelt, *B.* 16, 2622; Schleicher, *A.* 267, 123). *Obtained also by the action of KOHAq* on isopropyl-acetyl-succinic ether (Roser, *A.* 220, 276). According to Arppe (*J.* 1864, 377) it is not formed, as stated by Laurent (*A. Ch.* [2] 66, 163), by oxidation of oleïc acid. Nodules (from water) or triclinic crystals; *a*:*b*:*c* = ·497:1: ·599; $\alpha = 81° 50'$; $\beta = 100° 2'$; $\gamma = 85° 6'$ (Wreden, *A.* 163, 323; Von Zepharovitch, *Sitz. W.* [1] 73, 7). V. sol. water, alcohol, and ether. Yields butyric acid when fused with potash.

Salts.—$(NH_4)_2A''$. Hygroscopic leaflets.—Na_2A'' (dried at 130°).—CaA″aq: sandy crystalline powder. S. ·47 at 9°; ·25 at 100° (Bauer a. Schuler, *J.* 1878, 734; *B.* 10, 2031; *M.* 4, 345); ·30 at 13° (Roser).—SrA″: nearly insol. hot water, v. e. sol. cold water.—Ag_2A'': pp.

Ethyl ether Et_2A''. (236°–240°).

Chloride $C_7H_{10}O_2Cl_2$. (210°).

Anhydride $C_7H_{10}O_3$. (245°–250°). Got by distilling the acid. Reconverted into the acid by alkalis.

Imide $C_7H_{11}NO_2$. [60°]. Got by heating the ammonium salt. Tables (from water) or small needles (from alcohol-ligroïn). Insol. ligroïn, v. sol. alcohol and ether.

***n*-Pimelic acid** $CH_2(CH_2.CH_2.CO_2H)_2$. [103°]. (272° at 100 mm.) (Krafft a. Noerdlinger, *B.* 22, 818). S. 4·2 at 20°. H.C.p. 828,900. H.F. 243,100 (Stohmann, *J. pr.* [2] 45, 480).

Formation.—1. By heating suberone with HNO_3 (Dale a. Schorlemmer, *C. J.* 35, 686; *A.* 199, 147).—2. By heating furonic acid with HIAq and P at 200° (Baeyer, *B.* 10, 1358).—3. By heating pentane ω-tetra-carboxylic acid (Perkin, jun., *C. J.* 51, 242; 59, 825; *B.* 18, 3249).—4. By oxidation of myristic acid with HNO_3 (Noerdlinger, *B.* 19, 1898).—5. By reducing $CO(CH_2.CH_2.CH_2H)_2$ (*cf.* FURFURYL-ACRYLIC ACID) (Marckwald, *B.* 21, 1398).

Properties.—Rectangular trimetric plates (from water), v. sol. alcohol, ether, and hot benzene. May be sublimed. NaOEt forms $C_{17}H_{28}Na_2O_8$, a white powder, insol. ether, sol. water. Not converted into anhydride by AcCl or by PCl_5 (Volhard, *A.* 267, 82).

Salts.—BaA″aq.—CaA″. Deposited as granular powder when a cold saturated solution is heated.—Ag_2A'': white pp.

Ethyl ether Et_2A''. S.G. $\frac{4}{4}$ 1·0080; $\frac{15}{15}$ ·9988; $\frac{25}{25}$ ·9920. M.M. 11·424. Oil with penetrating odour (Perkin, *C. J.* 59, 826).

Pimelic acid $C_7H_{12}O_4$. [103° cor.]. Got by heating chelidonic acid with HIAq at 205° (Haitinger a. Lieben, *M.* 5, 358). Monoclinic tables, v. sol. hot benzene. Perhaps identical with *n*-pimelic acid.

(β)-Pimelic acid $C_5H_{10}(CO_2H)_2$. [106°]. Occurs among the products of oxidation of castor oil and earth-nut oil with nitric acid (Gantter a. Hell, *B.* 17, 2212). Large tables (from water). Readily forms supersaturated solutions.—BaA″aq: plates.—PbA″.—CuA″.—Ag_2A'': pp.

Iso-pimelic acid $C_5H_{10}(CO_2H)_2$. [104°]. Formed from amylene bromide by successive treatment with alcoholic KCy and HClAq at 170° (Bauer, *M.* 4, 345; Hell, *B.* 24, 1389). Prisms, v. sol. water and alcohol. Begins to form an anhydride at 135°.—$(NH_4)_2A''$.—BaA″1½aq: sandy powder.—CaA″. S. ·2 at 22°; ·14 at 100°.—SrA″4aq.—NiA″2½aq.—ZnA″.—PbA″. S. ·01 at 100°.—CuA″aq. S. ·04 at 16°; ·07 at 100°. Bluish-green plates.—CdA″2aq: needles. S. ·12 at 15°; ·13 at 100°.—Ag_2A''.

An amorphous pimelic acid was got by Bauer, as well as the preceding acid, from amylene bromide. Its Ca salt was more soluble (S. 4·7).

Pimelic acid $C_7H_{12}O_4$. [87°]. Got by oxidising menthol with $KMnO_4$ in acid solution (Arth, *A. Ch.* [6] 7, 455; *C. R.* 107, 107). Needles, v. sol. water. Can be extracted by ether from its aqueous solution.—Ag_2A''.

Isomerides—*v.* DI-METHYL-GLUTARIC ACID, METHYL-ETHYL-SUCCINIC ACID, TRI-METHYL-SUCCINIC ACID, and PROPYL-SUCCINIC ACID.

PIMENTO. The volatile oil obtained from the pods and seeds of *Myrtus Pimenta* contains eugenol and a terpene (255°) S.G. ^{15} ·98 (Bonastre, *J. Ph.* 11, 187; Oeser, *A.* 131, 277).

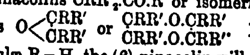
PINACOLIC ALCOHOL *v.* *Sec*-HEXYL ALCOHOL.

PINACOLIN *v.* METHYL *tert*-BUTYL KETONE.

Benzpinacolin *v.* vol. i. p. 488.

PINACONE $C_6H_{14}O_2$ *i.e.* $CMe_2(OH).CMe_2(OH)$. *Hexylene glycol.* [38°]. (170° cor.). S.G. $\frac{15}{15}$ ·9672; $\frac{25}{25}$ ·9609. M.M. 7·245 (Perkin, *C. J.* 45, 506). H.C. 897,697 (Louguinine, *A. Ch.* [5] 25, 143). Formed by the action of Na or sodium-amalgam on aqueous acetone (Fittig, *A.* 110, 25; 114, 54; Städeler, *A.* 111, 277; Friedel, *A.* 124, 324; *Bl.* [2] 19, 289; Linnemann, *A. Suppl.* 3, 374). Formed also from $CMe_2Br.CMe_2Br$ by successive treatment with AgOAc and baryta (Pawloff, *A.* 196, 122). Small needles (from CS_2), v. sol. cold alcohol and ether, sl. sol. cold CS_2. Sl. sol. cold water, but v. sol. hot water, separating on cooling as a hydrate $C_6H_{14}O_2 6aq$ [46·5°], crystallising in four-sided tables, decomposed by distillation into water and pinacone.

Reactions.—1. *Chromic acid mixture* reconverts it into acetone.—2. Gaseous HI yields PrI and some hexane (Linnemann, *Sitz. W.* [2] 63, 255). HIAq at 100° forms $C_6H_{11}I$ (Bouchardat, *Z.* 1871, 699).—3. Boiling dilute H_2SO_4 converts it into pinacolin. Heating with HOAc has the same effect.—4. $POCl_3$ forms di-chloro-hexane [160°] (Friedel a. Silva, *B.* 6, 35).—5. Does not form an acetal when heated with aldehyde (Lochert, *A. Ch.* [6] 16, 60).—6. When passed through a red-hot tube it yields acetone and isopropyl alcohol (Thörner a. Zincke, *B.* 13, 645).

PINACONES. Compounds of the form HO.CRR′.CRR′.OH, where R and R′ are alkyls. They are obtained by reduction of ketones. On treatment with dehydrating agents they yield (β)-pinacolins $CRR'_2.CO.R$ or isomeric (α)-pinacolins  $O\langle\begin{array}{l}CRR'\\CRR'\end{array}$ or $\begin{array}{l}CRR'.O.CRR'\\CRR'.O.CRR'\end{array}$. If in these formulæ R = H, the (β)-pinacolin will be an aldehyde; while if at the same time R′ = H, we find that glycol is the simplest pinacone, aldehyde the simplest (β)-pinacolin, and ethylene oxide the simplest (α)-pinacolin (Zincke, *A.* 216, 296). Some (β)-pinacolins are decomposed by heating with soda-lime or alcoholic potash, thus: $PhCX_2.COPh + H_2O = PhCX_2H + HOBz$ (Zincke

a. Thörner, *B.* 11, 65; Zagumenny, *J. R.* 12, 429); but phenyl (α)-naphthyl (β)-pinacolin reacts with alcoholic potash, thus:

$PhC(C_{10}H_7)_2COPh + H_2O = PhC(C_{10}H_7)_2OH + Ph.CO.H$

(Elbs, *J. pr.* [2] 35, 506).

PINE-APPLE OIL. Artificial pine-apple oil may be made by dissolving butyric ether in alcohol (Hofmann, *A.* 81, 87).

PINENE *v.* TERPENES.

PINEY TALLOW. A fat obtained by boiling the fruits of *Valeria indica* (of Malabar). Melts at 30° to 38°. Its fatty acids consist of palmitic acid (75 p.c.) and oleïc acid (25 p.c.) (Dal-Sie, *G.* 8, 107).

PINIPICRIN $C_{22}H_{36}O_{11}$. Occurs in the needles and bark of the Scotch fir (*Pinus sylvestris*) and in the green parts of *Thuja occidentale* (Kawalier, *Sitz. W.* 11, 350; 13, 515). Bright-yellow amorphous powder, beginning to soften at 55°, and quite liquid at 100°. Hygroscopic. Tastes bitter. V. sol. water, sol. alcohol, insol. ether. Boiling dilute H_2SO_4 yields glucose (2 mols.) and ericinol $C_{10}H_{16}O$ (1 mol.), *v.* vol. ii. p. 458.

PINITANNIC ACID $C_{14}H_{16}O_8$? Occurs in the needles of the Scotch fir and in the green parts of the *Arbor vitæ* (*Thuja occidentale*) (Kawalier, *Sitz. W.* 11, 357; 29, 19). Reddish-yellow powder, v. sol. water, alcohol, and ether. $FeCl_3$ colours its aqueous solution brown. Gives yellow pps. with lead acetate and subacetate. Not ppd. by gelatin.

PINITE $C_7H_{14}O_6$. *Methyl ether of dextrorotatory inosite.* [186°]. $[\alpha]_D = 65° 51'$. Supposed to be extracted by water from the hardened sap of *Pinus lambertiana* of California (Berthelot, *A. Ch.* [3] 46, 76; Johnson, *Am. S.* [2] 22, 6; Combes, *C. R.* 110, 46; Maquenne, *A. Ch.* [6] 22, 264). Crystalline crusts, v. e. sol. water, almost insol. alcohol. Tastes sweet. Dextrorotatory. Non-fermentable. Does not reduce Fehling's solution. HIAq splits it up into MeI and dextrorotatory inosite [248°]. Pinite is identical with matezite and sennite.

PINOL $C_{10}H_{16}O$ *i.e.* C_6H_6OMePr. (184°). S.G. $\frac{20}{}$ ·953; $\mu_D = 1{\cdot}469$. Formed, together with pinene nitroso-chloride when oil of turpentine is treated with HOAc, nitrous ether, and HClAq (Wallach, *A.* 253, 251; 259, 322; 268, 222; *B.* 24, 1552). Purified by conversion into the dibromide $C_{10}H_{16}Br_2O$ [94°], which is dissolved in dry benzene and treated with sodium-wire. Liquid, smelling like cineol.

Reactions.—1. Oxidised by $KMnO_4$ to CO_2, oxalic acid, and terebic acid [176°].—2. Br forms $C_{10}H_{16}Br_2O$ and $C_{10}H_{15}Br_3O$ [160°]. — 3. HBr forms an addition product converted by water into the hydrate $C_{10}N_{16}OH_2O$ [131°] which is not attacked by Ac_2O, but is reconverted into pinol by warming with dilute H_2SO_4, and yields terpenylic acid [57°] on oxidation by $KMnO_4$.

Dibromide $C_{10}H_{16}Br_2O$. [94°]. (144° at 11 mm.). Trimetric crystals; $a:b:c = {\cdot}570:1:1{\cdot}555$. Insol. water, volatile with steam. Converted by alcoholic potash into 'pinol glycollic ether' $C_{10}H_{16}(OEt)_2O$ [53°] (c. 115° at 14 mm.). AgOAc forms $C_{10}H_{16}(OAc)_2O$ [98°] (127° at 13 mm.), which on saponification by hot dilute H_2SO_4 yields 'pinol-glycol' $C_{10}H_{16}(OH)_2O$ [125°], crystallising in matted needles, v. e. sol. chloroform. Boiling with water and $Pb(OH)_2$ also converts the dibromide into the glycol. Silver propionate yields $C_{10}H_{16}(O.COEt)_2$ [106°]. Formic acid at 100° reduces the dibromide to cymene.

Nitroso-chloride $C_{10}H_{16}ONOCl$. [103°]. Formed by the action of amyl nitrite and HCl on pinol in HOAc (Wallach, *A.* 253, 261). Converted by alcoholic NH_3 into the nitrolamine $C_{10}H_{16}ONONH_2$ (130° at 14 mm.), a viscid mass which yields a crystalline hydrochloride, B'HCl. Aniline, piperidine, and benzylamine form the three analogous bodies $C_{10}H_{16}O.NO.NHPh$ [175°], $C_{10}H_{16}O.NO.NC_5H_{10}$ [154°], and the compound $C_{10}H_{16}O.NO.NHC_7H_7$ [136°], each of which forms a crystalline hydrochloride. (β)-Naphthylamine forms, in like manner, pinol-nitrol-naphthylamine $C_{10}H_{16}O.NO.NHC_{10}H_7$ [195°].

PINYLAMINE $C_{10}H_{15}NH_2$. (208°). S.G. $\frac{17}{}$ ·943. Formed by reducing with zinc-dust and HOAc nitroso-pinene $C_{10}H_{15}NO$ [132°], which is got from $C_{10}H_{16}NOCl$ and alcoholic NaOH (Wallach a. Lorenz, *A.* 268, 197; *B.* 24, 1550). Oil, turning yellow in air, and giving off NH_3. Absorbs CO_2 from air, forming a solid carbonate Benzoic aldehyde forms $C_{10}H_{15}N{:}CHPh$ [58°] furfuraldehyde gives $C_{10}H_{15}N{:}CH.C_4H_3O$ [81°] whilst salicylic aldehyde forms the compound $C_{10}H_{15}N{:}CH.C_6H_4.OH$ [109°].—B'HCl. [230°]. Needles (from water). Yields cymene on distillation.—$B'_2H_2PtCl_6$. Yellow plates or needles.—$B'HNO_3$. Crystals, sl. sol. cold water.—$B'_2H_2SO_4$.—B'HCyS. [136°]. Prisms (from water).—$B'_2H_2C_2O_4$. [248°]. Scales.

Acetyl derivative $C_{10}H_{15}NHAc$. [109°]

Benzoyl derivative. [125°]. Needles.

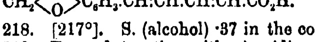
PINYL-UREA $NH_2.CO.NHC_{10}H_{15}$. [150°]. Formed from pinylamine hydrochloride and potassium cyanate (Wallach, *A.* 268, 204). Needles, v. sol. alcohol.

PIPECOLINE *v.* METHYL-PYRIDINE HEXAHYDRIDE.

PIPERAZINE *v.* PYRAZINE HEXAHYDRIDE.

PIPERHYDRONIC ACID *v.* *Methylene derivative* of DI-OXY-PHENYL-VALERIC ACID.

PIPERIC ACID $C_{12}H_{10}O_4$ *i.e.*



$CH_2{<}^{O}_{O}{>}C_6H_3.CH{:}CH.CH{:}CH.CO_2H$. Mol. w. 218. [217°]. S. (alcohol) ·37 in the cold; 2 at 78°. Formed, together with piperidine, by boiling piperine with alcoholic potash (Von Babo; Strecker, *A.* 105, 317; 118, 280; G. C. Foster, *C. J.* 15, 17; Fittig a. Mielk, *A.* 152, 25; 172, 134). Yellowish needles (from alcohol). After fusion it melts at 213°. Nearly insol. water, m. sol. hot alcohol and ether.

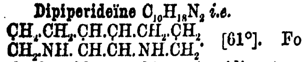
Reactions.—1. Reduced by sodium-amalgam to two hydropiperic acids, which are the methylene derivatives of di-oxy-phenyl-angelic acids $CH_2O_2{:}C_6H_3.CH_2.CH{:}CH.CH_2.CO_2H$ [78°] and $CH_2O_2{:}C_6H_3.CH_2.CH_2.CH{:}CH.CO_2H$ [131°] (Regel, *B.* 20, 414).—2. Dilute alkaline potassium permanganate at 4° oxidises piperic acid to piperonal $CH_2O_2{:}C_6H_3.CHO$ and racemic acid (Doebner, *B.* 23, 2375).—3. *Potash-fusion* yields protocatechuic, oxalic, and acetic acids.—4. *Bromine* in CC_2 forms a tetrabromide which decomposes at 160°–165°.

Salts.—NH_4A'. Satiny scales.—KA'.—BaA'_2. S. ·02 in the cold.—AgA': powder.

Ethyl ether EtA'. [78°]. Plates.

Reference.—BROMO-PIPERIC ACID.

PIPERIDEÏNE. A name for PYRIDINE TETRAHYDRIDE.

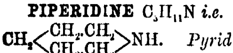
Dipiperideïne $C_{10}H_{18}N_2$ *i.e.*  $\begin{array}{l}CH_2.CH_2.CH.CH.CH_2.CH_2\\ CH_2.NH.CH.CH.NH.CH_2\end{array}$ [61°]. Formed by slowly adding *ν*-chloro-piperidine to a boiling 10 p.c. solution of potash in alcohol (Lellmann a. Schwaderer, *B.* 22, 1000, 1318). Monoclinic crystals, sl. sol. water, v. sol. alcohol and ether. Between 200° and 230° it begins to dissociate into (2 mols. of) pyridine tetrahydride; hence it has no constant boiling-point. Slightly volatile with steam. Ac_2O forms an acetyl derivative (220°). S.G. $\frac{16\cdot5}{4}$ 1·0531. Tin and conc. HClAq reduce it to piperidine. Phenyl thiocarbimide gives $C_{10}H_{17}N_2.CS.NHPh$ [144°]. CS_2 forms $C_{10}H_{18}N_2CS_2$, crystallising in needles, and melting at 150° with evolution of gas.

Salt.—$B''H_2Cl_2$ 2aq. [150°]. Plates, liquefies c. 80° when quickly heated.

Isodipiperideïne $C_{10}H_{18}N_2$. Formed by heating diazobenzene piperidide at 250° (Heusler, *A.* 260, 239). Thickish liquid, miscible with water, but can be extracted therefrom by ether. Reduces Fehling's solution and ammoniacal $AgNO_3$. Its salts are hygroscopic.

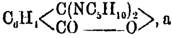
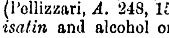
PIPERIDIC ACID $C_4H_9NO_2$ [184°], which is got by oxidising piperidine *ν*-carboxylic ether with fuming HNO_3 and heating the product with HClAq at 140°, is *γ*-amido-butyric acid (Schotten, *B.* 16, 643; Gabriel, *B.* 23, 1770).

PIPERIDINE $C_5H_{11}N$ *i.e.*

 $CH_2<\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}>NH$. *Pyridine hexahydride.* Mol. w. 85. (106°). S.G. $\frac{15}{15}$ ·8664; $\frac{25}{25}$ ·8591. M.M. 5·810 (Perkin, *C. J.* 55, 700). S.V. 108·76. S.H. ·533 (Colson, *Bl.* [3] 3, 8). H.F.v. 24,090. H.F.p. 26,990 (Thomsen, *Th.* 4, 145). Appears to occur in the husks of pepper (Johnstone, *C. N.* 58, 235; *An.* 14, 41).

Formation.—1. By distilling piperine with potash-lime or soda-lime, or by boiling it with alcoholic potash (Wertheim, *A.* 127, 75; Anderson, *A.* 75, 82; 84, 345; Cahours, *A. Ch.* [3] 38, 76; Von Babo a. Keller, *J. pr.* 72, 53).—2. By reduction of pyridine in alcoholic solution by sodium-amalgam; the yield being 75 p.c. of the theoretical (Ladenburg a. Roth, *A.* 247, 51). 3. By heating pentamethylene-diamine hydrochloride (Ladenburg, *B.* 18, 3100).—4. By heating hygric acid $C_6H_{11}NO_2$ with H_2SO_4 for a few minutes at 300° (Liebermann a. Kühling, *B.* 24, 413).

Properties.—Liquid, with ammoniacal and peppery smell, miscible with water. Alkaline in reaction. Caustic taste. Ppts. salts of zinc and copper, but does not redissolve the ppd. hydrates. Not attacked by fuming HClAq at 300° or by boiling HNO_3 (S.G. 1·5). Piperidine acts as an anæsthetic (*B.* 14, 713). Oxidised by H_2O_2 to glutaric acid and its imide and *δ*-amido-valeric aldehyde (Wolffenstein, *B.* 25, 2777).

Reactions.—1. *Bromine* and water at 200° yield di-bromo-oxy-pyridine and some $CHBr_3$ (Hofmann, *B.* 12, 984). Piperidine hydrochloride, heated with dry Br at 180, yields di-bromo-pyridine (Schotten, *B.* 15, 427). Bromine and NaOHAq give crystalline $C_5H_7Br_2NO$ (Hofmann, *B.* 16, 560). Bromine and lime-water yield bromo-piperidine $C_5H_{10}BrN$ [234°] (Lellmann, *B.* 22, 1327).—2. *Chlorine* acts with explosive violence on dry piperidine. In presence of water or chloroform it yields *ν*-chloro-piperidine, which may also be got by using bleaching-powder. It is an unstable, heavy oil (52° at 25 mm.), with pungent odour, and deposits piperidine hydrochloride when kept for some time (Bally, *B.* 21, 1772).—3. Conc. H_2SO_4 at 300° forms pyridine (Kœnigs, *B.* 12, 2341). Nitrobenzene at 260° also oxidises it to pyridine (L.). 4. *Chloroform*, on boiling for some days, yields $CH(C_5H_{10}N)_3$ aq (98° at 15 mm.) (Busz a. Kekulé, *B.* 20, 3246).—5. CH_3CCl_3 forms, on boiling, ethenyl tripiperidine $CH_3.C(C_5H_{10}N)_3$, a liquid (262°) yielding $B'''H_3Cl_3$ and $B'''_2 3H_2PtCl_6$ (B. a. K.).—6. Boiling *oxalic ether* (1 mol.) yields piperidyl-oxamic ether $C_5H_{10}N.CO.CO_2Et$ (289°) (Wallach, *A.* 214, 278; 237, 247). The corresponding acid [129°] splits up on fusion into CO_2 and the formyl derivative of piperidine. PCl_5 yields CO_2 and $C_5H_{10}N.COCl$ (238°), which acts upon piperidine forming $(C_5H_{10}N)_2CO$ [43°] (298°). NH_3Aq converts the ether into piperidyl-oxamide $C_5H_{10}N.CO.CO.NH_2$ [127°], crystallising in monoclinic prisms, converted by P_2O_5 into $C_5H_{10}N.CO.CN$, a heavy oil (264°). When piperidine (2 mols.) is distilled with oxalic ether (1 mol.) there is formed oxalyl-piperidine $C_5H_{10}N.CO.CO.C_5H_{10}N$ [89°] (above 350°).—7. By heating with *phthalic acid* (2 mols.) as long as phthalic anhydride sublimes there is formed 'piperilene-amine-phthaleïn' $C_{18}H_{24}N_2O_2$ or  $C_6H_4<\begin{array}{l}C(NC_5H_{10})_2\\ CO ——— O\end{array}>$, an oil which yields crystalline $C_{18}H_{24}Br_2N_2O_2$ (Piutti, *G.* 13, 535; *A.* 227, 197).—8. *Phthalic anhydride* unites in the cold with piperidine, forming a mixture of 'piperilene-phthalamic acid' $C_5H_{10}N.CO.C_6H_4.CO_2H$ and its piperidine salt (P.). On shaking with ether and water the acid goes into ethereal solution, and the salt into aqueous solution. Piperilene-phthalamic acid is a heavy oil, v. sol. alcohol. It yields AgA', $C_5H_{11}NHA'$ [c. 150°], and $C_{18}H_{26}Br_4N_2O_3$, crystallising in long needles. 9. *Alloxan* and aqueous sulphurous acid give $(C_4H_2N_2O_4)C_5H_{11}NH_2SO_3$, crystallising in plates (Pellizzari, *A.* 248, 150).—10. On heating with *isatin* and alcohol on the water-bath there is formed the compound $C_8H_5NO(C_5H_{10}N)_2$ or  $C_6H_4<\begin{array}{l}C(NC_5H_{10})_2\\ NH ——— CO\end{array}>$, crystallising in flat colourless prisms, m. sol. hot alcohol, turned red by HCl, and yielding a blue dye (indigo?) when treated with Ac_2O, or when rapidly heated to 125°–160°. Bromo-isatin forms, in like manner, $C_8H_4BrNO(C_5H_{10}N)_2$, crystallising in needles, while di-bromo-isatin reacts with production of $C_6H_2Br_2(NH_2).CO.CO.NC_5H_{10}$ [152°] (Schotten, *B.* 24, 1367, 2605).—11. A solution of *diazobenzene chloride* and sodium acetate forms $Ph.N{:}N.NC_5H_{10}$, which yields phenol and piperidine when treated with dilute H_2SO_4, and phenyl-hydrazine and piperidine when reduced by $SnCl_2$ and HCl (Nölting a. Binder, *B.* 20, 3016). Other diazo- compounds act in like manner. Diazobenzene piperidide is decomposed on heating to 250°, yielding benzene, N, and isopiperideïn (Heusler, *A.* 260, 239).—12. *Potassium cyanate* converts piperidine sulphate into $NH_2.CO.NC_5H_{10}$, crystallising from alcohol in needles (Cahours). *Methyl* and *ethyl cyanates* yield corresponding ureas. *Phenyl cyanate* forms $NHPh.CO.NC_5H_{10}$, crystallising from alcohol in prisms [172°]. $C_7H_7NH.COCl$ gives rise to $C_7H_7NH.CO.NC_5H_{10}$ [102°], crystallising from dilute alcohol in needles (Kühn a. Riesenfeld, *B.* 24, 3818).—13. *Methyl thio-carbimide* forms $NHMe.CS.NC_5H_{10}$ [129°] (Hecht, *B.* 23, 287; 25, 815), while *ethyl-*, *propyl-*, and *phenyl- thiocarbimides* form corresponding thio-ureas [46°], [75°], and [99°] respectively. *Phenyl-*, *o-*, and *p-tolyl-thiocarbimides* form $C_5H_{10}N.CS.NHPh$ [98°] (G.); [104°] (Skinner a. Ruhemann, *C. J.* 53, 558) and $C_5H_{10}N.CS.NHC_7H_7$ [98°] and [132°] respectively. *Potassium sulphocyanide* reacts with piperidine sulphate, forming $C_5H_{10}N.CS.NH_2$ [92°] Gebhardt, *B.* 17, 3039). *Allyl-thiocarbimide* forms oily $C_5H_{10}N.CS.NHC_3H_5$, which is converted by conc. HClAq at 100° into $C_5H_{10}N.C\left\langle\begin{array}{l}S.CHMe\\ N.CH_2\end{array}\right.$, a liquid (277°) yielding $B'C_6H_3N_3O_7$ [112°] and B'MeI [67°] (Avenarius, *B.* 24, 262).—14. *Benzoyl-thiocarbimide* added to a solution of piperidine in dry benzene forms $C_5H_{10}N.CS.NHBz$ [123°], crystallising in needles, sol. alcohol and ether (Dixon, *C. J.* 55, 624). *Benzyl-thiocarbimide* gives $C_5H_{10}N.CS.NHCH_2Ph$ [88°] (Dixon, *C. J.* 59, 568).—15. *Tri-methyl-trithiocyanurate* at 200° forms $C_{11}H_{24}N_3S$ [107°], which gives $B'_2H_2PtCl_6$ (Hofmann, *B.* 18, 2779).—16. *Quinone* forms red needles [178°], which are probably $C_6H_2O_2(NC_5H_{10})_2$ (Lachovitch, *M.* 9, 506).—17. *Benzoic aldehyde* in presence of K_2CO_3 forms $CHPh(NC_5H_{10})_2$ [80°] crystallising from alcohol in flat needles (Ehrenberg, *J. pr.* [2] 36, 130; Lachovitch, *M.* 9, 695).—18. *Tri-oxy-methylene* forms $CH_2(NC_5H_{10})_2$ (230°), which unites with CS_2 giving $C_{11}H_{20}N_2CS_2$ [58°].—19. *Pinene nitroso-chloride* in alcoholic or aqueous solution yields crystalline $C_{10}H_{16}NONC_5H_{10}$ [119°] which forms B'HCl. The corresponding terpine and dipentinene derivatives melt at 154° (Wallach, *A.* 241, 320; 245, 253).—20. *Amylene nitroso-nitrate* in boiling alcoholic solution forms $CMe_2(NC_5H_{10}).CMe{:}NOH$, which crystallises from ether in prisms [96°], and is converted by boiling dilute H_2SO_4 into $CMe_2(NC_5H_{10}).CO.CH_3$, an oil (220°), $\mu_D = 1{\cdot}934$, volatile with steam, yielding a very hygroscopic hydrochloride (Wallach, *A.* 248, 172).—21. *Fluorescein chloride* at 220° forms $C_6H_4{:}C_2O_2\left\langle\begin{array}{l}C_6H_3(NC_5H_{10})\\ C_6H_3(NC_5H_{10})\end{array}\right\rangle O$ which yields $B''H_2PtCl_6$ and $B''H_2Cl_2$ which is purple in dilute solution and yellow in conc. HClAq (Lellmann a. Büttner, *B.* 23, 1387).—22. *Bromo-phenanthrene* at 260° forms crystalline $C_{11}H_9NC_5H_{10}$ [113°] which yields $B'_2H_2PtCl_6$ 6aq (L. a. B.).—23. *Bromo-anthracene* at 260° reacts forming $C_{14}H_9NC_5H_{10}$ crystallising from ether in yellow prisms and giving $B'_2H_2PtCl_6$ 2aq (L. a. B.).—24. *Chloro-acetic acid* forms $C_5H_{10}N.CH_2.CO_2H$, which forms hemihedral prisms (containing aq) and yields CuA'_2 4aq, HA'HCl, $HA'HBiI_4$, $(HA')_4 3HAuCl_4$, and $HA'BaCl_2$ (Kraut, *A.* 157, 66).—25. *a-Chloro-propionic ether* produces $C_5H_{10}N.CHMe.CO_2H$ crystallising from water and alcohol in prisms and yielding $HA'HAuCl_4$ (Brühl, *B.* 9, 34).—26. *Benzene sulphochloride* and NaOHAq form $C_6H_5.SO_2.NC_5H_{10}$ [93°] (Hinsberg, *A.* 265, 182; Schotten a. Schlömann, *B.* 24, 3689). This body is oxidised by $KMnO_4$ to $C_6H_5.SO_2.NH.CH_2.CH_2.CH_2.CH_2.CO_2H$.—27. *Picryl chloride* forms $C_5H_{10}N.C_6H_2(NO_2)_3$ [106°] (S. a. S.).—28. *Glycerin dichlorhydrin* forms liquid $C_{10}H_{22}N_2O$ (280°-290°) which yields $B''H_2PtCl_6$ (Ladenburg, *B.* 14, 1879).—29. CS_2 forms $(C_5H_{11}N)_2CS_2$ or $C_5H_{10}N.CS.SNC_5H_{12}$ crystallising in slender monoclinic needles [174°], converted by an alcoholic solution of iodine to $(C_5H_{10}N.CS)_2S_2$ [130°].—30. *Dicyandiamide* reacts on 'piperyl-biguanide' with formation of $C_7H_{15}N_5$, *i.e.* $C_5H_{10}N.C(NH).NH.C(NH).NH_2$ [163°?] crystallising in silky needles, and yielding the salts $B'H_2Cl_2$ [217°], $B'H_2SO_4$ [173°], $B'_2H_2SO_4$ [219°], $B'H_2PtCl_6$ [252°], $B'H_2AuCl_5$, and the copper compound $Cu(C_7H_{11}N_5)_2H_2SO_4$ crystallising in rose-red needles (Bamberger, *B.* 24, 605, 904). Piperyl-biguanide is converted by $CHCl_3$ and caustic potash into 'piperyl-formoguanamine' $C_5H_{10}N.C\left\langle\begin{array}{l}N.C(NH_2)\\ N{=}CH\end{array}\right\rangle N$ [194·5°] which yields the salts B'HCl [201°], $B'_2H_2SO_4$aq [222°], $B'2C_6H_3N_3O_7$ [188°], $B'_2H_2PtCl_6$ [219°], $B'HAuCl_4$ [90°] and [158°], and B'_2AgNO_3 [229°-238°] (Hjelt, *B.* 25, 529). Piperyl-biguanide sulphate heated with NaOAc at 200° yields piperyl-acetoguanamine $C_5H_{10}N.C\left\langle\begin{array}{l}N.C(NH_2)\\ N{:}CMe\end{array}\right\rangle N$ [179°] (Hjelt, *B.* 25, 533). The acetyl derivative of piperyl-biguanide $C_5H_{10}N.C(NAc).NH.C(NH).NH_2$ [193°] is got by heating the copper salt with HOAc.

Salts.—B'HCl. [237°]. M.M. 10·034 in a 53 p.c. solution (Perkin, *C. J.* 55, 716). Needles, v. sol. water and alcohol.—$B'HAuCl_4$ [206°]. Not decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2PtCl_6$. [196°] (Ladenburg, *B.* 18, 3100); [200°] (Wallach a. Lehmann, *A.* 237, 241). Red needles. Not decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131). Crystallises also with EtOH in orange needles [191°].—B'_2PtCl_2.—$B'Zn_2OCl_2$: amorphous pp. got by adding piperidine to a solution of $ZnCl_2$ (Lachovitch, *M.* 9, 517).—B'HBr. Plates (Lellmann, *B.* 20, 680).—B'HI. Long needles.—$(B'HI)_3 2BiI_3$. Scarlet plates (from alcohol) (Kraut, *A.* 210, 319).—B'ICl. [143°]. White needles.—B'IClHCl. [90°]. Yellow crystals (from water) (Pictet a. Krafft, *Bl.* [3] 7, 72).—$B'HNO_3$. Small needles.—$B'_2H_2C_2O_4$: needles.—$B'_2H_4FeCy_6$ 3aq. Yellow triclinic crystals.—**Piperate** $B'C_{12}H_{10}O_4$. Silky laminæ [100°] (Babo a. Keller).—$B'_2H_2SO_4$.

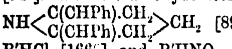
Nitrosamine $C_5H_{10}N.NO$. (218°). S.G. $^{16.5}$ 1·066. Formed from piperidine and nitrous acid (Wertheim, *A.* 127, 75; Schotten, *B.* 15, 425; Knorr, *A.* 221, 298). Pale-yellow liquid, sl. sol. water, v. sol. conc. HClAq, but reppd. on dilution. Zinc and HClAq reduce it to piperidine and NH_3. Heated in a current of HCl at 100° it gives piperidine and NOCl. Sodium-amalgam forms $C_5H_{10}N.NH_2$ and piperidine.—$B''H_2Cl_2$: syrupy.—$B''HCl$: crystalline mass.

Hydrazine $C_5H_{10}N.NH_2$. '*Piperyl-hydrazine.*' (146°) at 728 mm. S.G. $\underline{14.6}$ ·928. Got by reducing the nitrosamine with zinc-dust and HOAc (Knorr, *B.* 15, 859; *A.* 221, 299). Liquid, with ammoniacal odour, miscible with water, alcohol, and ether. Volatile with steam. Oxidised by HgO in the cold to the tetrazone $C_{10}H_{20}N_4$ [45°], which yields $B'_2H_2PtCl_6$. Reduces cold ammoniacal $AgNO_3$ and hot Fehling's solution. Nitrous acid converts it into piperidine. CS_2 gives rise to $(C_5H_{10}N.NH)_2CS$ [181°]. The compound

$C_5H_{10}N.NH.CS.NC_5H_{10}$ [86°] may also be obtained. BzCl in ether forms $C_5H_{10}N.NHBz$ [196°]. Benzoic aldehyde forms $C_5H_{10}N.N{:}CHPh$ [63°]. **Salt.**—B'HCl. [162°]. Tables (from alcohol). Reacts with potassium cyanate forming $C_5H_{10}N.NH.CO.NH_2$ [136°] and with potassium sulphocyanide forming $C_5H_{10}N.NH.CS.NH_2$ [167°].—*Methylo-iodide* B'MeI. [215°]. Begins to decompose at 150°.

Formyl derivative $C_5H_{10}N.CHO$. (222°). S.G. $^{23}_{4}$ 1·0193. Formed by the distillation of $C_5H_{10}N.CO.CO_2H$ (*v. Reaction* 6) (Wallach a. Lehmann, *A.* 228, 251; 237, 252). Got also by heating piperidine with formamide (Lachovitch, *M.* 9, 699). Liquid, miscible with water, alcohol, and ether. PCl_5 yields a base $C_{11}H_{20}N_2$.—B'HCl: deliquescent needles. — $B'_4H_2PtCl_6$. [172°]. Plates.—$B'HgCl_2$. [149°]. Needles.

Acetyl derivative $C_5H_{10}NAc$. (227°). S.G. ^{0} 1·011 (Wallach a. Kamensky, *A.* 214, 238; *cf.* Schotten, *B.* 15, 426). Liquid, miscible with water. When heated with BzCl it gives AcCl and benzoyl-piperidine (Pictet, *B.* 23, 3014). On heating with bromine it gives pyridine, bromo-pyridine, and di-bromo-pyridine (Hofmann, *B.* 16, 587). When Cl is passed into cooled acetyl-piperidine and the product is warmed with water, there is formed $C_7H_{11}Cl_2NO_2$ [122°] (Bally, *B.* 21, 1772).



Benzoyl derivative $C_5H_{10}NBz$. [48°]. (above 360°). Formed from piperidine, BzCl, and NaOHAq (Cahours; Schotten, *B.* 17, 2544; 21, 2238). Triclinic prisms (from alcohol). Oxidised by $KMnO_4$ to benzoyl-δ-amido-valeric acid [94°]. Benzoic aldehyde forms the compound $NH{<}\begin{matrix}C(CHPh).CH_2\\C(CHPh).CH_2\end{matrix}{>}CH_2$ [89°], which yields B'HCl [166°] and $B'HNO_3$ [98°], both being crystalline (Rügheimer, *B.* 24, 2186).

Bromo-benzoyl derivative $C_5H_{10}N.CO.C_6H_4Br$. The *o-* compound is an oil, while the *p-* compound crystallises from alcohol in rectangular monoclinic tables [95°] (Schotten, *B.* 21, 2248).

m-Nitro-benzoyl derivative $C_5H_{10}N.CO.C_6H_4NO_2$. [34°]. (184° at 54 mm.). S. (alcohol) 33 in the cold, 50 at 78°. Dark-yellow monoclinic crystals. Crystallises from water with about 5aq, and then melts at 84°. Yields, on reduction, the *m*-amido-benzoyl derivative [125°].

Oxy-benzoyl derivative v. Piperidide of OXY-BENZOIC ACID.

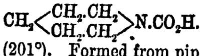
Cuminyl derivative $C_{15}H_{21}NO$. Tables.

Cinnamyl derivative $C_8H_7CO.NC_5H_{10}$. [122°]. Formed from the anhydride and piperidine (Herstein, *B.* 22, 2265). Stellate needles.

Alkyl-piperidines. On heating the alkylo-iodides of pyridine, a pair of alkyl-pyridines is produced, that of lower boiling-point being (α)-alkyl-pyridine, and the other (γ)-alkyl-pyridine. On reduction these give the corresponding alkyl-piperidines. The same isopropyl-pyridines are obtained both from pyridine isopropylo-iodide, and pyridine *n*-propylo-iodide, an intramolecular change taking place in the propyl group in the latter case. Conyrine is (α)-propyl-pyridine, coniine is (α)-propyl-piperidine (Ladenburg, *B.* 18, 1587). By adding potash to piperidine alkylo-iodides, ν-alkyl-piperidines can be obtained.

Methyl-, Ethyl-, Propyl-, Phenyl-, and Tolyl-Piperidines v. METHYL, ETHYL, PROPYL, PHENYL, and TOLYL PYRIDINE HEXAHYDRIDES.

PIPERIDINE ν-CARBOXYLIC ACID



$CH_2{<}\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}{>}N.CO_2H$. *Methyl ether* MeA'. (201°). Formed from piperidine, $ClCO_2Me$, and KOHAq (Schotten, *B.* 15, 425; 16, 647). Heavy oil. Converted by HNO_3, containing urea, into $C_5H_7(NO_2)N.CO_2Me$ [103°], whence Br forms a compound [130°].

Ethyl ether EtA'. *Piperyl-urethane.* (211°). Formed from piperidine and $ClCO_2Et$. Oil. Br in HOAc forms $C_5H_7BrN.CO_2Et$ [140°], while HNO_3 free from NO_2 forms 'nitrodehydro-piperyl urethane' $C_5H_7(NO_2)N.CO_2Et$ [52°], whence Br in HOAc forms $C_8H_{13}BrN_2O_5$ [157°].

Chloride $C_5H_{10}N.COCl$. (238°). Formed from $C_5H_{10}N.CO.CO_2H$ and PCl_5 (*v.* PIPERIDINE, *Reaction* 6). Liquid, slowly decomposed by cold water into piperidine, CO_2, and HCl.

Amide $C_5H_{10}N.CO.NH_2$. [106°]. Got from piperidine sulphate and potassium cyanate. Needles. Yields $B'HNO_3$. [67°] (Franchimont a. Klobbie, *R. T. C.* 8, 302).

Anilide. [172°]. Formed from piperidine and phenyl cyanate, or from the chloride and aniline (Gebhardt, *B.* 17, 3040; Wallach, *A.* 228, 250; 237, 250).

Piperidide $(C_5H_{10}N)_2CO$. [43°].

Isomeride *v. Hexahydride of* PYRIDINE CARBOXYLIC ACID.

DI-PIPERIDYL *v.* DIPYRIDYL *dodecahydride.*

PIPERIDYL-CYANURAMIDE *v. Cyanuramide* in article CYANIC ACIDS.

PIPERIDYL-MELAMINE *v.* CYANIC ACIDS.

PIPERILENE *v.* vol. iii. p. 807.

PIPERINE $C_{17}H_{19}NO_3$ *i.e.* $C_5H_{10}N.CO.CH{:}CH.CH{:}CH.C_6H_3{:}O_2CH_2$. *Piperyl-piperidine.* Mol. w. 285. [128°]. Occurs in black pepper (*Piper nigrum*), long pepper (*P. longum*), and in the black pepper of Western Africa (*Cubeba Clusii*) (Oersted, *S.* 29, 80; Pelletier, *A. Ch.* [2] 16, 344; 51, 199; Merck, *N. J. T.* 20, 1, 34; Wackenroder, *Br. Arch.* 37, 347; Duflos, *S.* 61, 22; Warrentrapp a. Will, *A.* 39, 283; Wertheim, *A.* 70, 58; Gerhardt, *Compt. Chim.* 1849, 375; *A. Ch.* [3] 7, 253; Anderson, *A.* 75, 82; 84, 345; Cahours, *A. Ch.* [3] 38, 76; Stenhouse, *A.* 95, 106; Von Babo a. Keller, *J. pr.* 72, 53; Strecker, *A.* 105, 317).

Formation.—By heating piperidine with the chloride of piperic acid (Rügheimer, *B.* 15, 1390).

Preparation.—Ground pepper (1 pt.) is boiled with slaked lime (2 pts.) and water, the filtrate evaporated to dryness at 100°, and the piperine extracted with ether and recrystallised from alcohol (Cazeneuve a. Caillot, *Bl.* [2] 27, 290).

Properties.—Monoclinic prisms, v. sl. sol. hot water, m. sol. alcohol and ether. Inactive to light. Insol. dilute acids and alkalis. Decomposed by alcoholic potash into piperic acid and piperidine. Conc. H_2SO_4 forms a blood-red solution. HNO_3 gives a greenish-yellow colour changing to red. Phosphomolybdic acid gives a flocculent pp.

Salts.—The hydrochloride is crystalline, but decomposed by water.—$B'_4H_2PtCl_6$: roseate monoclinic crystals. Not decomposed by hot water (De Coninck, *Bl.* [2] 45, 131).—B'_2HHgCl_3:

triclinic crystals.—B'_2HI_3. [145°]. Steel-blue needles (Jörgensen, *J. pr.* [2] 3, 328).

PIPEROKETONIC ACID *v.* Di-oxy-benzyl ethyl ketone carboxylic acid.

PIPERONAL *v.* *Methylene derivative* of Protocatechuic aldehyde.

PIPERONYL-ACRYLIC ACID *v.* *Methylene ether* of Caffeic acid.

PIPERONYL ALCOHOL *v.* *Methylene derivative* of Di-oxy-benzyl alcohol.

PIPERONYLIC ACID *v.* *Methylene derivative* of Protocatechuic acid.

PIPEROPROPIONIC ACID *v.* Di-oxy-phenyl-propionic acid.

PIPER-PROPYL-ALKINE *v.* Oxy-propyl-piperidine.

PIPERYL. This name is given to radicle $CH_2O_2:C_6H_3.CH:CH.CH:CH.CO$. *Piperyl* has also been used to denote C_5H_{10}, the divalent radicle which is united to NH in piperidine; many of the derivatives of this divalent 'piperyl' are described under Piperidine.

PIPERYLENE *v.* Pentinene.

PIPERYLENE TETRABROMIDE *v.* Tetra-bromo-pentane.

PIPITZAHOÏC ACID $C_{15}H_{20}O_3$. *Perezone.* [104°] (A. a. L.); [107°] (Mylius, *B.* 18, 480). May be extracted by alcohol from Pipitzahuac root or *Radix Perezia* (De la Sagra, *C. R.* 42, 873, 1072; Weldt, *A.* 95, 188; Anschütz a. Leather, *C. J.* 49, 715; *B.* 18, 709, 715). Flat golden plates (from alcohol), nearly insol. water, v. sol. alcohol and ether. May be sublimed. Volatile with steam. Aqueous alkalis form a violet solution. Aqueous methylamine forms methyl-amido-pipitzahoïc acid $C_{15}H_{19}(NHMe)O_3$ [114°], crystallising in blue needles, while aniline forms $C_{15}H_{19}(NHPh)O_3$ [139°], *o*-toluidine gives $C_{15}H_{19}(NHC_7H_7)O_3$ [110°], *p*-toluidine yields *p*-tolyl-amido-pipitzahoïc acid [134°]. Bromine forms $C_{15}H_{20}Br_2O_3$ [109°].

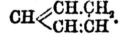
S a l t s.—$PbC_{15}H_{18}O_3$.—CuA'_2.—AgA': purple pp.

Ethyl ether EtA'. [141°].

Acetyl derivative $C_{15}H_{19}AcO_3$. [115°]. Trimetric plates; $a:b:c = \cdot629:1:\cdot845$.

Oxim? $C_{15}H_{21}NO_3$. *Amidopipitzahoïc acid.* [154°]. Flat violet-brown needles. Formed from the acid and alcoholic hydroxylamine (Mylius, *B.* 18, 936). The same body is got by boiling phenyl-amido-pipitzahoïc acid (*v. supra*) with NH_3Aq (A. a. L.).

Oxypipitzahoïc acid $C_{15}H_{18}(OH)_2O_2$. [129°] (A. a. L.); [134°] (M.). Formed by warming phenyl-amido-pipitzahoïc acid (*v. supra*) with alcoholic H_2SO_4. Orange plates, nearly insol. water. Its alkaline solutions are violet. Bromine forms an unstable dibromide [140°–146°]. On warming with H_2SO_4 it is converted into perezinone $C_{15}H_{18}O_3$ [144°], which crystallises in yellow needles or prisms, and yields $C_{15}H_{17}NaO_3$, crystallising in easily soluble yellow tables.



PIRYLENE C_5H_6 *i.e.* $CH\Big\langle{CH.CH_2 \atop CH:CH}$. (60°). **Formed by distilling with solid NaOH the methylo-iodide of the base obtained by the action of Ag_2O on the iodide formed from di-methyl-pyridine hexahydride and iodine (Ladenburg, *A.* 247, 60). Oil. Does not ppt. ammoniacal Cu_2Cl_2.**

PISCIDIN $C_{29}H_{24}O_8$. [192°]. The poisonous principle of Jamaica dogwood (*Piscidia Erythrina*), from which it can be extracted by lime-water (Hart, *Am.* 5, 39). Six-sided prisms (from alcohol), insol. water, sl. sol. cold alcohol, sol. benzene, $CHCl_3$, and conc. HClAq. Sedative and narcotic.

PITTAKAL *v.* Eupittonic acid.

PITURINE is Nicotine.

PLASMINE *v.* Proteïds.

PLATINAMMINES *v.* Platinum-ammonium compounds, p. 292.

PLATINATES. PtO_4H_4 acts as an acidic hydroxide towards strong bases, forming compounds of the type $xPtO_2.yMO$. These *platinates* are generally obtained by reacting on $PtCl_4Aq$ with caustic or carbonated alkalis, and sometimes by fusing $PtCl_4$ with bases and then washing with water.

Barium platinates. The compound $2PtO_2.3BaO$ was obtained, in hexagonal crystals, by Rousseau (*C. R.* 109, 144) by heating $PtCl_4$ with BaO for some time, then adding $BaCl_2$ equal to the quantity of BaO used, and heating to c. 1100° (m.p. of Cu) in a Pt dish for some hours, and washing with water. The crystals are insol. acetic acid, but sol. HClAq. The salt decomposes at an orange-red heat, in presence of $BaCl_2$, with separation of Pt. Topsöe (*B.* 3, 462) obtained $PtBaO_3.4H_2O$ by decomposing H_2PtCl_6Aq by excess of BaO_2H_2 in sunlight; to the pp. thus obtained Johannsen (*A.* 155, 204) gave the composition

$$3PtBaO_3.BaCl_2.PtOCl_2.11H_2O.$$

Calcium platinates. According to Herschel (*A.* 3, 317), CaOAq added to $PtCl_4Aq$ in sunlight produces a white pp. of

$$PtCaO_3.CaO.PtOCl_2.7H_2O.$$

Sodium platinates. When a mixture of Na_2CO_3Aq and H_2PtCl_6Aq stands for some days in a warm place, a pp. of $3PtO_2.Na_2O.6H_2O$ separates (Döbereiner a. Weiss, *A.* 14, 21). Rousseau (*C. R.* 109, 144) obtained crystals of Na platinate by heating a mixture of equal weights of NaOH and NaCl with some Pt black, in a Pt crucible, to c. 1100 for two or three hours.

For descriptions of the *bromoplatinates, chloroplatinates, iodoplatinates,* &c., *v.* Platini-bromides, Platini-chlorides, Platini-iodides, &c.

THIOPLATINATES. PtS_2 combines with some more basic sulphides to form salts which may be called *thioplatinates*; some salts are also known containing Pt and Sn combined with alkali metal and S, these may be called *thiostannoplatinates*. The alkali thioplatinates are obtained by fusing together spongy Pt, S, and alkali carbonate, and washing with water, wherein the thioplatinates are insoluble. Other thioplatinates—of Cd, Cu, Fe, Pb, Mn, Hg, Ag, Tl, Sr, and Zn—are obtained by double decomposition from the alkali salts. The thioplatinates belong to the forms $M^I_2Pt_4S_6$ and $M^I_4Pt_3S_6$; the corresponding *thioplatinic acids* $H_2Pt_4S_6$ and $H_4Pt_3S_6$ are obtained by decomposing $K_2Pt_4S_6$ and $Na_4Pt_3S_6$ respectively by dilute HClAq.

Potassium thioplatinate

$K_2Pt_4S_6 = K_2S.3PtS.PtS_2$ (*Potassium platin-thioplatinate*). Blue-grey, metal-like crystals; S.G. 6·44 at 15°. Glows like tinder when heated in air, forming K_2SO_4 and Pt; reduced in H with

evolution of H_2S and formation of Pt. Obtained by fusing an intimate mixture of 1–2 parts Pt black with 12 parts of a mixture of equal parts of S and K_2CO_3 in a porcelain crucible, keeping the molten mass over the blowpipe for a few minutes and extracting with water when cold.

Sodium thioplatinate $Na_4Pt_3S_6 = 2Na_2S.2PtS.PtS_2$ (*Disodium platinthioplatinate*). Copper-red, rhombic needles; decomposed in air. Obtained similarly to the K compound mentioned above.

For details regarding thioplatinates, and also thiostannoplatinates, *v.* Schneider, *P.* 136, 105; 138, 604; 139, 661; 141, 519; 148, 633; 149, 881 (*cf.* E. von Meyer, *J. pr.* [2] 15, 1).

M. M. P. M.

PLATINITES, *derivatives of*; *v.* Platino-bromides, Platino-chlorides, Platino-nitrites, &c.

PLATINI- and PLATINO- COMPOUNDS. Such compounds as *platini-bromides*, called also *bromoplatinates*, and *platino-nitrites* will be described here.

PLATINI- COMPOUNDS. These compounds are derived from platinic compounds, especially from $PtCl_4$, $PtBr_4$, and PtI_4; they generally react as salts of acids containing tetravalent atoms of Pt in their acidic radicles.

Platini-bromhydric acid $H_2PtBr_6.9H_2O$ (*Bromoplatinic acid*). Formed by heating spongy Pt with Br, and HBrAq (b.p. 126°), in a sealed tube, to 180° (Meyer a. Züblin, *B.* 13, 404; Halberstadt, *B.* 17, 2962). Also by dissolving Pt black in HNO_3Aq mixed with HBrAq, heating with repeated additions of HBrAq, evaporating over CaO, and washing the crystals, on an asbestos filter, with CS_2 (H., *l.c.*). Large, clear, carmine-red, monoclinic crystals; v. sol. water, alcohol, ether, acetic acid, and $CHCl_3$. Melts at 100° with partial decomposition (Topsöe, *Ar. Sc.* 35, 58; 45, 223).

Platini-bromides $M^I_2PtBr_6$ (*Bromoplatinates*). Thomsen (*Th.* 3, 430) gives $[Pt,Br^4,2RBrAq] = 57,160$ and $[Pt,O^2,6RBrAq] = 80,360$, where $R = H$, Na, K, Am, $\frac{1}{2}Ca$, $\frac{1}{2}Ba$, $\frac{1}{2}Sr$, $\frac{1}{2}Mg$. These salts are generally formed by evaporating H_2PtBr_6Aq, or a solution of Pt in Br and HBrAq, with metallic bromides. They are red crystalline solids, isomorphous with the corresponding Cl salts. As solutions of these salts give a pp. of Ag_2PtBr_6, and not AgBr, with a limited quantity of cold $AgNO_3Aq$, and on electrolysis of their solutions the Pt goes with the Br to the positive electrode, they are better regarded as ordinary salts than as double salts $2MBr.PtBr_4$.

Ammonium platini-bromide Am_2PtBr_6. Red octahedra; S.G. 4·2; sl. sol. cold water. S. at 20° = ·59 (Halberstadt, *B.* 17, 2962). Formed by evaporating $H_2PtBr_6Aq + NH_4Br$.

Potassium platini-bromide K_2PtBr_6. Red octahedra; S.G. 4·54 (Topsöe, *Ar. Sc.* 35, 58; 45, 228). S. 2·07 at 20°, 10 at 100° (H., *l.c.*). Obtained by ppg. H_2PtBr_6Aq by KBr, or by evaporating H_2PtCl_6Aq with KBr. Thomsen (*Th.* 3, 430) gives
$[Pt,Br^4,2KBr] = 59,260$; $[K^2PtBr^6,Aq] = -12,260$.

Double compounds with K_2PtCl_6 are described by Pitkin (*C. N.* 41, 118).

Sodium platini-bromide $Na_2PtBr_6.6H_2O$. Dark-red, triclinic prisms; S.G. 3·323; very sol. water and alcohol. Obtained by evaporating $PtCl_4Aq$ with HBr till the Cl is turned out, adding NaBrAq, evaporating to dryness, dissolving in a little water, and crystallising (Thomsen, *J. pr.* [2] 15, 294). Thomsen (*Th.* 3, 430) gives $[Pt,Br^4,2NaBr,6H^2O] = 65,330$; $[Na^2PtBr^6,6H^2O] = 18,540$; $[Na^2PtBr^6.6H^2O,Aq] = -8,550$. Platini-bromides of Ba with 10aq, Ca with 12aq, Co with 12aq, Cu with 8aq, Pb, Mg with 12aq, Mn with 12aq, Ni with 6aq, Sr with 10aq, and Zn with 12aq, are described by Topsöe (*Ar. Sc.* 35, 58; 45, 223); von Bonsdorff (*P.* 19, 343) describes a Mn salt with 6aq.

Platini-bromonitrites (*Nitro-bromoplatinates. Platini-nitrobromides*). Salts derived from the platini-bromides by replacing Br by NO_2. By gently heating $K_2Pt(NO_2)_4$ (*v.* Platino-nitrites, p. 284) with Br, *potassium platini-dibromonitrite*, $K_2PtBr_2(NO_2)_4$, is obtained as a yellow powder, sl. sol. cold, more sol. hot, water (Vèzes, *C. R.* 112, 616). When an aqueous solution of this salt is concentrated at a gentle heat, it yields crystals of *potassium platini-tribromonitrite*, $K_2PtBr_3(NO_2)_3$ (V., *C. R.* 115, 44). *Potassium platini-tetrabromonitrite*, $K_2PtBr_4(NO_2)_2$, is obtained by the regulated action of Br on $K_2Pt(NO_2)_4$; it forms red prisms, sol. water with partial decomposition (V., *C. R.* 115, 44).

Platini-chlorhydric acid $H_2PtCl_6.6H_2O$ (*Chloroplatinic acid*). A solution of this compound is the starting-point for the preparation of very many Pt compounds. Formed by dissolving Pt in *aqua regia*, repeatedly evaporating with conc. HClAq till every trace of HNO_3 is expelled, and allowing to crystallise (Weber, *P.* 131, 441; Jörgensen, *J. pr.* [2] 16, 345; Topsöe, *Ar. Sc.* 35, 58). Red-brown, very deliquescent crystals; S.G. 2·431. Easily sol. alcohol, forming $H_2PtCl_4(OEt)_2$ (Schützenberger, *A. Ch.* [4] 21, 362). Heated to 230°, gives $PtCl_2$ (*v.* Platinum dichloride, *Preparation*, p. 289). Heated in Cl to above 350° gives $PtCl_4$ (*v.* Platinum tetrachloride, *Formation*, p. 289). By adding much H_2SO_4 to $H_2PtCl_6.6H_2O$ in a little water, Pigeon (*C. R.* 112, 1218) obtained the hydrate with $4H_2O$; and by heating *in vacuo* at 100°, over fused KOH, he obtained $HPtCl_5.2H_2O$. Thomsen (*Th.* 3, 430) gives $[2HClAq,Pt,Cl^4] = 84,620$; $[6HClAq,Pt,O^2] = 64,060$. Pigeon (*C. R.* 110, 77) gives $[H^2PtCl^6.6H^2O,Aq] = 4,340$. H_2PtCl_6Aq reacts as a dibasic acid; the *platini-chlorides* are numerous and important; the Am and K salts are only sl. sol. water and insol. alcohol, and are much used as forms for estimating K and ammonia. Very many organic bases replace H and form salts analogous with the metallic platini-chlorides.

Platini-chlorides $M^I_2PtCl_6$ (*Chloroplatinates*). Thomsen (*Th.* 3, 430) gives $[Pt,Cl^4,2RClAq] = 84,620$; and $[Pt,O^2,6RClAq] = 64,060$; where $R = H$, Am, K, Na, $\frac{1}{2}Ba$, $\frac{1}{2}Ca$, $\frac{1}{2}Sr$, $\frac{1}{2}Mg$. Pigeon (*C. R.* 110, 77) gives $[PtCl^4,2HClAq] = 24,800$. These salts are generally obtained by evaporating H_2PtCl_6Aq with metallic chlorides. Most of them are yellow-red, crystalline solids; usually e. sol. water and alcohol. They are better regarded as ordinary salts than as double chlorides (*cf.* Platini-bromides, *supra*). The platini-chlorides were investigated by von Bonsdorff (*P.* 17, 250); later by Cleve (*Bl.* [2] 21, 118, 197, 247, 345); also by Topsöe (*Ar. Sc.* 35, 58); and by Nilson (*B.* 9, 1056, 1142). Crystallographically considered, these salts fall into four groups:—(1) M_2PtCl_6, where M = Am, Cs, K, Rb, Tl (and Pt may be replaced by Pd, Ir, or Sn); regular, isomorphous with Am_2(or K_2)$PtBr_6$, Am_2(or K_2)PtI_6, fluosilicates, fluostannates, and fluozirconates of similar composition. (2) $MPtCl_6.6aq$, where M = Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn (and Pt may be replaced by Pd or Sn); hexagonal. (3) $MPtCl_6.12aq$, where M = Mg or Mn; hexagonal; isomorphous with corresponding platini-bromides. (4) $M(PtCl_6)_2.24aq$, where M = Ce_2 or La_2; hexagonal.

AMMONIUM PLATINI-CHLORIDE Am_2PtCl_6 (*Ammonium chloroplatinate. Platinsalammoniac*). Ppd. on adding NH_4Cl to H_2PtCl_6Aq, $PtCl_4Aq$, or a solution of Pt in conc. HClAq with a little HNO_3. Yellow, regular, octahedral crystals. S.G. 3·065 (Topsöe, *l.c.*). S. ·665 at 20°, 1·25 at 100° (Michaelis, *G.-O.* 1, 1187). Scarcely sol. alcohol or ether. Decomposed at red heat, leaving Pt black. For reactions with NH_3 *v.* PLATINUM-AMMONIUM COMPOUNDS, p. 292.

POTASSIUM PLATINI-CHLORIDE K_2PtCl_6 (*Potassium chloroplatinate*). Ppd. by adding KCl, or other K salt, to conc. H_2PtCl_6Aq, or to a solution containing Pt which has been evaporated with excess of HClAq. Reddish-yellow regular octahedra. S.G. 3·586 (Bödeker). S. ·74 at 0°, 1·12 at 20°, 2·17 at 50°, 3·79 at 80°, 5·13 at 100° (Michaelis, *l.c.*). Almost insol. alcohol, or alcohol and ether. Slightly sol. dilute acids; sol. KOHAq. Reduced to Pt and KCl by heating to redness; more quickly by heating with reducing agents such as oxalic acid or sulphurous acid, or by heating in a stream of hydrogen. Vèzes (*C. R.* 110, 757) describes a *nitroso- derivative*, $K_2Pt(NO)Cl_5$. Pigeon (*C. R.* 110, 77; 112, 791) gives $[Pt,Cl^4,2KClAq] = 83,330$; $[PtCl^4,2KClAq] = 25,330$; $[PtCl^4,2KCl] = 29,700$. Thomsen (*Th.* 3, 430) gives $[Pt,Cl^4,2KCl] = 89,500$.

Potassium platini-bromochloride $K_2PtBr_2Cl_4$; by ppg. H_2PtCl_6Aq by KBr (Pitkin, *C. N.* 41, 118).

The following platini-chlorides have also been isolated: $AlCl_3.PtCl_4.15aq$ (Welkow, *B.* 7, 804; Salm-Horstmar, *P.* 99, 638); Ba, with 4aq (Topsöe; Bornsdorff, Precht, *Fr.* 1879. 509); Be, with 8aq (Welkow, *B.* 6, 1288; Thomsen, *B.* 3, 827); Cd, with 6aq (Topsöe); Cs (Crookes, *C. N.* 9, 37; Bunsen, *P.* 119, 371); Ca, with 9aq (Topsöe; Precht); Ce, various salts (Cleve, Marignac, Holzmann, *J. pr.* 84, 80); $CrCl_3.PtCl_4.10aq$ (Nilson, *B.* 9, 1056, 1142); Co, with 6aq (Topsöe); Cu, with 6aq (T.); Di, various salts (Frerichs a. Smith, *A.* 191, 331); $2InCl_3.5PtCl_4.36aq$ (Crookes, *J.* 1864. 256); Fe, various salts (T.; Bonsdorff; Nilson); La, various salts (Cleve, Marignac, Jolin, *B.* 11, 910); Pb, with 3 or 4aq (Birnbaum, *J.* 1867. 319; Topsöe); Li, with 6aq (Scheibler, *J. pr.* 67, 485; Jörgensen a. Topsöe, *Gm.-K.* 3, 1174); Mg, with 6aq (T.); Mn, with 6aq (T.); Ni, with 6aq (T.); Rb (Crookes; Bunsen); Ag (Birnbaum); Na, with 6aq (Marignac, Topsöe, Precht; for thermal data *v.* Thomsen, and Pigeon, *l.c.*); Sr, with 8aq (Bonsdorff); Tl (Crookes); Th, with 12aq (Cleve); Sn, with 12aq (Nilson). Compounds of $PtCl_4$ with chlorides of Er (Nilson), Hg (Birnbaum), VO (Brauner, *M.* 3, 89), and ZrO (Nilson) probably exist. No compounds are formed with $PtCl_4$ and chloride of Sb, As, or Bi.

Platini-chloronitrites (*Platini-nitrochlorides. Nitrochloroplatinates*). Salts derived from the platini-chlorides by replacing Cl by NO_2. A few of these salts are described by Vèzes (*C. R.* 115, 44); the principal are *dichloronitrite* $K_2PtCl_2(NO_2)_4$, *trichloronitrite* $K_2PtCl_3(NO_2)_3$, and *pentachloronitrite* $K_2PtCl_5(NO_2).H_2O$ (*v.* also Blomstrand, *J. pr.* [2] 3, 214).

Platini-iodhydric acid $H_2PtI_6.9H_2O$ (*Iodoplatinic acid*). Brown deliquescent crystals; probably monoclinic; by dissolving PtI_4 in HIAq, and evaporating. Easily decomposed, even in solution, rapidly at 100°, with separation of PtI_4 (Topsöe, *Ar. Sc.* 38, 297; Clementi, *J.* 1855. 420; Lassaigne, *A. Ch.* [2] 51, 113).

Platini-iodides $M^I_2PtI_6$ (*Iodoplatinates*). Reddish-brown, metal-like salts; generally formed by evaporating H_2PtCl_6Aq with excess of metallic iodides, or by adding iodides to PtI_4Aq. The following have been described (*v.* Topsöe, Clementi, Lassaigne, *l.c.*): Am; Ca, with 12aq; Co; Fe; Mg, with 9aq; Mn; Ni, with 6aq; K; Na, with 6aq; Zn, with 9aq.

Platini-iodonitrites (*Platini-nitro-iodides. Nitro-iodoplatinates*). $M^I_2PtI_{6-x}(NO_2)_x$. A few of these salts are described by Vèzes (*C. R.* 113, 696). A *nitroso-platini-iodide*, $K_2Pt(NO)I_5$, is also described.

Platini-molybdates. By boiling $Pt(OH_4)$ with an acidified solution of Na molybdate, Gibbs (*Am. S.* [3] 14, 61) obtained a complex compound which may provisionally be classed as a platini-molybdate, $4Na_2O.10MoO_3.PtO_2.29H_2O$.

Platini-nitrobromides; *v.* PLATINI-BROMONITRITES, p. 282.

Platini-nitrochlorides; *v.* PLATINI-CHLORONITRITES, *supra*.

Platini-nitro-iodides; *v.* PLATINI-IODONITRITES, *supra*.

Platini-tungstates. Complex compounds of PtO_2, WO_3, and strong bases (*v.* Gibbs, *Am. S.* [3] 14, 61; Rosenheim, *B.* 24, 2397).

PLATINO- COMPOUNDS. These compounds are derived from platinous compounds, especially from $PtCl_2$, $PtBr_2$, and PtI_2; they generally react as salts of acids of the form H_2PtX_4, where X is a monovalent negative radicle, generally Cl, Br, or I.

Platino-bromhydric acid H_2PtBr_4 (*Bromoplatinous acid*). This compound is probably contained in a solution of $PtBr_2$ in HBrAq.

Platino-bromides $M^I_2PtBr_4$ (*Bromoplatinites*). Only one of these salts, K_2PtBr_4, has been isolated. *Potassium platino-bromide* is obtained by adding a very little water to a mixture of the corresponding Cl salt and NaBr, in the ratio $K_2PtCl_4 : 4NaBr$, boiling, sucking up the clear liquid from ppd. NaCl, and allowing to cool, when the salt crystallises in dark-brown octahedra, or brown-red needles, which are very sol. water (Thomsen, *J. pr.* [2] 15, 294). Thomsen (*Th.* 3, 430) gives $[2KBr,Pt,Br^2] = 82,310$.

Platino-bromonitrites *v.* PLATINO-NITRITES, p. 284.

Platino-chlorhydric acid H_2PtCl_4 (*Chloroplatinous acid*). This acid has not been isolated; but it almost certainly exists in a solution of

$PtCl_2$ in HClAq, in the liquid obtained by decomposing $BaPtCl_4$ by the equivalent quantity of H_2SO_4Aq (Nilson, *J. pr.* [2] 15, 260), and in the solution formed when conc. H_2PtCl_6Aq is added to hot conc.K_2PtCl_4Aq (Thomsen, *J. pr.* [2] 15, 294). When these liquids are evaporated *in vacuo*, a residue is obtained agreeing in composition with the formula $HPtCl_3.2H_2O$ ($= HCl.PtCl_2.2H_2O = H_2PtCl_3(OH).H_2O$) ; at 100° this loses H_2O and HCl and leaves $PtCl_2$ (Nilson, *l.c.*).

Platino-chlorides $M^I{}_2PtCl_4$ (*Chloroplatinites*). These salts are obtained by evaporating metallic chlorides with $PtCl_2Aq$, or in many cases by reducing platini-chlorides. Most of the platino-chlorides are very soluble in water, and crystallise only from very conc. solutions, generally forming dark-red crystals. Many of them are described by Nilson (*J. pr.* [2] 15, 260). Thomsen (*Th.* 3, 430) gives $[Pt,Cl^2,2MClAq] = 41,830$; and $[Pt,O,4MClAq] = 31,550$; where $M^I =$ H, K, Na, Am, $\frac{1}{2}$Ba, $\frac{1}{2}$Ca, $\frac{1}{2}$Sr, or $\frac{1}{2}$Mg.

AMMONIUM PLATINO-CHLORIDE Am_2PtCl_4 (*Ammonium chloroplatinite*). Obtained, in four-sided prisms, by adding AmCl to $PtCl_2$ in HClAq, and evaporating; also by reducing hot Am_2PtCl_6Aq by SO_2, or hot H_2PtCl_6Aq by SO_2 and then adding AmCl (Peyrone, *A.* 55, 205; Thomsen, *B.* 2, 668; Grimm, *A.* 99, 95). $[Pt,Cl^2,2AmCl] = 43,550$ (*Th.* 3, 430).

POTASSIUM PLATINO-CHLORIDE K_2PtCl_4 (*Potassium chloroplatinite*). Large, ruby-red, four-sided prisms; S.G. 3·2909 at 21°; easily sol. water, insol. alcohol (Nilson). An aqueous solution is not ppd. by soda or potash when cold; on boiling, all the Pt is thrown down as $Pt(OH)_2$ (Thomsen, *J. pr.* [2] 15, 295). $[Pt,Cl^2,2KCl] = 45,170$ (*Th.* 3, 430). Obtained by adding KCl to $PtCl_2$ in HClAq, and evaporating (Magnus, *P.* 14, 241); also by reducing K_2PtCl_6Aq by H_2S (Böttger, *J. pr.* 91, 251), or better by Cu_2Cl_2 (Thomsen, *J. pr.* [2] 15, 294). K_2PtCl_6 is made into a paste with water, warmed, and moist Cu_2Cl_2 is added, little by little, until a small excess is present; the liquid, which is nearly black, is filtered, the red crystals which separate on cooling are washed with alcohol and re-crystallised.

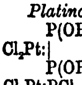
The following platino-chlorides have been isolated and described: Ba, with 3aq; Be, with 5aq; Ca, with 8aq; Cs (Böttger, *J. pr.* 91, 251); Co, with 6aq; Cu, with 6aq (Thomsen, *l.c.*; Millon a. Commaille, *C. R.* 57, 822); Fe^{ous}, with 6aq; Pb; Li, with 6aq; Mg, with 6aq; Mn, with 6aq; Ni, with 6aq; Rb; Ag; Na, with 4aq; Sr, with 6aq; Tl; Zn, with 6aq (Hünefeld, *S.* 60, 197). Compounds of $PtCl_2$ with the chlorides of the following metals are also described by Nilson (*l.c.*); Al, Ce, Cr, Di, Er, La, Th, and Y.

Platino-chloronitrites; *v.* PLATINO-NITRITES, *infra.*

Platino-chlorophosphates (*Phospho-platino-chlorides*). Several salts, and a few acids, containing Pt, Cl, and P have been isolated by Schützenberger (*Bl.* [2] 17, 482; 18, 101, 148). The classification of these compounds is very incomplete. The following scheme is accepted as provisional (*cf.* Seubert, *Ladenburg's Handwörterbuch der Chemie*, 9, 314):

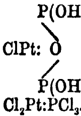
Platino-chlorophosphoric acid $Cl_2Pt:P(OH)_3$; by dissolving $Cl_2Pt.PCl_3$ in water and crystallising; $(Cl_2Pt:PO_3)_2Pb_3.8aq$, and various esters, isolated.

Platino-chlorodiphosphoric acid



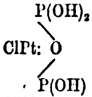
$Cl_2Pt:\begin{matrix}P(OH)_2\\|\\P(OH)_2\end{matrix}$; by the action of moist air on $Cl_2Pt:PCl_3.PCl_3$; ethyl ester also isolated.

Platino-chloropyrophosphoric acid



; by warming a solution of $Cl_2Pt:PCl_3.PCl_3$.

Platino-chloro-anhydropyrophosphoric acid



; by heating the foregoing acid to 150°.

Ethyl diplatino-chloro-phosphate $\begin{matrix}Cl_2Pt\\Cl_2Pt\end{matrix}\!>\!P(OEt)_3$; by dissolving $\begin{matrix}Cl_2Pt\\Cl_2Pt\end{matrix}\!>\!PCl_3$ in alcohol; corresponding acid not isolated (Cochin, *C. R.* 86, 1402).

Platino-cyanides and derivatives; *v.* vol. ii. p. 344.

Platino-iodhydric acid H_2PtI_4 (*Iodoplatinous acid*). This acid probably exists in a solution of PtI_2 in HIAq.

Platino-iodonitrites; *v.* PLATINO-NITRITES.

Platino-nitrites, *and derivatives.* Platinous nitrite $[Pt(NO_2)_2]$ has not been isolated; but several compounds are known in which the group $Pt(NO_2)_2$ forms part of the acidic radicle. These platino-nitrites belong to the form $M_2Pt(NO_2)_4$; they are not to be regarded as double salts, but as derivatives of the acid $H_2Pt(NO_2)_4$; the ordinary reagents for Pt do not show the presence of this metal in solutions of these salts, nor do these solutions give the reactions of nitrites; their solutions doubtless contain the ions M and $Pt(NO_2)_4$. Most of the platino-nitrites are obtained from the potassium salt $K_2Pt(NO_2)_4$, which is formed by the reaction of equivalent weights of K_2PtCl_4 and KNO_2.

PLATINO-NITROUS ACID $H_2Pt(NO_2)_4$ has not been obtained pure, but it doubtless exists in the solution obtained by decomposing $BaPt(NO_2)_4$ by H_2SO_4Aq; on evaporation, this solution gives red crystals (Lang, *J. pr.* 83, 415), but the process causes partial decomposition to *triplatino-octonitrous acid* $H_4Pt_3O(NO_2)_8.2H_2O$ (Nilson, *B.* 10, 934).

POTASSIUM PLATINO-NITRITE $K_2Pt(NO_2)_4$ (*Potassium nitroplatinite*). Small, lustrous, colourless, monoclinic prisms; by mixing solutions of equivalent weights of K_2PtCl_4 and KNO_2, and evaporating (Topsöe, *J.* 1879. 307). S. 3·8 at 15°; more sol. hot water. Combines with Br and Cl to form *potassium platini-dibromo-[dichloro-] nitrites*, $K_2PtBr_2[Cl_2](NO_2)_4$. Most of the other platino-nitrites are obtained from this salt, by adding $AgNO_3Aq$, separating $Ag_2Pt(NO_2)_4$, and decomposing this by metallic chlorides; or making $BaPt(NO_2)_4$, by the action of $BaCl_2Aq$ on the silver salt, and decomposing this by sulphates (Nilson, *B.* 9, 1722; 10, 930; 11, 879; *v.* also Blomstrand, *J. pr.* [2] 3, 186).

The other platino-nitrites which have been

isolated are: Al, Am, Cd, Ce, Cr, Co, Di, Sr, Fe, La, Pb, Li, Mg, Mn, Hg, Ni, Ag, Na, Tl, Y, and Zn.

PLATINO-BROMONITRITES $M^I_2Pt(NO_2)_{4-x}Br_x$. A few of these salts have been obtained by Vèzes (*C. R.* 113, 696; 115, 44). *Potassium platino-bromonitrite* $K_2PtBr(NO_2)_3$ and *dibromo-nitrite* $K_2PtBr_2(NO_2)_2$ are described.

PLATINO-CHLORONITRITES $M^I_2Pt(NO_2)_{4-x}Cl_x$. Vèzes (*l.c.*) has described the *potassium monochloro-salt* $K_2PtCl(NO_2)_3$, and the *dichloro-salt* $K_2PtCl_2(NO_2)_2$.

PLATINO-IODO-NITRITES $M_2Pt(NO_2)_{4-x}I_x$ (Nilson, *B.* 10, 930; 11, 879; Groth, *Z. K.* 4, 469; Vèzes, *C. R.* 115, 44). *Potassium platino-di-iodo-nitrite* $K_2PtI_2(NO_2)_2.2H_2O$ is obtained, in small, black crystals, by the action of an alcoholic solution of I on $K_2Pt(NO_2)_4$. The other salts isolated are those of Al, Am, Ba, Be, Cd, Cs, Ca, Ce, Co, Cu, Di, Fe, La, Pb, Li, Mg, Mn, Ni, Rb, Ag, Na, Sr, Tl, Y, and Zn.

Platino-nitrobromides; *v.* PLATINO-BROMONITRITES, *supra.*

Platino-nitrochlorides; *v.* PLATINO-CHLORONITRITES, *supra.*

Platino-nitro-iodides; *v.* PLATINO-IODONITRITES, *supra.*

Platino-oxalic acid and **platino-oxalates** $H_2Pt(C_2O_4)_2$ and $M^I_2Pt(C_2O_4)_2$ (Söderbaum, *Bl.* [2] 45, 188). The *sodium salt* $Na_2Pt(C_2O_4)_2.4H_2O$ is obtained, in copper-coloured crystals, by heating $Na_2O.3PtO_2.6H_2O$, with 1½ parts crystallised oxalic acid, cooling the blue-coloured liquid, treating the brown needles which separate with hot water, and crystallising; sometimes the salt separates with $5H_2O$ as golden-coloured crystals. The other salts are obtained by double decomposition from the Na salt; they seem to exist in two forms corresponding with the two sodium salts. *Platino-oxalic acid* $H_2Pt(C_2O_4)_2.2H_2O$ is obtained as red, lustrous, metal-like crystals by decomposing the silver salt with the equivalent weight of HClAq, filtering, and concentrating the blue solution *in vacuo.* Salts of the following metals are described by Söderbaum (*l.c.*): Am, Ba, Ca, Mg, Mn, Ni, K, Ag, Na, Sr, and Zn.

Platino-phosphochlorides *v.* PLATINO-CHLOROPHOSPHATES, p. 284.

Platino-seleno-stannates. Schneider (*J. pr.* [2] 44, 507) has described two salts, $K_2Pt_3SnSe_6$ and $Na_2Pt_3SnSe_6$, which may be called platino-seleno-stannates. They are formed by heating together Pt black, $SnSe_2$, K_2CO_3 or Na_2CO_3, and Se.

Platino-stannates. This name may be given to some compounds derived from the acids $H_4Pt_2Sn_2O_8$ and $H_2Pt_2Sn_2O_4$, described by Schneider (*P.* 136, 105) and Schützenberger (*C. R.* 98, 985); *cf.* also Lévy a. Bourgeois (*C. R.* 94, 1365).

Platino-sulphocyanhydric acid, and salts *v.* vol. ii. p. 357.

Platino-sulphonates, ***and derivatives*** (Liebig, *A.* 23, 23; Litton a. Schnedermann, *A.* 42, 316; Birnbaum, *A.* 139, 164; 152, 137; 159, 116; Döbereiner, *J. pr.* 15, 315; Lang, *J. pr.* 83, 415). (*Platino-sulphites. Sulpho-platinites.*) When K_2PtCl_4 is heated with $KHSO_3Aq$, or SO_2 is passed into K_2SO_3Aq holding $Pt(OH)_4$ in suspension, the liquid is neutralised by K_2CO_3 and evaporated, yellow, microscopic crystals are obtained of $K_2Pt(KSO_3)_4.2H_2O$. From this *potassium platino-sulphonate* other similar salts are obtained. These salts are better regarded as derived from *platino-sulphonic acid* $H_2Pt(HSO_3)_4$ than as double compounds of $PtSO_3$ and $K_2SO_3[K_2Pt(KSO_3)_4 = PtSO_3.3K_2SO_3]$; they are analogous to the platino-chlorides M_2PtCl_4 and the platino-nitrites $M_2Pt(NO_2)_4$. The *ammonium*, *sodium*, and *silver* salts have been isolated. *Sodium-platino-oxy-sulphonic acid* $Na_2Pt(HSO_3)_2O$ and *ammonium-platino-oxy-sulphonic acid* $Am_2Pt(HSO_3)_2O$ have also been isolated.

PLATINO-CHLOROSULPHONATES (*Platino-chlorosulphites. Sulpho-chloroplatinites*). $M^I_2Pt.Cl_3.M^ISO_3$. The *potassium salt* $K_2Pt.Cl_3.KSO_3$ is obtained by warming K_2PtCl_4 with SO_2Aq, evaporating, and adding KCl. *Ammonium platino-chlorosulphonic acid* $Am_2Pt.Cl_3.HSO_3$ crystallises from a solution of Am_2PtCl_6, or Am_2PtCl_4, in warm conc. SO_2Aq; the *potassium* and *sodium salts* of this acid are known. A complex acid, $AmH.Pt.Cl.SO_3.HSO_3$, and the salts $AmK.Pt.Cl.SO_3.KSO_3$ and $Am_2.Pt.Cl.SO_3.SO_3Am$ have been isolated.

Platino-thiosulphates. A few salts have been obtained which may be regarded as compounds of hypothetical platinous thiosulphate and sodium thiosulphate $PtS_2O_3.xNa_2S_2O_3.yH_2O$, where x is 3, 4, 6, and 7. They may also be looked on as derivatives of the hypothetical acid $H_2Pt(S_2O_3H)_x$, where H is replaced by Na (Schottländer, *A.* 140, 200; Jochum, *C. C.* 1885. 642).
M. M. P. M.

PLATINUM. Pt. At. w. 194·3. Mol. w. unknown. Melts at c. 1775° (Violle, *C. R.* 89, 702); older determinations generally gave m.p. c. 2000° (for references *v.* Carnelley's *Melting and Boiling Point Tables*, p. 10), although Becquerel (*C. R.* 57, 855) gave 1460°–1480°. S.G. 21·48 to 21·5 at 17·6°, after melting in H (Deville a. Debray, *C. R.* 81, 839; for other values *v.* Clarke's *Specific Gravity Tables*, 2nd edit. p. 15). S.H. ·03243 (Regnault); ·0314 (Dulong a. Petit); ·0317 + ·000012t at t° (Violle, *P. M.* [5] 4, 318). C.E. (linear at 40°) ·00000899 (Fizeau, *C. R.* 68, 1125, for Pt that had been melted); from 0° to 100°, ·00000881 (Calvert a. Johnson, *B. A.* 1858. for hammered Pt). T.C. (Ag = 1000) 379 (C. a. J., *l.c.*); c. 84 (Wiedemann a. Franz, *J.* 1855. 91). Heat of fusion c. 5276 (for 194 g.) (Violle, *l.c.*). E.C. (Ag = 100) 8·042 at 12°–13° (Becquerel, *A. Ch.* [3] 17, 242); 10·53 at 20·7° (Matthiessen, *P.* 103, 428). For electrical resistance of Pt wire *v.* Arndtsen (*P.* 104, 1). Crystallises in the regular system (*v. infra, Properties*). For chief lines in emission-spectrum *v. B. A.* 1884. 436.

Occurrence.—Alloyed with Ir, Pd, Rh, Au, Cu, and Fe in the sands of many rivers, often associated with titaniferous iron and chrome-iron, and in the older rocks in different parts of the world. The quantity of Pt in 'platinum ores,' varies from c. 50 to c. 90 p.c. A Canadian Ni ore was found by Clarke a. Catlett to contain from ·008 to ·02 p.c. Pt (*Am. S.* 37, 372). In 1741 Watson received some particles of a metal-like substance from the gold-bearing sand of the river Pinto in New Granada; the shining silvery particles were called in the district where they occurred *platina del Pinto* (*platina* = diminutive of Spanish *plata* = silver). Watson extracted a new metal from the substance sent him, and called it platinum (*T.* 1750. 585). For a short account of the history of the Pt metals, *v.* Noble metals, iv. 628.

Formation.—1. By decomposition of $PtCl_4$ or $(NH_4)_2PtCl_6$ by heat.—2. By heating an alloy of Pt and Pb in a current of air, whereby the Pb is oxidised and the Pt remains.—3. By reducing many Pt salts by Zn, Fe, NaOHAq and $FeSO_4$Aq, Na_2CO_3Aq and sugar, alcohol added to an alkaline solution, &c.

Preparation.—1. The Pt ore is obtained as a fine powder by fusing with 2 or 3 times its weight of Zn, powdering the brittle alloy so formed, and removing the Zn by dilute H_2SO_4Aq (Descotils, *G. A.* 27, 231; Hess, *J. pr.* 40, 498). The residue is heated to redness, then warmed with HClAq (to remove portions of the baser metals), and then treated with cold *aqua regia* which dissolves Au. The residue is heated, in retorts, with *aqua regia*; the solution contains most of the Pt, along with Rh, Pd, and a little Ir; in the residue are found osm-iridium (*v.* vol. iii. p. 47), Ru, and a little Pt. The acid is distilled off, carrying with it most of the Os as OsO_4; the concentrated solution is neutralised by Na_2CO_3, and the Pd is ppd. as $PdCy_2$ by $HgCy_2$; NH_4Cl is added to the filtrate, and $(NH_4)_2PtCl_6$ is thus ppd. mixed with some $(NH_4)_2IrCl_6$. The Ir salt may be removed by digesting with slightly warm KCNAq until the undissolved portion is light yellow; the salt $IrCl_3.3NH_4Cl$ is thus formed and dissolved, while $(NH_4)_2PtCl_6$ remains (Wöhler a. Mucklé, *A.* 104, 368). Or the NH_4.Pt and NH_4.Ir chlorides may be dissolved in hot water, and the Ir salt reduced to $IrCl_3.3NH_4Cl$, which dissolves, by SO_2 (*cf.* Iridium, vol. iii. p. 46). The residual ammonium platinichloride is then heated until all NH_3 and Cl are volatilised.—2. Finely-divided Pt ore is dissolved in *aqua regia* diluted with 2 pts. water, under increased pressure (which aids the solution); the solution is evaporated, and the residue is heated to 125°, whereby the chlorides of Pd and Ir are reduced to the lower chlorides; treatment with HClAq dissolves $PtCl_4$, which is ppd. as $(NH_4)_2PtCl_6$ by addition of NH_4Cl (Heræus, *v.* Hofmann's *Chem. Industrie auf der Wiener Weltausstellung*, 2, 999; *v.* also Dullo, *J. pr.* 78, 869).—3. Commercial Pt is melted with 6 times its weight of Pb, the granulated alloy is treated with dilute HNO_3Aq (1:8 by volume), which dissolves most of the Pb, Cu, Pd, and Rh; the black residue is dissolved in diluted *aqua regia*—Ir remains undissolved—the solution is evaporated with H_2SO_4Aq, whereby Pb is removed as $PbSO_4$, the filtrate and washings are mixed with excess of NH_4Cl and some NaCl, heated to 80°, and allowed to stand for some days; the pp. is washed repeatedly with saturated NH_4ClAq, and then with very dilute HClAq; it is then dried, heated to dull redness in a Pt vessel with $KHSO_4$ and a little NH_4HSO_4, and washed with boiling water—Rh goes into solution as Rh-K disulphate, and finely-divided Pt remains (Matthey, *Pr.* 28, 463). For other methods *v.* Deville a. Debray, *A. Ch.* [3] 56, 385; 61, 5.—4. Pure Pt is obtained by evaporating a solution of the ore in *aqua regia* with HClAq till HNO_3 is nearly removed, adding NaOHAq till strongly alkaline, boiling for a long time (the alkalinity gradually disappears, owing to formation of NaClOAq), adding alcohol, and then making the turbid liquid acid by HClAq, filtering from olive-green $IrCl_3$, and ppg. by conc. NH_4ClAq (W. von Schneider, *A. Suppl.* 5, 261). The Pt obtained by strongly heating the ppd. $(NH_4)_2PtCl_6$ should be dissolved in diluted *aqua regia*, and re-ppd. by addition of NH_4Cl; on heating this pp. pure Pt remains (Seubert, *A.* 207, 8). For another method of obtaining pure Pt, *v.* Mylius a. Förster, *B.* 25, 665.

The finely-divided Pt obtained by the above methods may be fused into a lump by the use of the O-H flame. The metal is placed in a cavity made in a block of lime (made by strongly heating marble), which is covered by another block, through the top of which a hole is pierced to admit the flame (*v.* Deville a. Debray, *A. Ch.* [3] 56, 385; *cf.* Platinum in Dictionary of Applied Chemistry).

Platinum black, which is extremely finely-divided Pt, is obtained by reducing solutions of some Pt salts by certain organic reducing compounds, or by Zn or Mg, &c. $PtCl_4$Aq may be reduced by Mg (Böttger, *J. pr.* [2] 2, 137), zinc-dust or Fe in powder (Brunner, *A.* 109, 253), $FeSO_4$Aq and NaOHAq (Hempel, *A.* 107, 97), sugar and Na_2CO_3Aq, or by alcohol. Pt black is also formed by fusing Pt with twice its weight of Zn, powdering the alloy, dissolving out Zn by H_2SO_4Aq, and washing with very dilute HNO_3Aq (Döbereiner, *A.* 17, 67). Loew (*B.* 23, 289) recommends to dissolve 50 g. $PtCl_4$ in 50-60 c.c. water, to add c. 70 c.c. formic aldehyde solution of 40 to 45 p.c., to cool, and then to add gradually 50 g. NaOH in 50 c.c. water, to set aside for 12 hours, and then to filter and wash until the washings pass through black, when the washing should be stopped for some hours, and continued when the washings again pass through colourless (O is absorbed and temperature rises); the residue is washed until quite free from NaCl, and dried over H_2SO_4. Liebig (*P.* 17, 101) dissolved $PtCl_2$ in warm conc. KOHAq, added alcohol to the hot liquid till CO_2 came off freely, decanted, washed the ppd. Pt, successively, with alcohol, HClAq, KOHAq, and finally, several times, with boiling water.

Crystals of platinum are obtained by heating Pt to redness, in a glass or porcelain tube, in a stream of dry Cl, for twenty-four hours (Hodgkinson a. Lowndes, *C. N.* 58, 158, 223; Seelheim, *B.* 12, 2066; Joly, *N.* 43, 541; *cf.* Troost a. Hautefeuille, *C. R.* 84, 94). Joly (*N.* 43, 541) obtained cubical crystals of Pt, about ·1 mm. in length, by sprinkling some finely-powdered topaz on a ribbon of Pt, and heating to bright redness by an electric current for c. two hours. Moissan (*C. R.* 109, 807) obtained crystalline Pt by heating dry PtF_4, in a Pt tube, to bright redness. Pt that has been melted shows a crystalline structure when touched with *aqua regia* (*cf.* Koettig, *J. pr.* 71, 190; Noguès, *C. R.* 47, 832; Kalischer, *B.* 15, 706; Mallet, *Am. S.* [2] 20, 340; Phipson, *C. N.* 5, 144).

Treatment of platinum residues.—Pt residues accumulated in the laboratory generally contain Pt as $(NH_4)_2PtCl_6$; the liquid portion usually contains alcohol. The solid part is warmed, in a water-bath, with K_2CO_3Aq, KOHAq, or NaOHAq, and the alcoholic liquid is added little by little, or HCO_2Na is added (Duvillier, *C. R.* 84, 444), till the salt is reduced to Pt. The black residue is washed, dried, boiled with HClAq, and again washed and dried (Knösel, *B.* 6, 1159).

Properties.—Compact platinum is a white metal with a greyish tinge; it is easily polished, thereby acquiring a very high lustre. Much softer than Ag, rather softer than Cu; thin plates or wire can be cut easily with scissors. Without taste or smell. Very malleable and ductile; a wire 2 mm. diameter breaks with a weight of 124 kilos; tenacity is, therefore, c. same as Fe. Pure Pt can be drawn into very thin wire; by fusing into Ag wire, drawing out, and dissolving away the Ag, a wire of Pt ·0009 mm. diameter is said to have been obtained (Gaiffe, *C. R.* 1877. 625). Most easily fused of Pt metals except Pd; very thin wire melts in the outer blow-pipe flame; larger masses require the O-H flame. Becomes soft and workable much below its m.p. Melts in an ordinary fire, owing to combination with C or Si (Heraeus, *D. P. J.* 167, 132; Deville, *A. Ch.* [3] 46, 182; Boussingault, *C. R.* 82, 591; Schützenberger a. Colson, *C. R.* 94, 1710). Crystallises in the regular system, chiefly in octahedral and dodecahedral forms (*v.* Seelheim, *B.* 12, 2066). Said to volatilise to some considerable extent when kept molten (Deville a. Debray, *C. R.* 44, 1101). By heating in certain gases, especially in Cl, volatile compounds are formed and again decomposed. Molten Pt absorbs O, and 'spits' when cooled rapidly.

Pt occludes H. According to Graham (*P. M.* [4] 36, 63), Pt foil absorbs five to six times its own volume of H at a dull-red heat; Berthelot (*C. R.* 94, 1383) says that Pt absorbs from 80 to 120 times its volume of H, probably with formation of definite compounds. Berliner (*W.* 35, 791; *cf.* Neumann, *M.* 13, 40) found that ordinary Pt foil absorbed 127 volumes of H; foil that had been quite freed from gases and cleaned absorbed 200 vols. of H and 80 vols. of O or CO. The whole of the occluded gas is removed, with difficulty, by strongly heating *in vacuo*; under ordinary conditions about 80 vols. of H are retained. O is also occluded by Pt foil, and the condensed O brings about oxidations, *e.g.* electrolytic gas (H_2+O) explodes when exposed to Pt foil at c. 180° (Berliner, *l.c.*). Pt is pervious to H at a bright-red heat; Graham (*P. M.* [4] 32, 401, 503) found that 489·2 c.c. H passed, per minute, through Pt foil 1·1 mm. thick and having a surface of 1 square metre. Gases other than H scarcely diffused through at all.

Pt is not acted on by pure HClAq, HNO_3Aq, or H_2SO_4Aq, nor is it attacked by O; various mixtures of acids dissolve it. Pt is acted on by Cl and by substances which evolve Cl; also, at high temperatures, by molten alkalis, nitrates, KCN, a mixture of alkali carbonates with S, by P and Si, and by most of the metals.

Platinum black is a porous, heavy, very finely-divided black powder, which becomes metal-like, grey, and lustrous when rubbed; S.G. 15·8 to 17·6. Pt black absorbs large quantities of certain gases, especially O; according to Döbereiner (*A.* 17, 67), from 173 to 253 vols. O are occluded by 1 vol. Pt black. The O condensed in Pt black is able to bring about many processes of rapid oxidation: H, CO, C_2H_4, C_2H_6O gas, Et_2O vapour, &c., are rapidly oxidised, generally with ignition (*v.* von Mulder, *R. T. C.* 2, 44; Schönbein, *J. pr.* 98, 76; *P.* 105, 258; von Mulder a. van der Meulen, *R. T. C.* 1, 167); alcohol is oxidised to acetic acid, formic and oxalic acids to CO_2 and H_2O, As_2O_3 to As_2O_5 (von Mulder, *R. T. C.* 2, 44). Pt black charged with H acts as a reducer; water is formed when the hydrogenised Pt black is brought into O (Wilm, *B.* 14, 878; Berthelot, *C. R.* 94, 1377); aqueous solutions of $KClO_3$, KNO_3, K_4FeCy_6, also $C_6H_5NO_2$, &c., are reduced (Gladstone a. Tribe, *C. N.* 37, 245); ozone is reduced to O (von M. a. van der M., *l.c.*). One cause of these actions is probably the heat produced during the condensation of the gases in the porous Pt (*cf.* Berthelot, *A. Ch.* [5] 30, 519); it is not probable that an oxide of Pt is formed and then reduced (*v.* V. Meyer, *J. pr.* [2] 14, 124; *cf.* Tommasi, *B.* 11, 811).

The at. w. of Pt has been determined (1) by strongly heating $PtCl_2$ (Berzelius, *P.* 8, 179 [1813]); (2) by determining Pt in K_2PtCl_6, and by finding the ratio of Pt:KCl in the same salt (B., *P.* 13, 469 [1826]; Andrews, *Chem. Gazette*, 1852. 379); (3) by analyses of K_2PtCl_6 and $(NH_4)_2PtCl_6$ (Seubert, *A.* 207, 29 [1800]; Halberstadt, *B.* 17, 2962 [1884]; *cf.* Dittmar a. McArthur, *E. Tr.* 33, 561 [1888], and criticism thereon by Seubert, *B.* 21, 2179); (4) by determining S.H. of solid Pt (Violle, *P. M.* [5] 4, 318). As no V.D. of a Pt compound has yet been determined, the at. w. cannot be found by the direct application of the law of Avogadro. The older determinations gave 196 to 197; Seubert proved that the true value is c. 194·5, which is between the values for Ir (192·5) and Au (196·8). No compound of Pt has been gasified from which the valency of the atom of Pt in gaseous molecules can be determined. Pt is closely allied to Ir, and less closely to Os, in its chemical properties. It is distinctly metallic physically, and, on the whole, chemically also. PtO_2 is both basic and acidic; Pt forms numerous acids by combining with H and negative radicles such as Cl_6, $(NO_2)_4Cl_2$, $(CN)_4$, $(SCN)_6$, &c. For a fuller account of the chemical relations of Pt *v.* NOBLE METALS, vol. iii. p. 628, and *cf.* IRON GROUP OF ELEMENTS, vol. iii. p. 67.

Pt is used for making crucibles &c. for laboratory use, and vessels for evaporating conc. oil of vitriol, &c. Apparatus is sometimes platinised by placing in hot $PtCl_4Aq$ containing KOH and some organic reducing compound.

Reactions and Combinations.—1. Is *not* acted on by *oxygen*; concerning absorption of O by Pt *v. Properties.*—2. Heated to redness with *sulphur*, in presence of borax, PtS is formed (Deville a. Debray, *C. R.* 89, 587).—3. Said to form a compound by heating Pt black with *selenion.*—4. With *chlorine*, *bromine*, and *iodine* Pt reacts at temperatures above c. 300° (Langer a. Meyer, *Pyrochemische Untersuchungen* [Braunschweig, 1885] 44, 57). Cl and Br attack Pt in presence of water.—5. Scarcely acted on by *fluorine* below 100° (Moissan, *A. Ch.* 1892. 125). 6. *Hydrogen* is occluded by Pt; a considerable quantity of heat is produced, and perhaps compounds are formed (*v.* PLATINUM HYDRIDE, p.

290).—7. Heated with *arsenic*, a compound $PtAs_2$ is said to be formed (*v. Gm.-K.* 3, 1192–1193).—8. *Phosphorus* combines when heated with finely-divided Pt (Schrötter, *J.* 1849. 246). 9. A boride is formed by heating Pt black with amorphous *boron* (Descotils, *A. Ch.* [3] 67, 88; Deville a. Wöhler, *J.* 1856. 279).—10. Heated to whiteness with *silicon*, Pt forms several compounds; also combines with Si when heated with *silica and carbon* (*v.* PLATINUM SILICIDES, p. 291).—11. Softens when heated with *carbon* (*v.* PLATINUM CARBIDE, p. 289).—12. Alloys with many of the more easily fusible *metals* (*v.* PLATINUM ALLOYS, *infra*).—13. Pt is not acted on by pure *hydrochloric*, *nitric*, or *sulphuric acid* (Scheurer-Kestner, *C. R.* 86, 1082; 91, 59). It dissolves in warm *aqua regia*, forming $PtCl_4$ (*v.* Dullo, *J. pr.* 78, 369). Alloying modifies the solubility in acids; alloys of Pt with small quantities of Ir or Rh are scarcely sol. in *aqua regia*, while an alloy with much Ag dissolves in conc. HNO_3Aq; Pt ppd. by zinc dissolves in conc. HNO_3Aq (*v.* Winkler, *Fr.* 13, 369; van Riemsdyk, *B.* 16, 387; Wilm, *B.* 13, 1198).—14. *Conc. sulphuric acid containing a little nitrous acid* dissolves small quantities of Pt (Scheurer-Kestner, *C. R.* 86, 1082; 91, 59). *Nitric acid, containing bromine or bromhydric acid*, and also *hydrochloric acid, into which chlorine is passed*, dissolve Pt, forming $PtBr_4$ and $PtCl_4$ respectively (Wagner, *W. J.* 1876. 149; Seubert, *A.* 207, 16).—15. Pt is acted on, at red heat, by *molten alkalis*, *baryta*, *nitrates*, *potassium cyanide*, and by a mixture of *alkali carbonate and sulphur*.—16. $PtCl_2$ or $PtBr_2$ and PtI_2 are formed when Pt wire is heated in *iodine mono-* or *tri-chloride*, or in *chlorine mixed with iodine or iodine bromide*; with *phosphorus pentachloride* Pt phosphide is formed; with *carbon tetrachloride* C, C_2Cl_6, and Cl are produced; *hydrogen chloride* forms $PtCl_2$; *hydrogen fluoride* produces a soluble Pt salt; and with *mercurous chloride* Hg and $PtCl_2$ are obtained (Hodgkinson a. Lowndes, *C. N.* 58, 223).

Platinum, acids of. The hydroxide $Pt(OH)_4$ reacts with strong bases as an acid. Several acids have been isolated containing Pt in combination with more or less complex negative radicles; these are H_2PtCl_4, H_2PtCl_6, H_2PtBr_6, H_2PtI_6; $H_2Pt(NO_2)_4$, $H_4Pt_3O(NO_2)_8$; H_2PtCy_4, $H_2PtCy_4Cl_2$, $H_2Pt(SCN)_6$; $H_2Pt_4S_6$; $Pt(NH_3)_2.Cl.SO_3H$; $PtCl_2.P(OH)_3$. These acids are described as *platino-* and *platini-chlorhydric acid*, &c. (pp. 283 and 282); *platino-nitrous acid*, &c. (p. 284); *platino-cyanhydric acid*, &c. (vol. ii. pp. 344–5); *thioplatinic acid* (p. 281); *platosammine-chloro-sulphonic acid* (p. 293); *platino-chloro-phosphoric acid* (p. 284).

Platinum, alloys of. Pt alloys with many metals by fusing it with them; with Sb, As, Pb, Sn, and Zn heat and light are produced. Alloys which seem to be definite compounds have been obtained with *arsenic* ($PtAs_2$, Gehlen, *Gm.-K.* 3, 1192); *antimony* ($PtSb_2$, Christofle); *cadmium* ($PtCd_2$, Deville a. Debray, *A. Ch.* [3] 56, 385); *lead* (PtPb, Bauer, *B.* 3, 836; 4, 449; D. a. D., *C. R.* 90, 1195); *tin* (Pt_2Sn_3, $PtSn_4$, and Pt_4Sn_3, D. a. D., *A. Ch.* [3] 56, 385; Debray, *C. R.* 104, 1470); and *zinc* (Pt_2Zn_3, D. a. D., *l.c.*). Alloys have also been formed with *bismuth* (Gehlen, *Gm.-K.* 3, 1192); *copper* (D. a. D., *A. Ch.* 1859. 611; Hélonis, *B.* 6, 42); *gold* (Dodé, *B.* 6, 1278); *iridium* (D. a. D., *A. Ch.* [3] 56, 385; Pelouze, *C. R.* 49, 896; Matthey, *Pr.* 28, 463; D. a. D., *C. R.* 81, 839; Morin, *C. R.* 78, 1502); *iron* (D. a. D., *C. R.* 89, 587; Daubrée, *C. R.* 80, 526); *nickel* (Hélonis, *B.* 6, 42); *potassium* (V. Meyer, *B.* 13, 392); *silver* (D. a. D., *A. Ch.* 1859. 611; H., *l.c.*); *sodium* (V. M., *l.c.*).

Amalgams of platinum. According to Crafts (*Bl.* [2] 49, 856), Hg has no action on Pt at the ordinary temperature, but Pt dissolves to a very small extent in boiling Hg, air being excluded. When acid is present Hg alloys with Pt (Casamajor, *Am.* 6, 540; Skey, *C. N.* 22, 282; Krouchkoll, *J. de Ph.* [3] 3, 139). The amalgams are most easily formed by adding sodium-amalgam to $PtCl_4Aq$; with 13·5 p.c. Pt the amalgam is a thick liquid; with 25·8 p.c. Pt it is solid; an amalgam with c. 30 p.c. Pt has also been obtained (Joule, *C. J.* [2] 1, 378).

Platinum, antimonide of. An alloy of Pt and Sb, approximating to the composition $PtSb_2$, is obtained by melting the elements together in the ratio Pt : 2Sb; also by passing SbH_3 into H_2PtCl_6Aq, and removing ppd. Sb and $PtCl_2$ by washing with K_2SAq and KCNAq mixed (Christofle, *Recherches sur les Combin. de l'Antimoine*, Göttingen, 1863).

Platinum, arsenides of. An alloy $PtAs_2$ is said to be formed by heating Pt black with As (Gehlen, *Gm.-K.* 3, 1192). By passing AsH_3 into $PtCl_4Aq$, and heating the pp. in dry CO_2, Pt_3As_2 is said to be formed (Tivoli, *G.* 1885. 487).

Platinum-arsenic hydroxide. According to Tivoli (*G.* 1885. 487) a compound PtAsOH is produced by passing AsH_3, containing H but no other impurity, into $PtCl_4Aq$ (corresponding with 2 g. Pt in 60 c.c. water), and drying the black flocculent pp. at 120°–130°. The compound is decomposed by washing with alcohol or water; hot conc. H_2SO_4 at once separates Pt; heating in dry CO_2 produces As_2O_3, Pt_3As_2, and H_2O. Gibbs (*Am.* 8, 289) described some compounds of Pt and As_2O_3.

Platinum, boride of. Pt and B combine when melted together (Descotils, *A. Ch.* [3] 67, 88). It is best to heat Pt black and amorphous B under borax (Wöhler a. Debray, *A.* 101, 113). When excess of B is used, a crystalline compound containing 91·8 p.c. Pt., S.G. 17·3, is formed (Martius, *A.* 109, 79).

Platinum, bromides of. Pt and Br combine when heated together to above 300° (Langer a. Meyer, *Pyrochemische Untersuchungen* [Braunschweig, 1885], pp. 44, 57). Two bromides are known, $PtBr_2$ and $PtBr_4$; the V.D. of neither has been determined.

PLATINUM DIBROMIDE $PtBr_2$ (*Platinous bromide.*) Formed by heating HBrAq, b.p. 126°, with Br and spongy Pt to 180° in a sealed tube—$H_2PtBr_6.xH_2O$ is thus formed—evaporating to dryness, heating to c. 200°, and washing the residue with boiling water (Topsoë, *J.* 1868. 273). Pullinger (*C. J.* 59, 602) heats spongy Pt with Br and HBrAq in a flask with a reflux-condenser, evaporates to dryness, and heats the residue to c. 280°. $PtBr_2$ is a brown powder; decomposes slowly at c. 300° in an air-current (P., *l.c.*); insol. water, sol. HBrAq and KBrAq. With KBr forms K_2PtBr_4 (*v.* PLATINO-BROMIDES,

p. 282). **Combines with CO at c. 180° to form $PtBr_2.CO$, a bright red, crystalline solid; melts at 177·7°; not very hygroscopic; sol. alcohol; decomposed by water (Pullinger, *l.c.*). This compound is called by P. *carbonyl-bromoplatinite*.**

PLATINUM TETRABROMIDE $PtBr_4$ (*Platinic bromide*). Formed by heating spongy Pt with Br and HBrAq in a sealed tube to 180°—or by boiling Br, Pt, and HBrAq in flask with reflux-condenser (Pullinger, *C. J.* 59, 602)—filtering, evaporating, heating residue at 180° till HBr ceases to come off; treating with boiling water, filtering from traces of $PtBr_2$, evaporating, and drying at 180° (H. Meyer a. Züblin, *B.* 13, 404; Halberstadt, *B.* 17, 2963). A dark-brown, non-hygroscopic powder; sol. aqueous alcohol, more sol. absolute alcohol or ether, v. sl. sol. water (S. at 20° = ·41) (H. *l.c.*); somewhat sol. glycerin. Pt black separates when solution in alcohol, ether, or glycerin is heated. With HBr forms H_2PtBr_6 (*v.* PLATINI-BROMHYDRIC ACID, p. 282). With many metallic bromides forms salts $M_2^IPtBr_6$ (*v.* PLATINI-BROMIDES, p. 282). When spongy Pt is heated with HBrAq and excess of HNO_3, small, dark-brown, very hygroscopic crystals of *platinum nitrosyl bromide*, $PtBr_4.2NOBr$, are obtained (Topsoë, *J.* 1868. 273).

Platinum, carbide of. Pt becomes brittle and more friable when heated to redness with charcoal. By heating the compound which $PtCl_4$ forms with acetone, Zeise (*J. pr.* 20, 209) obtained a black solid, to which he gave the composition PtC_2.

Platinum, chlorides of. Two chlorides of Pt are known, $PtCl_2$ and $PtCl_4$. When Pt black is heated in dry Cl at 240°–250°, $PtCl_2$ is formed, according to Schützenberger (*C. R.* 70, 1134, 1287). Pigeon (*C. R.* 108, 1009) says that at 360° $PtCl_2$ and $PtCl_4$ are formed, but the action is incomplete. Troost a. Hautefeuille (*C. R.* 84, 94) found that $PtCl_2$ was formed when Pt was heated in Cl to 1400°, and the tube was suddenly cooled.

PLATINUM DICHLORIDE $PtCl_2$ (*Platinous chloride. Platinochloride*). V.D. not determined.

Formation.—1. By heating H_2PtCl_6 to c. 230° (Berzelius, *Gm.-K.* 3, 1081).—2. By heating Pt black in Cl at 240°–250° till no more Cl is taken up (Schützenberger, *C. R.* 70, 1134, 1287).—3. By decomposing $Na_2Pt(NaSO_3)_4$ by HClAq (Liebig, *A.* 23, 23; for formation of $Na_2Pt(NaSO_3)_4$ *v.* PLATINOSULPHONATES, p. 285).—4. A solution of $PtCl_2$ is obtained by passing SO_2 into $PtCl_4Aq$ till the liquid becomes red.

Preparation.—1. H_2PtCl_6Aq is evaporated to dryness, and the residue is heated in a bath of molten tin, *i.e.* at c. 230°, with constant stirring as long as Cl is given off (Berzelius, *Gm.-K.* 3, 1081). Or the heating is stopped before much of the solid is decomposed, the residue is dissolved in water, the dark-brown opaque liquid is evaporated, and the $PtCl_2$ which separates is dried at c. 150° (*cf.* Magnus, *P.* 14, 239).—2. $H_2PtCl_6.6H_2O$ is heated *in vacuo*, in presence of molten KOH, at 100° for 2 or 3 days; the temperature is then raised to 360°, and maintained thereat so long as Cl is given off (Pigeon, *C. R.* 112, 1218). Shenstone a. Beck (*C. J.* 61, 445) say that $PtCl_2$, prepared as directed above, always contains small quantities of some basic compound; and that when the salt is strongly heated small quantities of HCl and O are obtained, as well as Cl. Shenstone (*C. J. Proc.* 1892 93. 38) finds that $PtCl_2$ almost free from basic compounds can be prepared by heating $PtCl_4$ in a stream of dry HCl; a sample prepared in this way gave only ·15 p.c. of HCl and O when decomposed by heat.

Properties and Reactions.—A brown powder; S.G. 5·87 at 11° (Bödeker). H.F. $[Pt,Cl^2] = 22,600$ (Berthelot, *C. R.* 87, 615). Insol. water, sol. HClAq in absence of air. Decomposed by heating to redness, giving off all Cl, and leaving Pt. According to Shenstone a. Beck (*v. Preparation*), the Cl thus obtained contains a little HCl and O, and H_2O is also given off. Not acted on by HNO_3Aq or dilute H_2SO_4Aq; decomposed by KOHAq, giving $Pt(OH)_2$; by heating with conc. H_2SO_4, and then with water, Kane obtained a black powder to which he gave the composition $PtCl_2.3PtO$ (*B. J.* 24, 238).

Combinations.—$PtCl_2$ combines with many metallic chlorides; the compounds are described as *platino-chlorides* (p. 284). With HCl an acid H_2PtCl_4 is formed (*v.* PLATINO-CHLORHYDRIC ACID, p. 283). With CO the compounds $PtCl_2.CO$, $PtCl_2.2CO$, and $2PtCl_2.3CO$ are formed. These compounds are produced by passing alternate currents of Cl and CO over spongy Pt at 250° (Schützenberger, *A. Ch.* [4] 21, 350). Pullinger (*C. J.* 59, 598) found that a fourth compound is also formed—$PtCl_2.2COCl_2$ (or $PtCl_4.2CO$). *Carbonyl chloroplatinite* ($PtCl_2.CO$) combines with HCl, and with various hydrochlorides of organic bases (*v.* Mylius a. Förster, *B.* 24, 2424). $PtCl_2$ combines with PCl_3 to form $PtCl_2.PCl_3$ and $PtCl_2.2PCl_3$; and from these is derived a number of complex bodies. By treating $PtCl_2.PCl_3$ with H_2O an acid $PtCl_2.P(OH)_3$ is obtained, from which various salt-like compounds are derived; similarly $PtCl_2.2PCl_3$ yields an acid $PtCl_2.P_2(OH)_6$, and this gives many salt-like derivatives (Schützenberger, *A. Ch.* [4] 15, 100; 21, 350; Baudrimont, *C. R.* 53, 637: *cf.* PLATINO-CHLOROPHOSPHATES, p. 284). By heating $PtCl_2.PCl_3$ with $PtCl_2$ Colchin (*C. R.* 86, 1402) obtained $2PtCl_2.PCl_3$. For ammoniacal derivatives of the platino-phosphorus chlorides *v.* Colchin (*l.c.*) and Quesneville (*M. S.* [3] 6, 659), also Schützenberger (*Bl.* [2] 14, 97; 17, 482; 18, 101, 148).

PLATINUM TETRACHLORIDE $PtCl_4$ (*Platinic chloride. Platinichloride*). V.D. not determined.

Formation.—1. By heating Pt in Cl to c. 1700° (Langer a. Meyer, *l.c.* 44, 57); if a thin wire of Pt is heated by an electric current nearly to melting, in a stream of Cl, $PtCl_4$ is formed (Hodgkinson a. Lowndes, *C. N.* 58, 158, 223).—2. By allowing $H_2PtCl_6.6H_2O$ to remain over KOH, when it loses $4H_2O$, and then heating in Cl to c. 350° (Pigeon, *C. R.* 110, 77).—3. By heating Pt and Se, mixed with $AsCl_3$, in Cl (*v. Preparation*).—4. $PtCl_4.5H_2O$ is obtained by adding $AgNO_3Aq$ to H_2PtCl_6Aq in the ratio of $H_2PtCl_6:2AgNO_3$, heating, filtering from AgCl, and evaporating finally over H_2SO_4 (Norton, *J. pr.* [2] 2, 469; 5, 365; Engel, *Bl.* [2] 50, 100; Quesneville, *M. S.* [3] 6, 659).

Preparation.—1. Spongy Pt is mixed with rather less than its own weight of Se, the mixture is placed in a tube of hard glass filled to one-third with $AsCl_3$, and heated in a stream of Cl till the mass liquefies and boils, when the tube is sealed and heated for some hours at 250°; on cooling, the colourless crystals are separated from the pale-yellow crystals and the yellow liquid, and are heated *in vacuo* at 110°, whereby $PtCl_4$ and $SeCl_4$ remain; this residue is then heated at 360° in a stream of Cl, when $SeCl_4$ sublimes and $PtCl_4$ remains (Pigeon, *C. R.* 108, 1009).—2. Dry H_2PtCl_6 is placed in a porcelain boat which is heated, in a tube of hard glass, to 165° for about 15 hours in a stream of dry HCl (Pullinger, *C. J.* 61, 422).

Properties and Reactions. — H.F. $[Pt,Cl^4] = 59,800$; $[Pt,Cl^4,Aq] = 79,400$ (Pigeon, *C. R.* 110, 77; 112, 791). A brown solid, said by Pigeon to be deliquescent; described by Pullinger as very soluble in water, but not deliquescent. The hydrate (*v. Formation*, No. 4) forms large, red, monoclinic crystals; according to Norton this compound has $5H_2O$, according to Engel $4H_2O$; all H_2O except one molecule is removed at 100°, but the last molecule is not removable without decomposition. Decomposed by heating to dull redness (Pigeon, *C. R.* 110, 77); in presence of Cl, may be heated to c. 360°; in dry HCl slight decomposition occurs at c. 200° (Pullinger, *l.c.*). HClAq produces H_2PtCl_6Aq; NH_4Cl ppts. $(NH_4)_2PtCl_6$. $AgNO_3Aq$ ppts. Ag_2PtCl_6 from cold $PtCl_4Aq$, but on heating AgCl is formed and $PtCl_4$ goes into solution (Jörgensen, *J. pr.* [2] 16, 345). Pigeon (*C. R.* 112, 791) gives $[Ag^2PtCl^6,Aq] = 12,160$, to form $PtCl_4Aq$ and 2AgCl; $PtCl_4Aq$ is decomposed by light, for some measurements *v.* Foussereau (*C. R.* 103, 248).

Combinations.—1. With *water* (*v. Formation*, No. 4, and *Properties*). — 2. With *hydrogen chloride* to form $H_2PtCl_6.6H_2O$; the compound $HPtCl_5.2H_2O$ was obtained by Pigeon by heating $H_2PtCl_6.6H_2O$ *in vacuo* at 100° (*v.* PLATINICHLORHYDRIC ACID, p. 282). Pigeon (*C. R.* 110, 77) gives $[PtCl^4,2HClAq] = 24,800$. — 3. With many *metallic chlorides* to form *platinichlorides* (*q. v.*, p. 282).—4. A compound with *phosphorous chloride* $PtCl_4.PCl_3$ is formed by treating $PtCl_2.PCl_3$ with Cl (Schützenberger, *Bl.* [2] 14, 97; 17, 482; 18, 101, 148; *cf.* Baudrimont, *C. R.* 53, 637).—5. A compound with *nitrosyl chloride*, $PtCl_4.2NOCl.H_2O$, is one of the products of the action of fuming HNO_3 on H_2PtCl_6Aq (Weber, *P.* 131, 441).—6. Combines with *alcohol*, and with *ethyl sulphide*, to form $PtCl_4.2C_2H_6O$ and $PtCl_4.2(Et)_2S$ respectively (Schützenberger, *C. R.* 70, 1134; Blomstrand, *J. pr.* [2] 17, 189).—7. Compounds with various *organic bases and metallic chlorides*, $EtNH_2$, &c., are described by Jörgensen (*J. pr.* [2] 33, 409).

Platinum, chloro-iodides of; *v.* PLATINUM IODOCHLORIDES, *infra*.

Platinum, cyanides of; *and derivatives*: *v.* vol. ii. p. 343.

Platinum, fluoride of. Only one fluoride of Pt has been isolated, PtF_4. Prepared by heating Pt wire in F, in a Pt or fluorspar tube, to c. 500°; if HF is mixed with the F combination occurs at the ordinary temperature (Moissan, *C. R.* 109, 807). Small buff-coloured crystals, or fused masses of a deep red colour. Dissolves in a little water, forming fawn-coloured solution, which almost at once decomposes, with rise of temperature and production of $PtO_2.xH_2O$ and HFAq. Heated to bright redness in Pt tube, PtF_4 is decomposed to F, and Pt which separates in crystals. A compound with PF_3, viz. $PtF_4.2PF_3$, is formed by passing PF_5 over spongy Pt heated to dull redness (M., *Bl.* [3] 5, 454). The decomposing action of H_2O on PtF_4 explains the failure of former attempts to prepare a fluoride of Pt in the wet way.

Platinum-iridium, or *platin-iridium*. An alloy of Pt and Ir which remains, mixed with osm-iridium, when many samples of Pt ore are heated with *aqua regia* (*cf.* IRIDIUM, vol. iii. p. 46).

Platinum, hydride of. Pt black absorbs considerable quantities of H. According to Berthelot (*A. Ch.* [5] 30, 519), the relative weights of Pt and H are approximately 15:1 and 10:1; a considerable quantity of heat is produced. No certain evidence of the formation of hydrides has been obtained; but Thoma's result (*Z. P. C.* 3, 69), that the excess of H, above a definite quantity, absorbed by Pt when Pt is the negative electrode during the electrolysis of dilute sulphuric acid, is not easily given up, indicates the probable existence of a compound or compounds (*cf.* PALLADIUM, vol. ii. p. 720).

Platinum, hydroxides of; *v.* PLATINUM, OXIDES AND HYDROXIDES OF, p. 291.

Platinum, iodides of. Pt and I combine directly to form PtI_4; the lower iodide PtI_2 has also been obtained, but not pure.

PLATINUM DI-IODIDE PtI_2 (*Platinous iodide. Platino-iodide*). This compound is described as a black, heavy powder, insol. water, alcohol, and acids; giving Pt and I at 300°-350°; decomposed by NaOHAq to PtO_2H_2. It is produced by boiling $PtCl_2$ with fairly conc. KIAq (Lassaigne, *A. Ch.* [2] 51, 113); but it has not been obtained pure (Clementi, *J.* 1858. 420; Topsoë, *Ar. Sc.* 38, 297). The compound $PtI_2.CO$, *carbonyl iodoplatinite*, is described by Mylius a. Förster (*B.* 24, 2424).

PLATINUM TETRA-IODIDE PtI_4 (*Platinic iodide. Platini-iodide*). V.D. not determined. Prepared by heating PtO_2 with HIAq (Clementi, *J.* 1855. 420); also by the action of cold HIAq on $H_2PtCl_6.6H_2O$ (Topsoë, *Ar. Sc.* 38, 297), and evaporating. Pullinger (*C. J.* 59, 602) obtained PtI_4 by dissolving spongy Pt in a hot solution of I in HIAq, evaporating to dryness, heating to 180°, and washing with water. A brown-black amorphous powder, insol. water; sol. HIAq and metallic iodide solutions (Topsoë, *l.c.*); not wholly decomposed by heating with Na_2CO_3 to the m.p. of the carbonate (Pullinger, *l.c.*). Combines with HI to form $H_2PtI_6.9H_2O$ (*v.* PLATINI-IODHYDRIC ACID, p. 283), and with metallic iodides to form salts (*v.* PLATINI-IODIDES, p. 283).

Platinum, iodochlorides of. A compound PtI_2Cl_2 is said to be formed, in large red plates, by dissolving Pt and I in *aqua regia* and evaporating at 100° (Kämmerer, *A.* 148, 329). Another compound PtI_3Cl was obtained by Mather, as a black powder, by evaporating H_2PtCl_6 with a small excess of HIAq, and heating the residue to 150° (*Am. S.* 27, 257).

Platinum-nitrosyl bromide and Platinum-nitrosyl chloride, *v.* PLATINUM TETRABROMIDE,

p. 289; and Platinum tetrachloride, *Combinations*, No. 5, p. 290.

Platinum, oxides and hydroxides of. Three oxides have been isolated; PtO, Pt_3O_4, and PtO_2; hydrates of all are known. PtO forms a few salts; it also dissolves in molten KOH and $NaOH$. PtO_2 forms corresponding salts, and also combines with alkaline oxides to form *platinates* (*q.v.* p. 281).

Platinum monoxide PtO (*Platinous oxide*). Obtained as a violet powder, by strongly heating the pp. formed by $CaOAq$ acting on H_2PtCl_6Aq in sunlight, and washing with water and then with HNO_3Aq (Döbereiner, *P.* 28, 181). Also by carefully heating PtO_2H_2. Reduced to Pt at red heat, also by action of reducers such as HCO_2HAq. Dissolves in molten KOH and $NaOH$, but the compounds thus formed have not been examined. A compound which is perhaps $PtO.CO$ is described by Mylius a. Förster (*B.* 24, 2440).

Platinous hydroxide PtO_2H_2 was obtained by Thomsen (*J. pr.* [2] 15, 294) by adding $NaOHAq$ to K_2PtCl_4Aq (1:12) in the ratio $2NaOH{:}K_2PtCl_4$, and heating to boiling. A black powder, sol. $HClAq$, $HBrAq$, and SO_2Aq, forming corresponding salts. Freshly ppd. PtO_2H_2 dissolves in excess of $NaOHAq$.

Tri-platinum tetroxide Pt_3O_4 (*Platino-platinic oxide*). A black powder, insol. acids; obtained by heating dehydrated Na_2PtCl_6 with 4 parts dry Na_2CO_3 till fusion begins, boiling with water, then with dilute HNO_3Aq, and finally with *aqua regia* (Jörgensen, *J. pr.* [2] 16, 344). Loses its O at red heat; easily reduced to Pt by H or coal-gas, even without heating. Prost (*Bl.* [2] 46, 156) describes a hydrate $Pt_3O_4.9H_2O$.

Platinum dioxide PtO_2 (*Platinic oxide*). A black powder, obtained by gently heating PtO_4H_4. PtO_2 is insol. acids, but salts of this oxide are formed from the hydroxide.

Platinic hydroxide PtO_4H_4. Formed by boiling $PtCl_4Aq$ for a considerable time with a large excess of $NaOHAq$, acidifying by acetic acid, drying the white flocculent pp. in the air, and heating the yellow hydrate, $PtO_4H_4.2H_2O$, to 100° (Topsoë, *B.* 3, 462; Fremy, *A. Ch.* [3] 31, 478). Also obtained by evaporating H_2PtCl_6Aq with excess of Na_2CO_3, rubbing up the residue in water, and treating with acetic acid (Döbereiner, *P.* 28, 181; Topsoë, *l.c.*; *cf.* Wittstein, *R. P.* 74, 43). A hydrate $PtO_4H_4.H_2O$ was obtained by Prost (*Bl.* [2] 46, 156) by adding water to a solution of PtO_4H_4 in conc. HNO_3Aq. A reddish-brown powder; dehydrated by heating gently; at a higher temperature gives Pt and O. Heated in H gives Pt. Sol. $NaOHAq$, $HClAq$, HNO_3Aq, and H_2SO_4Aq. With acids forms platinic salts, PtX_4, where $X = \frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, NO_3, &c.; with strongly basic oxides forms platinates, $PtO_2.xMO$ (*v.* Platinates, p. 281). Compounds with SnO and SnO_2 are described by Delachanel a. Mermet (*C. R.* 81, 370), Schneider (*P.* 136, 105), Lévy a. Bourgeois (*C. R.* 94, 1365), and Schützenberger (*C. R.* 98, 985). PtO_4H_4 dissolves in solutions of certain molybdates and tungstates, forming *platini-molybdates* and *platini-tungstates* (*q.v.* p. 283).

Platinum, oxychlorides of. When $AgNO_3Aq$ is added to $PtCl_4Aq$ in the ratio $PtCl_4{:}2AgNO_3$, or when $AgNO_3Aq$ and H_2PtCl_6Aq are heated together in the ratio $H_2PtCl_6{:}4AgNO_3$, a pp. is obtained which has the empirical composition $PtCl_2(OH)_2.2AgCl$; this substance may be regarded as a compound of the hydrated oxychloride $PtOCl_2.H_2O$ (Jörgensen, *J. pr.* [2] 16, 345). The pps. formed by $CaOAq$ and $BaOAq$ in $PtCl_4Aq$ are supposed to contain oxychlorides of Pt (*v.* Johannsen, *A.* 155, 204).

Platinum, oxysulphide of, $2PtOS.H_2O$. PtS_2 slowly oxidises by exposure to air; by washing the product (to dissolve H_2SO_4 and SO_2) and drying in a stream of CO_2, a black powder is obtained having the composition $2PtOS.H_2O$ (perhaps $HO.PtS.O.SPt.OH$). This substance is an energetic oxidiser; H, CO, H_2S, SO_2 take fire when brought into contact with it; NH_3 is absorbed and oxidised to HNO_2 and HNO_3 (E. von Meyer, *J. pr.* [2] 15, 1).

Platinum, phosphides of. Pt and P combine when strongly heated together. Schrötter obtained a grey metal-like mass, S.G. 8·77, to which he gave the composition PtP_2, by heating Pt black in vapour of P (*J.* 1879. 246). By heating Pt and P to white heat, Clarke a. Joslin (*Am.* 5, 231) obtained Pt_3P_5; and by heating in a muffle they got Pt_2P, sol. *aqua regia* but changed to insoluble PtP.

Platinum, salts of. But few salts, excepting the halides, are known wherein Pt replaces the H of acids; Pt more frequently enters into the acid radicle, than the positive radicle, of salts.

Platinum, selenide of. By heating Pt and Se, Berzelius obtained a grey, infusible powder; perhaps $PtSe$ (*Gm.-K.* 3, 1081).

Platinum, selenocyanides of; for a double salt *v.* vol. ii. p. 348.

Platinum, silicides of. A white, crystalline, brittle solid, Pt_4Si_3, was obtained by Guyard (*Bl.* [2] 25, 510) by heating together equal parts of Pt black and powdered crystalline Si (*cf.* Winkler, *J. pr.* 91, 203). According to Miles (*Am.* 8, 428), the conditions favourable to the formation of compounds of Pt and Si are a high temperature, the presence of a reducer such as CO, a basic substance such as MgO, and SiF_4, in contact with Pt (*v.* also Brown, *Am.* 7, 173).

Platinum, sulphides of. Pt and S combine when heated together. Two sulphides have been isolated, PtS and PtS_2; there is also evidence of the existence of Pt_2S_3.

Platinum monosulphide PtS (*Platinous sulphide*). Obtained by heating Pt black and S, and volatilising excess of S, in absence of air; also by heating $(NH_4)_2PtCl_6$ with S, out of contact with air, till NH_4Cl and excess of S are volatilised; also by passing H_2S into $PtCl_2Aq$ (Berzelius). Prepared in crystals by heating to redness a mixture of 1 pt. Pt, 1 pt. borax, and 10 pts. pyrites (Deville a. Debray, *A. Ch.* [2] 55, 215). A grey, lustrous solid; S.G. 6·2. PtS prepared in the wet way is a black powder. Unchanged in air, even when moist; unacted on by boiling acids; loses S when heated in air, leaving Pt; reduction in H begins at 19°. A compound with CO—$PtS.CO$—was obtained by Mylius a. Förster (*B.* 24, 2438) by the action of H_2S on $PtCl_2.CO$.

Platinum disulphide PtS_2 (*Platinic sulphide*). Obtained by passing H_2S into Na_2PtCl_6Aq, or by dropping H_2PtCl_6Aq into solution of an alkali hydrosulphide. Also formed by digesting, in a strong closed flask, 1 pt. $PtCl_4$, 4 pts. alcohol, and 5 pts. CS_2 (Böttger, *J. pr.* 3, 274); and by decolourising H_2PtCl_6Aq by SO_2, and then heating in a sealed tube at 200° (Geitner, *A.* 129, 358). PtS_2 is also a product of the action of HClAq in air on $Na_4Pt_3S_6$ or $H_2Pt_4S_6$ (*v.* THIOPLATINATES, p. 281). Colloidal soluble PtS_2 was obtained by Winssinger (*Bl.* [2] 49, 452) by passing H_2S into very dilute $PtCl_4Aq$, and dialysing. A black solid; as obtained from $Na_4Pt_3S_6$ forms steel-grey needles, S.G. 5·27. PtS_2 prepared by one of the wet methods must be dried in absence of air, else it is partially decomposed. Heated out of air forms PtS, and Pt and S. Oxidised to sulphate by strong oxidisers, such as *aqua regia*, Cl, fuming HNO_3, molten $KClO_3$ or KNO_3. Freshly ppd. PtS_2 dissolves in alkali sulphide solutions forming *thioplatinates* (*q. v.*), from which solutions it is reppd. by acids. Clässon (*J. pr.* [2] 15, 193) describes a compound with EtSH.

PLATINUM SESQUISULPHIDE, Pt_2S_3. This compound is said to be formed, as a steel-grey, metal-like solid, S.G. 5·52, by the oxidation in air of $H_2Pt_4S_6$ (Schneider, *P.* 136, 105; 138, 604; 139, 661; 141, 519; 148, 633; 149, 381). Schneider also describes a compound $4PtS.PtS_2 = Pt_5S_6$.

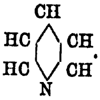
Platinum, sulphocyanides of; *v.* vol. ii. p. 357; *v.* also Guareschi, *Giorn. della R. Accad. di Med.* 1891. No. 5; abstract in *B.* 25, *Ref.* 7.

Platinum, thiocarbide of. Pt_2CS_2. This compound is described by Schützenberger (*C. R.* 111, 391). It is a black powder; obtained by passing a stream of N, or H, charged with CS_2, over spongy Pt heated to 400°–450°.

M. M. P. M.

PLATINUM-AMMONIUM COMPOUNDS (*Ammonio-platinum compounds. Ammoniacal platinum bases. Platinammines*). When a solution of $PtCl_2$ in HClAq reacts with NH_3, more than one compound of the form $PtCl_2.2NH_3$ is obtained. These compounds react with acids, oxidisers, &c., to form many derivatives containing Pt, N, H, and negative radicles, in which the reactions of Pt and NH_3 are more or less modified.

The platin-ammonium compounds may be regarded as salts of bases derived from two or more NH_4 groups, in which part of the H is replaced by Pt; thus $PtCl_2.2NH_3$ may be called platoso-diammonium chloride, and formulated as $N_2H_6Pt.Cl_2$. Similarly $PtCl_2.4NH_3$ may be regarded as $Pt\left\langle\begin{array}{l}NH_2(NH_4)Cl\\NH_2(NH_4)Cl\end{array}\right.$, and called ammonium platoso-diammonium chloride. The compounds derived from $PtCl_4$ are regarded, in this scheme, as platini-ammonium compounds; thus, $PtCl_4.2NH_3$ is $Cl_2Pt.NH_2.NH_4.Cl_2$ (*v.* Hofmann, *T.* 1851. [2] 357; Weltzien, *A.* 97, 19; Kolbe, *J. pr.* [2] 2, 217; Grimm, *A.* 99, 67).

This view of the constitution of the compounds in question was opposed by Claus (*J. pr.* 63, 99), Blomstrand (*B.* 4, 40, 639, 673; 6, 1469), Jörgensen (*J. pr.* [2] 33, 489), and others. Jörgensen found that pyridine, $N.C_5H_5$, forms a compound with platinous chloride similar to $PtCl_2.4NH_3$; in this pyridine compound, which has the composition $PtCl_2.4NC_5H_5$, the atoms of hydrogen cannot be in direct union with N; for the constitution of pyridine is known to be 

. Now if the ammoniacal platinum bases are all to be derived from NH_4, by substituting H by NH_4 groups, it is evident that the substituted H atoms must always be directly bound to N atoms. But the existence of the pyridine compound shows that this is not necessary. Hence $PtCl_2.4NH_3$ may be regarded as $Pt\left\langle\begin{array}{l}NH_3.NH_3Cl\\NH_3.NH_3Cl\end{array}\right.$.

The classification and nomenclature of the platin-ammonium compounds proposed by Blomstrand (*Chemie der Jetztzeit*, Heidelberg, 1869; *B.* 2, 202; 4, 40, 639, 673; 6, 1469) is now usually adopted. In the following formulæ R stands for a monovalent negative radicle. Blomstrand uses the term *ammine* to distinguish these compounds from the *amines*, which contain the group NH_2.

Class I. PLATO- OR PLATOSO- COMPOUNDS.

Series 1. *Platosemiammines*, $RPtNH_3R$.
" 2. *Platosammines*, $Pt(NH_3R)_2$.
" 3. *Platodiammines*, $Pt(NH_3.NH_3R)_2$.
" 4. *Platosemidiammines*, $Pt(NH_3.NH_3R)R$.
" 5. *Platomonodiammines*, $Pt(NH_3.NH_3R)(NH_3R)$.

Series 2 and 4 are isomeric. Cleve has isolated two distinct aniline compounds, $Pt(NH_3)_2.(C_6H_5NH_2)_2.R_2$ (*cf.* Jörgensen, *J. pr.* [2] 33, 489).

Class II. PLATINI- OR PLATIN- COMPOUNDS.

Series 1. *Platinammines*, $R_2Pt(NH_3R)_2$.
" 2. *Platinidiammines*, $R_2Pt(NH_3.NH_3R)_2$.
" 3. *Platinisemidiammines*, $R_2Pt(NH_3.NH_3R)R$.
" 4. *Platinimonodiammines*, $R_2Pt(NH_3.NH_3)R(NH_3R)$.
" 5. *Platinitriammines*, $R_2Pt(NH_3.NH_3.NH_3R)_2$.

Series 1 and 3 are isomeric.

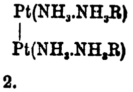
The prefixes *mono*, *di*, &c., are used to denote the number of NH_3 groups in direct union with one another, and not the number of NH_3 groups in union with the atom of Pt. As the compounds in Series 3 contain one diammine chain, $(NH_3.NH_3)$, they are called *semidiammines*; and as those in Series 4 contain a diammine and a monammine chain, they are called *monodiammines*.

Class III. DIPLATINUM COMPOUNDS.

These contain 2 Pt atoms; the group Pt_2 may be divalent, tetravalent, or hexavalent.

Series 1.

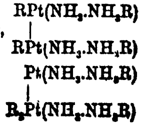
Diplatodiammines,



$$\begin{array}{l}Pt(NH_3.NH_3R)\\ \mid\\ Pt(NH_3.NH_3R)\end{array}$$

Series 2.

Diplatosindiammines,



$$\begin{array}{l}RPt(NH_3.NH_3R)\\ \mid\\ RPt(NH_3.NH_3R)\end{array}\quad\text{or}\quad\begin{array}{l}Pt(NH_3.NH_3R)\\ \mid\\ R_2Pt(NH_3.NH_3R)\end{array}$$

Series 3.

Diplatinammines,
$$\begin{array}{c} RPt(NH_3R)_2 \\ | \\ RPt(NH_3R)_2 \end{array}$$

Series 4.

Diplatinidiammines,
$$\begin{array}{c} RPt(NH_3.NH_3R)_2 \\ | \\ RPt(NH_3.NH_3R)_2 \end{array}$$

Iodides of platinum bases with 4 and 8 atoms Pt are also known; $I_2Pt_4.8NH_3.I_8$, and $I_2Pt_8.16NH_3.I_{16}$.

Many organic bases, such as aniline, pyridene, &c., can take the place of NH_3 in these compounds, and the N of NH_3 is often replaceable by P or As.

Class I. Plato- or Platoso- compounds.

Series 1. *Platosemiammines*, $RPtNH_3R$. None of these has been isolated, but Cossa (*B.* 23, 2503) has obtained a compound which probably contains platosemiammine chloride; the compound is $2PtNH_3Cl_2.Pt(NH_3)_4Cl_2$.

Series 2. *Platosammines*, $Pt(NH_3R)_2$. These compounds are generally obtained by heating the corresponding platodiammines, $Pt(NH_3.NH_3R)_2$, which thus lose $2NH_3$; by heating with NH_3Aq, platodiammines are re-formed; with oxidisers, platini- compounds are obtained.

PLATOSAMMINE CHLORIDE $Pt.NH_3Cl.NH_3Cl$ (Peyrone, *A.* 51, 1; 55, 205; 61, 178). Obtained by heating $Pt(NH_3)_4Cl_2$ (plato-diammine chloride) to 250°, or by evaporating that compound with HClAq at 100° and dissolving out AmCl in water; also by evaporating with HCl the solution of the corresponding nitrate or sulphate. Microscopic, sulphur-yellow crystals. S. ·022 at 0°, ·77 at 100°. Sol. NH_3Aq, forming $Pt(NH_3.NH_3Cl)_2$ (platodiammine chloride); in *aqua regia* forms $Cl_2Pt(NH_3Cl)_2$ (platinammine chloride). With $AgNO_3Aq$, in the ratio $2Pt(NH_3Cl)_2:AgNO_3$, one half of the chloride remains unchanged and one half gives $Pt(NH_3.NO_3)_2$. Heated to 270°, the chloride is decomposed thus:

$$3Pt(NH_3Cl)_2 = 3Pt + 4NH_4Cl + 2HCl + N_2.$$

Platosemidiammine chloride $Pt(NH_3.NH_3Cl)Cl$, and *platodiammine chloride platinous chloride* $Pt(NH_3.NH_3Cl)_2.PtCl_2$ (Magnus' green salt), are isomeric or polymeric with platosammine chloride. Other compounds, perhaps also isomeric, were obtained by Peyrone (*l.c.*) and by Cossa (*B.* 23, 2503).

Grimm (*A.* 99, 67) obtained a double compound with AmCl; $Pt(NH_3Cl)_2.2AmCl$. Jörgensen (*J. pr.* [2] 33, 489) obtained the pyridine compound $Pt(NC_5H_5Cl)_2$; and also the mixed compound $PtNC_5H_5Cl.NH_3Cl$ (*v.* also Hedin, *Dissertation*, Lund; *B.* 20, *Ref.* 108).

PLATOSAMMINE HYDROXIDE $Pt.NH_3OH.NH_3OH$. Said to be obtained, as a crystalline, very soluble solid, by decomposing the sulphate, $Pt(NH_3.NH_3)SO_4$, by BaOAq (Odling, *C. N.* 21, 269, 289). The compound thus formed may have been the isomeric *platosemidiammine hydroxide*, $OH.Pt(NH_3.NH_3OH)$. A solution of Odling's hydroxide reacts strongly alkaline, absorbs CO_2 from the air, neutralises acids, decomposes salts of NH_4 giving off NH_3, and ppts. many metallic hydroxides from salts of the metals.

PLATOSAMMINE OXIDE $Pt(NH_3.NH_3)O$. A grey solid, insol. water or NH_3Aq; heated in a retort to 195° gives N, NH_3, H_2O and Pt. Obtained by heating platodiammine hydroxide $(Pt[NH_3.NH_3.OH]_2)$ to 110° (Reiset, *A. Ch.* [3] 11, 417).

PLATOSAMMINE SULPHONATES and CHLOROSULPHONATES $Pt.NH_3SO_3M.NH_3SO_3M$ and $Pt.NH_3Cl.NH_3SO_3M$. *Ammonium platosammine sulphonate*, $Pt(NH_3.SO_3Am)_2$, is formed by the reaction of excess of Am_2SO_3Aq on $Pt(NH_3Cl)_2$ (Peyrone, *A.* 51, 1; 55, 205; 61, 178). The salts of Ba, Co, Cu, Pb, Mn, Ni, Ag, Na, UO_2, and Zn have been obtained. *Ammonium platosammine chlorosulphonate*, $Pt.NH_3Cl.NH_3SO_3Am.H_2O$, is obtained, in colourless rhombic tablets, by leading SO_2 into a boiling solution of $Pt(NH_3Cl)_2$, and neutralising with NH_3Aq. If the neutralisation is omitted, *platosammine chlorosulphonic acid*, $Pt.NH_3Cl.NH_3.SO_3H$, is obtained (Peyrone, *l.c.*).

The other salts of the platosammine series which have been isolated are the following; $M = Pt(NH_3)_2$:—*bromide*, MBr_2 (Jörgensen, *J. pr.* [2] 33, 521, 531, 535); *cyanide*, MCy_2 (Buckton, *A.* 92, 280); *iodide*, MI_2 (Cleve, *Bl.* [2] 7, 12; 17, 482; Reiset, *A. Ch.* [3] 11, 417); *nitrate* and *nitrite*, $M(NO_3)_2$ and $M(NO_2)_2$ (Cleve, *l.c.*); *sulphate* and *sulphite*, $MSO_4.H_2O$ and $MSO_3.H_2O$ (Cleve, *l.c.*); and *sulphocyanide*, $M(CyS)_2$ (Buckton, *l.c.*). Substituted derivatives of the bromide, of the form $Pt(NH_2RBr)_2$ and $Pt.NH_3Br.NH_2RBr$, where R = Et, Me, or Pr, have been obtained (Jörgensen, *l.c.*).

Series 3.—*Platodiammines* $Pt(NH_3.NH_3R)_2$. Formed by action of NH_3Aq on platinous salts, platosammine or platosemidiammine compounds. Easily lose NH_3 on heating, giving platosammine compounds. Give platinidiammine compounds by action of oxidisers.

PLATODIAMMINE CHLORIDE $Pt(NH_3.NH_3Cl)_2.H_2O$ (Reiset, *A. Ch.* [3] 11, 417). Sometimes called *Reiset's first chloride.* Obtained by the prolonged action of boiling NH_3Aq on $PtCl_2$, Magnus's green salt (*v. infra*), platosammine chloride $Pt(NH_3Cl)_2$, or platosemidiammine chloride $Pt(NH_3.NH_3Cl)Cl$, precipitation by alcohol, and crystallisation from water. Also formed by reduction of platinidiammine chloride $Cl_2Pt(NH_3.NH_3Cl)_2$, by H_2S (Thomsen, *J.* 1868. 278). Large, colourless, tetragonal crystals; S. 25 at 16·5°, more sol. hot water; insol. absolute alcohol and ether. Addition of H_2SO_4Aq, HNO_3Aq, or $H_2C_2O_4Aq$ ppts. the corresponding sulphate, nitrate, or oxalate. By gently warming with HNO_3Aq the salt $(NO_3)_2Pt(NH_3.NH_3Cl)_2$ is formed; Cl, Br, and $FeCl_3Aq$ react similarly. At 240°–270° NH_3 is given off, and $Pt(NH_3Cl)_2$ is formed (*v.* PLATOSAMMINE CHLORIDE, *supra*). Combines with $PtCl_2$, and $PtCl_4$, to form $M.PtCl_2$ and $M.PtCl_4$ respectively $[M = Pt(NH_3.NH_3Cl)_2]$. Compounds are known in which NH_3 is wholly or partly replaced by pyridine, also by alkyl radicles (Jörgensen, *J. pr.* [2] 33, 489), and also by PEt_3 (Cahours a. Gal, *C. R.* 70, 1381).

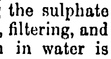
Double compounds. Combines with various metallic chlorides to form compounds of the form $M.XCl_2$, where $M = Pt(NH_3.NH_3Cl)_2$, and X = Pt, Cu, Pb, Hg, Sn, and Zn (*v.* Thomsen, *J.* 1868. 278; Buckton, *C. J.* 5, 213; Millon a. Commaille, *C. R.* 57, 822).

The most important of these compounds is PLATODIAMMINE CHLORIDE PLATINOUS CHLORIDE, known as *Magnus's green salt*, $\mathrm{Pt(NH_3.NH_3Cl)_2.PtCl_2}$. This salt is obtained by the action of $\mathrm{NH_3Aq}$ on $\mathrm{PtCl_2}$ in HClAq, or on $\mathrm{PtCl_4}$ in HClAq after passing in $\mathrm{SO_2}$ till AmCl ceases to give a pp. (Magnus, *P.* 14, 242; Gros, *A.* 27, 241). Also by adding $\mathrm{Pt(NH_3.NH_3Cl)_2}$ to $\mathrm{PtCl_2}$ in HClAq. It is best prepared by making $\mathrm{Am_2PtCl_4}$, from $\mathrm{PtCl_4}$ in HClAq treated with $\mathrm{SO_2}$ and crystallised from AmClAq, and heating this with HClAq and $\mathrm{NH_3Aq}$ (Claus, *A.* 107, 138). Green, microscopic prisms or needles; insol. water, alcohol, and dilute HClAq. Digestion with hot $\mathrm{NH_3Aq}$ forms $\mathrm{Pt(NH_3.NH_3Cl)_2}$; Cl, Br, or $\mathrm{HNO_3Aq}$ produces platinidiammines (Gros, *l.c.*; Raewsky, *A. Ch.* [3] 22, 278). Boiling with $\mathrm{AgNO_3Aq}$ produces $\mathrm{PtCl_2}$ and $\mathrm{Pt(NH_3.NH_3NO_3)_2}$. If the empirical formula $n\mathrm{Pt(NH_3)_2Cl_2}$ is given to Magnus's green salt, it is seen to be isomeric, or polymeric, with platosammine chloride $\mathrm{Pt(NH_3Cl)_2}$, platosemidiammine chloride $\mathrm{Cl_2Pt.NH_3.NH_3Cl}$, platomonodiammine chloride platinous chloride $\mathrm{2[Pt(NH_3.Cl)(NH_3.NH_3Cl)].PtCl_2}$, diplatosindiammine chloride $\mathrm{Cl_2Pt_2(NH_3.NH_3Cl)_2}$, and with a double salt obtained by Cossa (*B.* 23, 2503), $\mathrm{2[Pt.NH_3.Cl_2].Pt(NH_3)_4Cl_2}$.

PLATODIAMMINE HYDROXIDE $\mathrm{Pt(NH_3.NH_3OH)_2}$. Sometimes called *Reiset's first base* (Reiset, *A. Ch.* [3] 11, 417). White, crystalline, deliquescent needles; by decomposing the sulphate by the proper quantity of BaOAq, filtering, and evaporating *in vacuo*. Solution in water is strongly alkaline, absorbs $\mathrm{CO_2}$ from the air, and drives out $\mathrm{NH_3}$ from $\mathrm{NH_4}$ salts. $\mathrm{NH_3}$ is not given off when an aqueous solution is boiled alone or with potash. Melts at c. 110°; at a higher temperature gives off $\mathrm{NH_3}$ and $\mathrm{H_2O}$ and leaves platosammine oxide $\mathrm{Pt(NH_3)_2O}$ (*q. v.* p. 293).

The other chief compounds of the platodiammine series are the following; $\mathrm{M = Pt(NH_3)_4}$:— *carbonates*, $\mathrm{MCO_3.4aq}$ and $\mathrm{M(CO_3H)_2}$ (Peyrone, *A.* 51, 14; Reiset, *A. Ch.* [3] 11, 417); *chromates* $\mathrm{MCrO_4}$ and $\mathrm{MCr_2O_7}$; *bromide*, $\mathrm{MBr_2.3aq}$ (Cleve, *J.* 1867. 321); *iodide*, $\mathrm{MI_2}.x\mathrm{aq}$ (Cleve); *nitrate* and *nitrite*, $\mathrm{M(NO_3)_2}$ and $\mathrm{M(NO_2)_2.2aq}$ (Peyrone, *l.c.*); *phosphate*, $\mathrm{MHPO_4.aq}$ (Cleve, *Bl.* [2] 7, 12; 17, 482); *sulphate* and *sulphites*, $\mathrm{MSO_4}$, $\mathrm{MSO_3}$, $\mathrm{M(SO_3H)_2.2aq}$ (Cleve, *l.c.*).

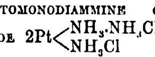
Series 4. *Platosemidiammines*, $\mathrm{Pt(NH_3.NH_3R)R}$. Generally formed from the chloride by double decomposition; the chloride is a product of the action of $\mathrm{NH_3Aq}$ or $\mathrm{(NH_4)_2CO_3Aq}$ on $\mathrm{PtCl_2}$. Prolonged treatment of the platosemidiammines with $\mathrm{NH_3Aq}$ produces diammine compounds. Jörgensen (*J. pr.* [2] 33, 489) has replaced $\mathrm{NH_3}$ in these compounds by alkyl radicles and by pyridine.



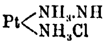
PLATOSEMIDIAMMINE CHLORIDE $\mathrm{Pt}<\begin{matrix}\mathrm{NH_3.NH_3Cl}\\ \mathrm{Cl}\end{matrix}$. Sometimes called *Peyrone's chloride*. $\mathrm{PtCl_2}$ is formed by the action of $\mathrm{SO_2}$ on $\mathrm{PtCl_4}$ in HClAq, and the solution is heated to boiling with excess of $\mathrm{(NH_4)_2CO_3}$ until the red solution has become light-yellow and a greenish-brown pp. forms, when the liquid is rapidly filtered. The chloride separates as the liquid cools; it must be filtered off at once (else it may re-dissolve), and crystallised from boiling water (Peyrone, *A.* 51, 14; 55, 209; *v.* also Thomsen, *Gm.-K.* 8, 1115; Cleve, *Bl.* [2] 7, 12, 17, 482). Small yellow crystals. S. ·26 at 0°, 3·6 at 100°. Decomposes at 270°, giving off $\mathrm{NH_3}$ and HCl. Boiling $\mathrm{NH_3Aq}$ forms platodiammine chloride, $\mathrm{Pt(NH_3.NH_3Cl)_2}$; Cl, Br, I, and some other oxidisers produce platinisemidiammine compounds, $\mathrm{R_2Pt(NH_3.NH_3R)R}$. With $\mathrm{AgNO_3}$, and $\mathrm{Ag_2SO_4}$, the corresponding nitrate and sulphate are formed.

It is doubtful whether the *hydroxide* $\mathrm{Pt(NH_3.NH_3OH)OH}$ has been prepared; the compound obtained by Odling (*C. N.* 21, 269, 289) was this or the isomeric platosammine hydroxide, $\mathrm{Pt(NH_3OH)_2}$ (*v.* PLATOSAMMINE HYDROXIDE, p. 293). The other compounds of this series which have been obtained are the following; $\mathrm{M = Pt.NH_3.NH_3}$:—*bromide*. $\mathrm{MBr_2}$; *chloro-sulphonic acid*, $\mathrm{MCl.SO_3H}$ (Cleve. *l.c.*); *iodide*, $\mathrm{MI_2}$; *nitrate* and *nitrite*, $\mathrm{M(NO_3)_2}$ and $\mathrm{M(NO_2)_2}$; *sulphate*, $\mathrm{MSO_4}$; *double sulphites*, $\mathrm{MSO_3.2X_2SO_3}$, $\mathrm{X_2 = 2NH_4}$, Ba. Co, $\mathrm{Ag_2}$; these may be regarded as compounds of sulphites with salts of the *hypothetical platosemiammine sulphonic acid* $\mathrm{Pt(NH_3.NH_3.SO_3H)SO_3H}$.

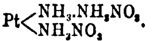
Series 5. *Platomonodiammines* $\mathrm{Pt(NH_3.NH_3R)(NH_3R)}$. Most of the salts of this series are prepared from the double salt of the chloride with $\mathrm{PtCl_2}$.



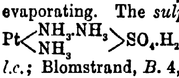
PLATOMONODIAMMINE CHLORIDE PLATINOUS CHLORIDE $\mathrm{2Pt}<\begin{matrix}\mathrm{NH_3.NH_3Cl}\\ \mathrm{NH_3Cl}\end{matrix}\mathrm{.PtCl_2}$. This compound is one product of the action of $\mathrm{NH_3Aq}$ on $\mathrm{PtCl_2}$ in HClAq; it is prepared by neutralising $\mathrm{PtCl_2}$ in HClAq by $\mathrm{(NH_4)_2CO_3Aq}$, heating to boiling, and adding $\mathrm{(NH_4)_2CO_3Aq}$ drop by drop, when it separates in small red tablets (Peyrone, *A.* 55, 209). Fairly sol. cold water, more sol. hot water. Boiled with $\mathrm{NH_3Aq}$ forms Magnus's green salt, $\mathrm{Pt(NH_3.NH_3Cl)_2.PtCl_2}$. Isomeric, or polymeric, with Magnus's green salt, platosammine chloride, and platosemidiammine chloride.



PLATOMONODIAMMINE CHLORIDE $\mathrm{Pt}<\begin{matrix}\mathrm{NH_3.NH_3Cl}\\ \mathrm{NH_3Cl}\end{matrix}$. Obtained, in lustrous colourless crystals, by adding HClAq to an ice-cold solution of the nitrate.



PLATOMONODIAMMINE NITRATE $\mathrm{Pt}<\begin{matrix}\mathrm{NH_3.NH_3NO_3}\\ \mathrm{NH_3NO_3}\end{matrix}$. Formed by decomposing the chloride in solution by $\mathrm{AgNO_3Aq}$, filtering, and evaporating. The *sulphate*



$\mathrm{Pt}<\begin{matrix}\mathrm{NH_3.NH_3}\\ \mathrm{NH_3}\end{matrix}>\mathrm{SO_4.H_2O}$ is also known (*v.* Cleve, *l.c.*; Blomstrand, *B.* 4, 40, 639, 673; 6, 1469).

Class II. Platini- or Platin- compounds.

Series 1. *Platinammines*, $\mathrm{R_2Pt(NH_3R)_2}$. These compounds are formed by the addition of Cl, Br, or I to platosammines, or by the action of such oxidisers as $\mathrm{HNO_3Aq}$ on platosammines; they are generally changed to platinidiammines by heating with $\mathrm{NH_3Aq}$, and are reduced to platosammines by $\mathrm{SO_2Aq}$. The radicles in direct union with Pt are replaced with more difficulty than those in union with $\mathrm{NH_3}$. The nomenclature is arranged to indicate, first, the nature of the radicles in direct union with Pt, and then those in direct union with $\mathrm{NH_3}$.

I. *Chloro- compounds* $\mathrm{Cl_2Pt(NH_3R)_2}$.

CHLOROPLATINAMMINE CHLORIDE $\mathrm{Cl_2Pt(NH_3Cl)_2}$. Formed by suspending platosammine chloride,

$Pt(NH_3Cl)_2$ in boiling water, and passing in Cl until the original citron-yellow particles are changed to microscopic yellow octahedra (Gerhardt a. Laurent, *C. R.* 30, 273), or until the liquid, which is yellow at first, begins to turn reddish. *Aqua regia*, or $KMnO_4Aq$ and HClAq, may be used instead of Cl (Odling, *C. N.* 21, 269, 289). A heavy, yellow, crystalline powder. S. 1 at 0°; 3 at 100°. Unacted on by boiling conc. HNO_3 or H_2SO_4; sol. boiling KOHAq without evolution of NH_3; sol. NH_3Aq, with formation of chloroplatinidiammine chloride, $Cl_2Pt(NH_3.NH_3Cl)_2$. The Cl is ppd. as AgCl only after long boiling with $AgNO_3Aq$ (Grimm, *A.* 99, 67).

CHLOROPLATINAMMINE NITRITE

$Cl_2Pt(NH_3.NO_2)_2$. Ppd. in colourless rhombic plates by addition of excess of HClAq to solution of the nitrato-nitrite, $(NO_3)_2Pt(NH_3.NO_2)_2$, which is formed by boiling platosammine nitrite, $Pt(NH_3.NO_2)_2$, with HNO_3Aq.

CHLOROPLATINAMMINE CHLORONITRITE

$Cl_2Pt(NH_3Cl)(NH_3.NO_2)$, is produced by the reaction of K_2PtCl_4 and $(NO_3)_2Pt(NH_3NO_2)_2$.

II. *Hydroxyl compounds*

$(OH)_2Pt(NH_3R)_2$.

HYDROXYL PLATINAMMINE HYDROXIDE

$(OH)_2Pt(NH_3.OH)_2$. Yellow, lustrous crystals; by adding excess of NH_3Aq to a boiling solution of the nitrato-nitrate $(NO_3)_2Pt(NH_3.NO_3)_2$, and allowing to cool. Scarcely sol. water; easily sol. dilute acids. Boiling KOHAq does not evolve NH_3; decomposes above 130°, giving off NH_3 and H_2O, and leaving Pt (Gerhardt a. Laurent, *C. R.* 30, 273).

HYDROXYL PLATINAMMINE NITRATE

$(OH)_2Pt(NH_3.NO_3)_2.2aq$. Crystalline pp. by decomposing $Cl_2Pt(NH_3Cl)_2$ by $AgNO_3Aq$. Not acted on by cold HClAq; evaporation with HNO_3Aq produces $(NO_3)_2Pt(NH_3.NO_3)_2$ (G. a. L., *l.c.*; Cleve, *Bl.* [2] 7, 12; 17, 482).

HYDROXYL PLATINAMMINE SULPHATE

$(OH)_2Pt(NH_3)_2SO_4.aq$. Formed as a pale-yellow, hard crust of needle-shaped crystals, by decomposing $Cl_2Pt(NH_3.Cl)_2$ by Ag_2SO_4Aq. Evaporation with H_2SO_4Aq produces the sulphato-sulphate, $SO_4.Pt.(NH_3)_2SO_4.3aq$; when HClAq is used, $Cl_2Pt(NH_3)_2SO_4$ and $Cl_2Pt(NH_3Cl)_2$ are produced (Cleve, *l.c.*).

The following salts of this series have also been isolated: *Bromo-bromide*, $Br_2Pt(NH_3Br)_2$ (Cleve, *l.c.*); *bromo-nitrite*, $Br_2Pt(NH_3.NO_2)_2$ (Cleve, *l.c.*); *iodo-iodide*, $I_2Pt(NH_3I)_2$ (Cleve, *l.c.*); *nitrato-nitrate*, $(NO_3)_2Pt(NH_3.NO_3)_2$; *nitrato-nitrite*, $(NO_3)_2Pt(NH_3.NO_2)_2$; *nitrato-chloro-nitrite*, $NO_3.Cl.Pt(NH_3NO_2)_2$ (Cleve, *l.c.*); *sulphato-sulphate*, $SO_4.Pt(NH_3)_2SO_4.3aq$ (Cleve, *l.c.*).

Series 2. *Platinidiammines*,

$R_2Pt(NH_3NH_3R)_2$. Generally formed by action of Cl, Br, I, and other oxidisers on platodiammines. A large number of these compounds is known. R attached directly to Pt may be the same as, or different from, R united directly to NH_3. The nomenclature is similar to that of the platinammine series. The radicles in direct union with Pt are removed with more difficulty than those united with NH_3.

I. *Chloro-compounds*

$ClR.Pt(NH_3.NH_3R)(NH_3.NH_3R)$; the R's may be the same or different.

CHLOROPLATINIDIAMMINE CHLORIDE

$Cl_2Pt(NH_3.NH_3Cl)_2$. By passing Cl into a fairly conc. boiling solution of platodiammine chloride, $Pt(NH_3.NH_3Cl)_2$, till the liquid begins to turn red (Raewsky, *A. Ch.* [3] 22, 278); also by dissolving chloroplatinammine chloride, $Cl_2Pt(NH_3Cl)_2$, in NH_3Aq (Gerhardt a. Laurent, *C. R.* 30, 273). Pale-yellow, crystalline powder; scarcely sol. cold water, sl. sol. boiling water. HNO_3Aq produces the *chloro-nitrate* $Cl_2Pt(NH_3.NH_3.NO_3)_2$; a little $AgNO_3Aq$ produces the *chloro-hydroxyl-nitrate* $Cl(OH)Pt(NH_3.NH_3.NO_3)_2$; long boiling with $AgNO_3Aq$ is needed to remove all Cl as AgCl. Reduced by H_2S, or action of Ag, to $Pt(NH_3.NH_3Cl)_2$ (Thomsen, *J.* 1868. 278; Jörgensen, *J. pr.* [2] 33, 489). Forms double compounds with $PtCl_2$ and $PtCl_4$ (Reiset, *A. Ch.* [3] 11, 417; G. a. L., *l.c.*; Cleve, *Bl.* [2] 7, 12; 17, 482).

The other chloro- compounds which are known are the following: *Chloro-nitrate*, $Cl_2Pt(NH_3.NH_3.NO_3)_2$ (Gros, *A. Ch.* [2] 69, 204; Raewsky, *A. Ch.* [3] 22, 278; Hadow, *C. J.* [2] 4, 345); *chloro-chloro-nitrite*, $Cl_2Pt(NH_3.NH_3.NO_2)(NH_3.NH_3Cl)$; *chloro-hydroxyl-chloride*, $Cl(OH)Pt(NH_3.NH_3Cl)_2$ (Cleve, *l.c.*; Hadow, *l.c.*); *chloro-hydroxyl-carbonate*, $Cl(OH)Pt(NH_3.NH_3)_2CO_3.H_2O$ (Raewsky, *l.c.*; Gros, *l.c.*); *chloro-hydroxyl-chromate* and *dichromate*, $Cl(OH)Pt(NH_3.NH_3)_2CrO_4$ and $Cl(OH)Pt(NH_3.NH_3)_2Cr_2O_7$ (Cleve, *l.c.*); *chloro-hydroxyl-nitrate*, $Cl(OH)Pt(NH_3.NH_3.NO_3)_2$, (Raewsky, *l.c.*; G. a. L., *l.c.*; Cleve, *l.c.*); *chloro-chromate* and *dichromate*, and *chloro-sulphate*, $MCrO_4$, MCr_2O_7, and MSO_4, where $M = Cl_2Pt(NH_3.NH_3)_2$ (Cleve, *l.c.*).

II. *Bromo-compounds.* The following members of this class have been isolated (Cleve, *l.c.*); *bromo-bromide*, MBr_2; *bromo-chloride*, MCl_2; *bromo-dichromate*, MCr_2O_7; *bromo-nitrate*, $M(NO_3)_2$; *bromo-phosphate*, $M(PO_4H_2)_2.2aq$ (in these formulæ $M = Br_2Pt(NH_3.NH_3)_2$); *bromo-chloro-chloride*, $BrClPt(NH_3.NH_3Cl)_2$; *bromo-hydroxyl-chloride* and *nitrate*, MCl_2 and $M(NO_3)_2$, where $M = Br(OH)Pt(NH_3.NH_3)_2$.

III. *Hydroxyl compounds. Hydroxyl-nitrate* and *sulphate*, $M(NO_3)_2$ and MSO_4, where $M = (OH)_2Pt(NH_3.NH_3)_2$.

IV. *Iodo-compounds. Iodo-iodide*, MI_2; *iodo-nitrate*, $M(NO_3)_2$; *iodo-sulphate*, MSO_4; where $M = I_2Pt(NH_3.NH_3)_2$.

IV. *Carbonato-compounds. Carbonato-bromo-carbonate*, *carbonato-chloro-carbonate*, and *carbonato-nitrato-carbonate*, $Br_2(CO_3)R$, $Cl_2(CO_3)R$, and $(NO_3)_2CO_3R$, where

$$R = 2[Pt(NH_3.NH_3)_2].(CO_3)_2.$$

V. *Nitrato-compounds* (Cleve, *l.c.*; Gerhardt a. Laurent, *C. R.* 30, 273):

$(NO_3)_2Pt(NH_3.NH_3Cl)_2.2aq$;

$(NO_3)_2Pt(NH_3.NH_3NO_3)_2$;

$(NO_3)_2Pt(NH_3.NH_3)_2CrO_4$;

$(NO_3)_2Pt(NH_3.NH_3)_2Cr_2O_7$;

$OH(NO_3)Pt(NH_3.NH_3.NO_3)_2$;

$Cl(NO_3)Pt(NH_3.NH_3)_2SO_4.aq$;

$Cl(NO_3)Pt(NH_3.NH_3.NO_3)_2$.

VI. *Nitrito-compounds* (Cleve, *l.c.*; Hadow, *C. J.* [2] 4, 345):

$(NO_2)_2Pt(NH_3.NH_3.NO_3)_2$;

$I(NO_2)Pt(NH_3.NH_3.NO_3)_2$.

VII. ***Sulphato- compounds*** (Cleve, *l.c.*): $(SO_4)Pt(NH_3.NH_3)_2SO_4.aq$;

$$\begin{array}{c} OH.Pt(NH_3.NH_3)_2Cl.2aq; \\ \diagdown SO_4 \diagup \end{array}$$

$OH(SO_4)Pt(NH_3.NH_3)_2SO_4.3aq$; $Br_2(SO_4)Pt(NH_3.NH_3)_4(SO_4)_2.aq$.

Series 3. *Platinisemidiammines*, $R_2Pt(NH_3.NH_3R)R$. These compounds are isomeric with the platinammines, $R_2Pt(NH_3R)_2$. They are generally formed by oxidising the platosemidiammines, $Pt(NH_3.NH_2R)R$.

CHLOROPLATINISEMIDIAMMINE CHLORIDE $Cl_2Pt(NH_3.NH_3Cl)Cl$. By chlorinating platosemidiammine chloride, $Pt(NH_3.NH_3Cl)Cl$, by Cl or *aqua regia* (Cleve, *l.c.*). Orange, crystalline powder; S. ·33 at 0°, 1·52 at 100°. Not acted on by conc. H_2SO_4 or alkali solutions.

The following salts of this series are known (Cleve, *l.c.*):
bromo-bromide, $Br_2Pt(NH_3.NH_3Br)Br$;
bromo-nitrite, $Br_2Pt(NH_3.NH_3.NO_2)NO_2$;
chloro-nitrite, $Cl_2Pt(NH_3.NH_3.NO_2)NO_2$;
chloro-hydroxyl-nitro-nitrite, $Cl(OH)Pt(NH_3.NH_3.NO_2)NO_2$;
trihydroxyl-nitrate, $(OH)_2Pt(NH_3.NH_3.NO_3)OH$;
hydroxyl-sulphate, $\begin{array}{c} (OH)_2PtNH_3.NH_3 \\ \diagdown SO_4 \diagup \end{array}$.

Series 4. *Platinimonodiammines*, $R_2Pt(NH_3.NH_3R)(NH_3R)$. Of this series the following have been isolated (Cleve, *l.c.*): *bromo-nitrate*, $Br_2Pt(NH_3.NH_3.NO_3)(NH_3.NO_3)$; *bromo-sulphate*, $Br_2Pt(NH_3.NH_3.SO_4.NH_3).aq$; *chloro-chloride*, $Cl_2Pt(NH_3.NH_3Cl)(NH_3Cl)$; *hydroxyl-nitrate*, $(OH)_2Pt(NH_3.NH_3.NO_3)(NH_3.NO_3).aq$; *hydroxyl-bromo-nitrate*, $(OH)BrPt(NH_3.NH_3.NO_3)(NH_3.NO_3).aq$; *iodo-bromide*, $I_2Pt(NH_3.NH_3Br)(NH_3Br)$.

Series 5. *Platinitriammines*, $R_2Pt(NH_3.NH_3.NH_3R)_2$. This constitution is probably to be given to salts formed by electrolysing ammonium carbamate or carbonate solution, using electrodes of Pt (Drechsel, *J. pr.* [2] 20, 378; 26, 277; Gerdes, *J. pr.* [2] 26, 257). The salt formed as described is probably ***carbonato-platinitriammine carbonate***, $(CO_3).Pt\begin{array}{c}\diagup NH_3.NH_3.NH_3 \diagdown \\ \diagdown NH_3.NH_3.NH_3 \diagup\end{array}CO_3$. By the action of HNO_3, H_2SO_4, and HCl, respectively, on this compound are obtained the *nitrato-nitrate*, *sulphato-sulphate*, and *chloro-chloride*, $(NO_3)_2.M.(NO_3)_2$, $SO_4.M.SO_4.aq$, and $Cl_2.M.Cl_2$, where $M = Pt(NH_3.NH_3.NH_3)_2$.

Class III. Diplatinum compounds.

Series 1. *Diplatodiammines*, $\begin{array}{l} Pt(NH_3.NH_3R) \\ | \\ Pt(NH_3.NH_3R) \end{array}$ (Blomstrand, *J. pr.* [2] 3, 207). Cleve (*l.c.*) gives to these compounds the formula

$$Pt_2(NH_3)_2(NH_2)_2R_2.$$

The following members of this series are known: *chloride*, MCl_2; *hydroxide*, $M(OH)_2$; *nitrate*, $M(NO_3)_2$; and *sulphate*, MSO_4; where $M = Pt_2(NH_3)_4$.

Series 2. *Diplatosindiammines*, $\begin{array}{l} RPt(NH_3.NH_3R) \\ | \\ RPt(NH_3.NH_3R) \end{array}$. The only compound of this series is the *chloride* $Cl_2Pt_2(NH_3)_4Cl_2$.

Series 3. *Diplatinammines*, $\begin{array}{l} RPt(NH_3R)_2 \\ | \\ RPt(NH_3R)_2 \end{array}$. The only compound of this series is the *iodide* $I_2Pt_2(NH_3)_4I_4$ (Cleve, *l.c.*); by treatment with HIAq, the compound $Pt_4I_{10}(NH_3)_8$ and $Pt_8I_{13}(NH_3)_{16}$ are produced.

Series 4. *Diplatinidiammines*, $\begin{array}{l} RPt(NH_3.NH_3R)_2 \\ | \\ RPt(NH_3.NH_3R)_2 \end{array}$ (Cleve, *l.c.*). The iodo-nitrate, $I_2Pt_2(NH_3)_8(NO_3)_4$, is formed by reacting on $I_2Pt(NH_3)_4(NO_3)_2$ with NH_3Aq and treating the product with HNO_3Aq; most of the other compounds of the series are formed from the iodo-nitrate. Various classes of compounds of this series are formed by varying the composition of the radicles, R; the nomenclature is similar to that used for the platinidiammines. The compounds which have been isolated are *bromo-nitrate*, *bromo-anhydronitrate*, and *bromosulphate*, $M(NO_3)_4$, $M(NO_3)_2O$, and $M(SO_4)_2.2aq$, where $M = Br_2Pt_2(NH_3)_8$; *hydroxyl-chloride*, *dichromate*, *phosphate*, and *sulphate*, $MCl_4.aq$, $M(Cr_2O_7)_2$, $M(HPO_4)_2$, and $M(SO_4)_2.2aq$, where $M = (OH)_2Pt_2(NH_3)_8$; *iodo-iodide*, *anhydro-iodide*, *nitrate*, *anhydronitrate*, *phosphate*, and *sulphate*, MI_4, MI_2O, $M(NO_3)_4.4aq$, $M(NO_3)_2O$, $M(HPO_4)_2$, and $M(SO_4)_2$, where $M = I_2Pt_2(NH_3)_8$; *nitrato-nitrate*, $(NO_3)_2Pt_2(NH_3)_8(NO_3)_4.4aq$.

M. M. P. M.

PLATINUMS, FULMINATING. Various compounds of Pt, N, Cl, O, and H, all of which explode when heated, are formed by the action of KOHAq on $(NH_4)_2PtCl_6$, or by ppg. $Pt(SO_4)_2$ with NH_3Aq and boiling the pp. with KOHAq (Proust, *Gehlen's J.* 1, 348; Döbereiner, *G. A.* 72, 194; Fourcroy a. Vauquelin, *Gehlen's J.* 1, 348; Davy, *S.* 19, 91). These compounds are classed together as *fulminating platinums*. E. von Meyer (*J. pr.* [2] 18, 305) classifies according to the quantities of Cl they contain; all contain Pt and N in the ratio of equal numbers of atoms: *tetrachloro- compound* $Pt_4N_4Cl_4O_{12}H_{24}$, *trichloroxy-* $Pt_4N_4Cl_3(OH)O_{12}H_{24}$, *dichloro-* $Pt_4N_4Cl_2O_{12}H_{22}$, *chloroxy-* $Pt_4N_4Cl(OH)O_{12}H_{22}$. Tetrachloro-fulminating platinum is formed by adding KOHAq drop by drop to Am_2PtCl_6, in the ratio 4·6KOH : Am_2PtCl_6, and washing the pp. by repeatedly boiling with acetic acid solution and then with water. At 150° $4H_2O$ is given off; explosion occurs at a higher temperature. Dilute H_2SO_4Aq produces $H_2C_2O_4$ and evolves CO_2. By treatment with KOHAq, or NH_3Aq, Cl_2 is easily removed, a third Cl is removed with difficulty, but the fourth Cl remains unattacked.

M. M. P. M.

PLUMBAGO. A name sometimes given to graphite; *v.* CARBON, vol. i. p. 686.

PLUMBATES. Salts wherein PbO_2 acts as acidic radicle, *v.* vol. iii. p. 132.

PLUMBITES. Salts wherein PbO acts as acidic radicle, *v.* vol. iii. p. 129.

PLUMERIC ACID $C_{10}H_{10}O_5$. [139°]. Occurs as calcium salt in the milky juice of *Plumeria acutifolia* (Oudemans, *A.* 181, 154). Minute crystals (from water), v. sol. alcohol and ether, sl. sol. cold water. Yields salicylic acid on fusion with KOH. Reduced by sodium-amalgam to crystalline 'hydroplumeric' acid $C_{10}H_{12}O_5$.—K_4A^{iv} 8aq. — $Ca(H_3A^{iv})_2$ 4aq. S. ·5 at 20°. — CaH_2A^{iv} 5aq. S. ·25 at 20°.—$Ca_3(HA^{iv})_2$ 8aq.— $Ag_2H_2A^{iv}$ aq. — Ag_3HA^{iv} $1\frac{1}{2}$aq: needles (from water).

PODOCARPIC ACID $C_{17}H_{22}O_3$ *i.e.* $C_8H_{15}.C_6H_2Me(OH).CO_2H$. Mol. w. 274. [188°]. $[\alpha]_D = 136°$. Constitutes at least 90 p.c. of the resin found by de Vrij in the trunk of an old tree, *Podocarpus cupressina*, var. *imbricata* (Oudemans, *A.* 170, 213). Plates (from dilute alcohol), insol. water, v. sl. sol. benzene, v. e. sol. alcohol and ether. Dextrorotatory. Resolved at 300° into water and anhydride $C_{34}H_{42}O_5$. Yields methanthrene $C_{15}H_{12}$ on distillation with zinc-dust. The Ca salt on distillation yields *p*-cresol, hydrocarpol, carpene C_9H_{14}, and methanthrol $C_{15}H_{12}O$. Br added to its alcoholic solution forms $C_{17}H_{20}BrEtO_3(EtOH)$ [above 80°], which gives off alcohol when heated for some time, leaving $C_{17}H_{20}BrEtO_3$ [158°].

Salts.—NaA' 7aq. S. 33 at 21°. Needles.—KA' 3aq.—KA' 4aq.—$(NH_4)HA'_2$ aq.—BaA'_2 3aq.—BaA'_2 8aq. — BaA'_2 9aq. — BaA'_2 15aq. — $BaC_{17}H_{20}O_3$ 8aq. — CaA'_2 5aq. — PbA'_2 4aq.—$PbC_{17}H_{20}O_3$ aq. — $PbH_2A'_4$ 10aq. — CuA'_2 10aq.—AgA' $2\frac{1}{2}$aq.

Methyl ether MeA'. [174°]. Grains.

Ethyl ether EtA'. [146°]. Needles.

Acetyl derivative $C_{17}H_{21}AcO_3$. [152°]. Small needles (from dilute alcohol).

Nitropodocarpic acid $C_{17}H_{21}(NO_2)O_3$. [205°]. Formed, as well as the di-nitro- acids, by the action of HNO_3 (S.G. 1·34). Small crystals, insol. water, m. sol. hot alcohol. May be reduced to unstable amido-podocarpic acid, which forms $C_{17}H_{23}NO_3HCl$ $\frac{1}{2}$aq.

Salts.—$(NH_4)_2C_{17}H_{19}NO_5$ 4aq.—$K_2C_{17}H_{19}NO_5$ $5\frac{1}{2}$aq. Red needles with green lustre, v. sol. water.—$Na_2C_{17}H_{19}NO_5$ 9aq. Scarlet plates. — $BaC_{17}H_{19}NO_5$ 7aq. Red needles. — $BaC_{17}H_{19}NO_5$ 3aq.—BaA'_2 4aq: yellow needles, sl. sol. water.—$CaC_{17}H_{19}NO_5$ 4aq: orange needles.

Di-nitro-podocarpic acid $C_{17}H_{20}(NO_2)_2O_3$. [203°]. Pale-yellow crystals, insol. water, m. sol. alcohol.—Salts: $K_2C_{17}H_{18}N_2O_7$ 5aq. Crimson needles, with green reflex.—$BaC_{17}H_{18}N_2O_7$ 4aq.—$Ag_2C_{17}H_{18}N_2O_7$ 4aq: orange pp.

Sulpho-podocarpic acid $C_{17}H_{21}(SO_3H)O_3$ 8aq. Got by warming with H_2SO_4. Amorphous mass. Salts: Na_2A'' 7aq: easily soluble rosettes.—$Ba(HA'')_2$ 6aq. — BaA'' 8aq: white laminæ. — CaA'' 7aq: thin laminæ.

Hydrocarpol $C_{16}H_{20}O$. (220° *in vacuo*). A product of the distillation of calcium podocarpate. Viscid oil, v. sol. alcohol and ether. Yields *p*-cresol, carpene, and methanthrol $C_{15}H_{12}O$ [122°] when distilled. Methanthrol is crystalline, sol. KOHAq.

PODOPHYLLIN. The resin extracted from the root of *Podophyllum peltatum* (Guareschi, *B.* 12, 683; *G.* 10, 16; Busch, *Ph.* [3] 8, 443; Senier a. Lowe, *Ph.* [3] 8, 445). It contains bitter and physiologically active 'picropodophyllin' crystallising in needles [200°-210°], and several resins, *e.g.* 'podophyllo- quercetin' [247°-250°] and 'podophyllic acid' (Podwissotzky, *Ph.* [3] 12, 1011).

POLYCHROÏTE *v.* SAFFRON.

POLYMERISM; a term generally applied to the phenomena of the existence of more than one substance having the same composition, and related in properties, but with different molecular weights; *v.* ISOMERISM, vol. iii. pp. 79-81.

M. M. P. M.

POLYPORIC ACID $C_{18}H_{14}O_4$. [above 300°]. Occurs in a fungus belonging to the genus *Polyporus*, which grows on the bark of diseased or dead oaks. The fungus is yellow, but is turned violet by ammonia (Stahlschmidt, *A.* 187, 177; 195, 365). Bronzed tables (from alcohol), insol. water, ether, benzene, CS_2, and HOAc, sl. sol. chloroform and alcohol. Alkalis form purple solutions, decolourised by zinc-dust. Yields a tetrahydride when boiled with conc. KOHAq. Yields benzene on distillation with zinc-dust. Conc. HNO_3 forms $C_{18}H_{12}(NO_2)_2O_4$ [230°]. $KClO_3$ and HCl give $C_{18}H_{14}Cl_4O_4$ [108°] and $C_{18}H_{12}Cl_4O_2$ [110°].

Salts.—K_2A'' 2aq: purple monoclinic crystals.—Na_2A'' 2aq: violet needles.—$(NH_4)_2A''$ 2aq.—BaA'' 4aq.—BaA'' 2aq.—SrA'' 4aq.—SrA'' aq.—CaA'' 3aq: pale-violet needles. MgA'' 3aq.—Ag_2A'': insoluble pp.

Methyl ether Me_2A''. [187°].

Ethyl ether Et_2A''. [134°]. Needles.

Diacetyl derivative $C_{18}H_{12}Ac_2O_4$. [205°]. Yellow needles, sl. sol. alcohol.

Hydride $C_{18}H_{18}O_4$. [163°]. Formed, together with the acid $C_{20}H_{18}O_2$ [156°] which yields Ag_2A'', by boiling polyporic acid with conc. KOHAq. White crystalline powder (from hot water), sol. alcohol.—Na_2A'' 4aq.—BaA''.—MnA'' 6aq.—Ag_2A'': crystalline pp.

POPPY OIL. The oil expressed from the seeds of *Papaver somniferum* contains glycerides of linoleïc, stearic, and palmitic acids (Oudemans, *J.* 1858. 301; 1863. 333; *cf.* Mulder, *J.* 1865. 323).

POPULIN is the *Benzoyl derivative* of SALICIN.

PORPHYRINE $C_{21}H_{25}N_3O_2$. [97°]. Occurs, together with alstonine and alstonidine, in the bark of *Alstonia constricta* (Hesse, *A.* 205, 366). White amorphous substance, sol. alcohol, ether, and chloroform. Conc. H_2SO_4 gives a purple solution. Its acid solutions exhibit blue fluorescence.—$B'_2H_2PtCl_6$ 4aq.

POTASH. *Potassium hydroxide*, *q. v.*, p. 302.

POTASSIUM. K. At. w. 39·04. Mol. w. probably 39·04 (Ramsay, *C. J.* 55, 521; *v. infra*). M.P. 58° (Quincke, *P.* 135, 642); 62·5° (Bunsen, *A.* 125, 368). B.P. 719°-731° (Carnelley a. Williams, *C. J.* 35, 563); 667° (Perman, *C. J.* 55, 326). S.G. ·865 at 15° (Gay-Lussac a. Thénard); ·875 at 13° (Baumhauer, *B.* 6, 655). V.D. not known with certainty; *v. infra, molecular weight.* S.H. from −78° to +10° ·166 (Regnault, *A. Ch.* [3] 26, 286). C.E. (linear, 0°-50°) ·00008415 (Hagen, *Verhandl. d. physikal. Ges. zu Berlin*, 1882. No. 13). Volume at $t°$ = vol. at 0° $(1 + \cdot00023935t + \cdot0000002\!9925t^2)$ for interval 10° to 95° (Hagen, *l.c.*). E.C. at 0° (Hg at 0° = 1) 11·23; at 100° (liquid) 5·586 (Matthiessen, *P.* 100, 177). Refraction-equiv 7·51 (Kanonnikoff, *J. R.* 1884 (1), 119). The emission-spectrum is characterised by a line K_α in the extreme red, and a line K_β in the violet; for measurements of all the chief lines *v. B. A.* 1884. 436; for the absorption-spectrum *v.* Roscoe a. Schuster, *C. N.* 29, 268. H.C. $[K^2,O] = 66{,}050$ (Woods, *P. M.* [4] 2, 268).

Occurrence.—Compounds of K are widely distributed in large quantities. *Felspar, mica, &c.*, contain silicates of this metal; *carnallite, sylvine, &c.*, contain KCl; *alum-stone* and other minerals contain K_2SO_4; *saltpetre* is chiefly KNO_3. Sea-water contains c. ·5 to ·7 g. KCl per litre. Potassium salts, *e.g.* acid tartrate and oxalate, are found in plants. Animals contain salts of K, chiefly phosphate and chloride.

Historical.—Potash was decomposed by Davy (*T.* 1808. [1] 5) in 1807, by passing the electric current from a Volta-pile of 200 plates, through a piece of potash placed in a Pt basin. Gay-Lussac a. Thénard, in 1808, reduced potash and obtained the metal, by heating it to whiteness with iron filings (*A. Ch.* 65, 325). In the same year Curaudan (*A. Ch.* 66, 97) showed that charcoal could be used instead of iron. Brunner (*S.* 88, 517) made this process applicable on the large scale, and B.'s method was modified by several workers, especially by Donny a. Mareska (*A. Ch.* [3] 35, 147).

Formation.—1. By electrolysing KOH. The most effective method is to place a little conc. KOHAq, with pieces of solid KOH in it, in a Pt basin, to connect this with the negative pole of a powerful battery, to pour a little Hg into the basin, and place therein the wire from the positive pole. The K which is thus formed amalgamates with the Hg; the amalgam, after drying, is heated in a small retort, along with a little mineral oil, which drives out the air, and the K remains when the Hg has been distilled off.—2. By electrolysing a molten mixture of KCl and $CaCl_2$ in the ratio $2KCl:CaCl_2$. Temperature is arranged so that a solid crust remains on the surface of the molten mixture. Electrodes of gas-coke are used. After electrolysis the mixture is allowed to cool for twenty minutes, and the contents of the crucible are scraped out under petroleum (Matthiessen). Linnemann electrolyses molten KCN (*J. pr.* 73, 415).—3. By heating KOH to redness with iron filings or charcoal.—4. By heating an intimate mixture of K_2CO_3 and C, or a mixture of K_2CO_3 or KOH, C, and very finely-divided iron (Castner, *C. N.* 54, 218).—5. By heating sulphide of K with iron filings (Dolbear, *C. N.* 26, 33).—6. By heating potash with sodium under petroleum to c. 170° (Williams, *C. N.* 3, 21).—7. By the action of Na on dry molten K acetate (Wanklyn, *C. N.* 3, 66).

Preparation.—An intimate mixture of K_2CO_3 and C is formed by heating cream of tartar (K-H tartrate) in a closed crucible. The mixture is then strongly heated in an iron bottle, connected with a flat receiver about 30 centim. long, 12 centims. wide, and 6 centims. from the inner surface of one side to that of the other; this receiver is made of two pieces of sheet-iron (about 4 mm. thick) screwed together, and has an opening at the end farthest from the retort, to allow the escape of CO. The reaction may be represented thus: $K_2CO_3 + 2C = 2K + 3CO$. The K distils over and condenses in the receiver; when full the receiver is removed, plunged under mineral oil and there opened, and the K is removed by a chisel. K combines with CO at a red heat to form a black, very explosive substance; the more rapidly the distilled K is cooled the less of this explosive compound is formed. The distilled metal is purified by wrapping it, when under oil, in a piece of linen, heating the oil to c. 65°, and pressing the molten K through the linen; the metal is then redistilled, from an iron bottle, into a copper tube partly filled with mineral naphtha, and having an opening through which an iron rod may be passed to clear the tube which carries the K from the bottle into the receiver (Donny a. Mareska, *A. Ch.* [3] 35, 147). Castner (*C. N.* 54, 218) uses as reducer a mixture of C and a metallic carbide, or a mixture of very finely-divided metal and C (conveniently prepared by heating a mixture of Fe_2O_3 and tar in a covered vessel), and heats in an iron crucible with an exit-tube passing through the lid. The reaction, using KOH, Fe, and C, may be formulated as $3KOH + Fe + 2C = 3K + Fe + CO + CO_2 + 3H$.

Properties.—A silver-white, lustrous metal. As soft as wax at ordinary temperatures, brittle at 0°, melts at c. 60°. Boils when heated in a stream of H to c. 700°, and forms a bright-green vapour. A sublimate, in a very thin film on glass, shows a rich purple colour in transmitted light (Dudley, *C. N.* 66, 163; Newth, *N.* 47, 55). Crystallises in quadratic octahedra, which have a greenish-blue sheen. These crystals are obtained by melting K in a glass tube, narrowed at one place, and filled with coal-gas, and allowing the semi-solidified metal to flow slowly through the constricted part of the tube (Long, *C. J.* 13, 122). Sol. liquid NH_3, forming a blue liquid, from which the metal is obtained by allowing the NH_3 to evaporate (Seeley, *C. N.* 23, 169; *v.* POTASSAMMONIUM, p. 299). Combines very rapidly with O; on exposing a freshly-cut surface to air, oxidation occurs at once. Decomposes cold water rapidly. K must be kept under a liquid free from O, such as mineral naphtha or rock-oil.

The *atomic weight* of K was determined by Berzelius, Penny, Marignac, Pelouze, Millon, Faget, and Maumené, from 1813 to 1846, by reducing $KClO_3$, $KClO_4$, and KIO_3 to KCl and KI, and by converting KCl, KBr, and KI to AgCl, AgBr, and AgI. The researches of Stas, in 1860 and 1865, have determined the at. w. with great accuracy. Stas heated $KClO_3$, thus getting KCl, decomposed $KClO_3$ by HClAq, determined the ratio of KCl and KBr to Ag required for complete ppn., converted KCl into KNO_3 and KBr into AgBr, and determined the ratio of KBr to $AgNO_3$ required for ppn. (Stas, *Rech.* 69, 70, 91, 118; *Nouv. R.* 244, 303).

The *molecular weight* of K is not known with certainty. Dewar a. Dittmar (*C. N.* 27, 121) and Dewar a. Scott (*Pr.* 29, 206, 490) determined the V.D. of K at c. 1000°; the earlier results pointed to a mol. w. of c. 90, and the later numbers to a value c. 45. V. Meyer (*B.* 13, 391) showed that the results were untrustworthy, as vapour of K attacks glass vessels. It has also been shown that vessels of Cu, Ag, Pt, or Fe cannot be used (Rieth, *B.* 4, 807; Meyer, *l.c.*). Ramsay (*C. J.* 55, 521) attempted to find mol. w. of K by dissolving in Hg, and finding the decrease of the vapour-pressure of Hg thereby produced. Assuming the mol. w. of liquid Hg to be 200, and also assuming that equal vols. of dilute solutions contain equal numbers of molecules, the results gave mol. w. of K as 29·1 and 30·2; it seems probable that the mol. of K is monatomic.

The only compound of K whose V.D. has been determined is KI; in this molecule the atom of K is monovalent.

K is a very strongly positive element. In all

its compounds it reacts as a metal, and does not enter into the composition of any negative radicles. K forms very few basic salts, and no oxyhaloid compounds; its halide compounds are very stable towards heat. K is closely related to Cs, Li, Na, and Rb (*v.* ALKALIS, METALS OF THE, vol. i. p. 114).

Reactions.—1. Heated in dry *air* or *oxygen*, K_2O and K_2O_4 are formed (*v. Oxides*, p. 304).—2. At about 300° K absorbs *hydrogen* readily, probably forming K_2H (*v. Hydride*, p. 301).—3. Combines with *chlorine*, *bromine*, and *iodine* when heated (*v. Chlorides, bromides, iodides*, pp. 299, 300, 302).—4. Forms compounds with *sulphur*, *selenion*, and *tellurium* when heated (*v. Sulphides, selenides, tellurides*, pp. 305, 306).—5. Combines with *phosphorus* (*v. Phosphide*, p. 305).—6. Alloys with several *metals* (*v. Alloys*, *infra*).—7. Reacts rapidly with *water*, forming KOHAq and H.—8. Heated with *hydrogen sulphide* forms KHS (*v. Hydrosulphide*, p. 302).—9. Dissolves in *liquid ammonia* (Seeley, *C. N.* 23, 169; *v. infra*, POTASSAMMONIUM). Heated in dry *ammonia gas*, KNH_2 is formed (*v. Amide*, *infra*).—10. Combines with *carbon monoxide* to form KCO (*v. Carbonyl compound*, p. 300). At red heat decomposes CO with separation of C.—11. Decomposes *carbon dioxide*, and *nitrous* and *nitric oxide*, when strongly heated with these compounds.—12. Reacts with *moist carbon dioxide* to form K_2CO_3 and HCO_2K (Kolbe a. Schmitt, *A.* 119, 251).—13. Decomposes *silica* and *boric acid*, when heated with these compounds, probably forming silicide and boride (*q. v.*, pp. 299, 305).

Potassium, alloys of. Alloys of K with most metals are known; K alloys easily with the more fusible metals. The alloys generally oxidise in air, and decompose cold water. K forms amalgams with Hg; according to Joannis (*C. R.* 113, 795), $Hg_{18}K$ is formed by letting potassammonium (*q. v.*) in liquid NH_3 drop on to Hg. For polarisation of K amalgam in KClAq against Zn amalgam *v.* Le Blanc, *Z. P. C.* 5, 467. For supposed alloy with NH_4, *v. infra*, POTASSAMMONIUM.

Potassium, aluminate of; *v.* vol. i. p. 141.

Potassium amide, KNH_2. Gay-Lussac a. Thénard (*G. A.* 29, 135; 32, 23) obtained dark olive-green crystals by heating K in dry NH_3. Baumert a. Landolt (*A.* 111, 1) confirmed G. a. T.'s formula KNH_2. The compound is formed by passing dry NH_3 into a flask of c. 50 c.c. capacity, fitted with a cork carrying an inlet and exit tube, quickly throwing in pieces of K, continuing the passage of NH_3, and heating very gently till the metal just ceases to dissolve in the greenish-blue liquid that is formed; on cooling, a yellowish-brown solid is obtained. KNH_2 is a non-conductor of electricity. Melts at a little over 100°, at a higher temperature NH_3 is given off, along with H and N, and K_3N remains (*v.* POTASSIUM NITRIDE, p. 304). Burns when heated in O, or heated to redness in air, giving N and KOH; decomposes in moist air to KOH and NH_3; must, therefore, be kept under rock oil. Reacts energetically with water, giving NH_3 and KOHAq.

Potassium-ammonium or Potassammonium. By evolving dry NH_3, from $AgCl.xNH_3$, in a Faraday tube containing K in the other end, Weyl (*P.* 121, 697) obtained a substance which he regarded as an alloy, or compound, of K and NH_4. Seeley (*C. N.* 23, 169) regarded the blue liquid formed by dissolving K in liquid NH_3 as a solution, inasmuch as K was obtained again when the NH_3 was allowed to evaporate. Joannis (*C. R.* 109, 900, 965; 110, 238) examined the vapour-pressures of a solution of K in liquid NH_3, and also the thermal phenomena attending the formation of the solution. He found the vapour-pressure to decrease till a certain value was reached, when it became constant, provided temperature was not changed; on removal of more NH_3 a copper-red solid separated, and thereafter NH_3 was given off at constant pressure, till only K remained. This last part of the process was regarded by J. as a dissociation of NH_3K; analysis showed this ratio (NH_3:K) to be always attained when the final part of the change commenced. The heat of formation of NH_3K is given by J. as 6,300 when NH_3 is gas and K solid, and as 1,900 when NH_3 is liquid and K solid. Joannis (*C. R.* 113, 795) found that NH_3K in liquid NH_3 is decomposed by Sb, Pb, and Hg, but not by Al, Cu, Ag, or Zn; by dropping the liquid on to Hg, and washing the product with liquid NH_3, he obtained a crystalline amalgam $Hg_{18}K$.

By measuring the depression of the vapour-pressure of liquid NH_3 by solution of K therein, J. concludes that the mol. formula of potassammonium is $N_2H_6K_2$ (*C. R.* 115, 820).

Potassium, antimonide of. Probably SbK_3. A greyish-white, lustrous solid; decomposes water, giving KOH, Sb, and H. Formed by heating the elements together, or by fusing Sb_2O_3 with K_2CO_3 and C.

Potassium, antimonates of; *v.* vol. i. p. 286.

Potassium, arsenates of; *v.* vol. i. p. 309.

Potassium, arsenites of; *v.* vol. i. p. 306.

Potassium, auricyanide of; *v.* vol. ii. p. 332.

Potassium, borates of; *v.* vol. i. p. 529.

Potassium, boride of. The brown solid formed when boric acid is reduced by heating K may contain a compound of B and K.

Potassium, borofluoride of; *v.* vol. i. p. 526.

Potassium, boronitride of. By very strongly heating a mixture of 7 parts B_2O_3 with 20 parts KCN, Balmain (*J. pr.* 27, 422) obtained a white, infusible solid; insol. water or KOHAq; decomposed by boiling *aqua regia*, leaving BN (vol. i. p. 527); heated in steam gave off NH_3, and left KOH and boric acid.

Potassium, bromide of, KBr. Formula probably molecular, from analogy of KI. Melts at 699° (Carnelley, *C. J.* 33, 279). S.G. 2·695 to 2·72 at 4° (Schröder, *P.* 106, 226); 2·712 at 12·7° (Clarke's *Tables of Spec. Gravities*, 2nd ed., 31); 2·199 *fused* (Quincke, *P.* 138, 141): *v.* also Spring (*B.* 16, 2724). S.H. (16° to 98°) ·11322 (Regnault, *A. Ch.* [3] 1, 129). Vol. at 40° = vol. at 0° (1 + ·00012602) (Fizeau, *C. R.* 64, 314). S. 53·48 at 0°, 64·6 at 20°, 74·62 at 40°, 84·74 at 60°, 93·46 at 80°, 102·04 at 100° (Kremers, *P.* 25, 119); Coppet (*A. Ch.* [5] 30, 411) gives S. 54·43 + ·5128*t* where *t* varies from −13·4° to 110°. Gerlach (*Fr.* 8, 285) calculated the following from Kremer's data:

S.G. KBrAq

5 p.c.	1·037	30 p.c.	1·256
10 „	1·075	35 „	1·309
15 „	1·116	40 „	1·366
20 „	1·159	45 „	1·430
25 „	1·207		

H.F. [K,Br] = 95,310; [K,Br,Aq] = 90,230 (*Th.* 3, 235). [KBr,O³] = 84,060 (*Th., l.c.*).

Formation.—1. K and Br combine with production of much heat (*v.* Balard, Merz, a. Weith, *B.* 6, 1518).—2. By treating BrAq with iron filings and ppg. with K_2CO_3.—3. By neutralising HBrAq by KOHAq or K_2CO_3Aq, and evaporating.—4. By decomposing $CaBr_2$Aq by K_2SO_4, filtering after 12 hours, adding K_2CO_3 as long as turbidity is produced, filtering, and evaporating (Klein, *A.* 128, 237).

Preparation.—A moderately conc. solution of KOH, free from K_2CO_3, is prepared from pure K_2CO_3 and pure CaO (*v.* Potassium hydroxide, p. 302); to this solution Br is added, little by little, till the liquid is slightly yellow; very finely-powdered charcoal, equal to about one-tenth of the quantity of Br used, is added, and the liquid is evaporated to dryness ($6KOHAq + 3Br_2 = 5KBrAq + KBrO_3Aq + 3H_2O$); the dry residue is well powdered, and heated to dull redness in a closed crucible for some time ($2KBrO_3 + 3C = 2KBr + 3CO_2$); the residue is extracted with warm water, the solution is filtered, and evaporated to the crystallising point.

Properties and Reactions.—KBr crystallises in very lustrous, white cubes, sometimes elongated to prisms or flattened to plates; it has a strongly saline taste. Easily sol. water, with considerable lowering of temperature; [KBr,Aq] = −5,080 (*Th.* 3, 235). *Chlorine* reacts with KBrAq to give KClAq and Br; Br is not set free by H_2SO_4 containing N_2O_3, nor by KNO_2Aq + dil. H_2SO_4Aq. KBr heated with *potassium chromate and sulphuric acid* gives off Br; KCl under similar conditions gives CrO_2Cl_2. *Conc. sulphuric acid* produces HBr, Br, and SO_2; the amount of HBr (the primary product of the reaction) thus decomposed varies very nearly in proportion to the quantity of H_2SO_4 used; if the H_2SO_4 is in such large excess that the water formed in the reaction causes no sensible dilution, only SO_2 and Br are produced; by using dil. H_2SO_4Aq (c. 30 p.c.) a mere trace of Br is obtained, the products being almost wholly $KHSO_4Aq$ and HBrAq (*v.* Addyman, *C. J.* 61, 94). *Hypochlorous acid* solution produces KClAq and $KBrO_3Aq$, with evolution of Br and Cl. *Potassium permanganate* solution has no action even when boiled; but Br is set free if a little H_2SO_4 is added, even without warming, the decomposition being soon completed (Hempel, *A.* 107, 160). Fusion with *potassium chlorate* produces $KBrO_3$.

Combinations.—With many *bromides of less positive metals* to form double salts; some of these are best regarded as K salts of acids containing Br and a metal less positive than K, *e.g.* $AuBr_3.KBr$ is best looked on as $KAuBr_4$ (*v.* the various metallic bromides). Also with *iodine bromide*, to form KBr.IBr (Wells a. Wheeler, *Am. S.* [3] 43, 475). Also with some *metallic chlorides*; thus $SbCl_3$ forms $SbCl_3.3KBr$ identical with $SbBr_3.3KCl$, and therefore to be regarded as $SbK_3Cl_3Br_3$ (Atkinson, *C. J.* 43, 290). Feit (*J. pr.* [2] 39, 378) describes $MgBr_2.KBr.6aq$, analogous to *carnallite* ($MgCl_2.KCl.6aq$). Schiff (*A.* 228, 72) describes a compound with *arsenious oxide* $KBr.As_4O_6$.

Potassium tribromide KBr_3. According to Berthelot (*A. Ch.* [5] 21, 370), orange crystals of this composition are formed by adding Br to KBrAq; no analyses are given. The substance decomposes rapidly. B. gives [KBr,Br²] = 2940.

Potassium, carbonyl compound of. (*Carbonic oxide potassium.*) The black solid formed in the preparation of K was thought by Berzelius (*P.* 4, 31) to be a carbide; Liebig (*A.* 11, 182) found that the same compound was formed by passing CO over K heated just to melting; Brodie (*C. J.* 12, 269) confirmed Liebig's result, and determined that one molecule CO is absorbed for each atom K; hence the empirical formula is probably KCO. This substance is extremely explosive; many serious accidents have occurred with it. If the CO used is quite dry, and the substance is washed rapidly in alcohol as soon as it is prepared, the residue is not nearly so explosive (Nietzki a. Benckiser, *B.* 18, 1833, where details of the method of preparation are given); probably the alcohol dissolves out unchanged K. *Potassium carbonyl* is a greyish solid; on standing in air it becomes yellowish and very explosive; it dissolves in water, with evolution of much gas (according to E. Davy [*A.* 23, 144] this gas contains C_2H_2), and generally with combustion or explosion; heated to redness it is resolved into K and CO. By exposure to moist air, or by other processes of oxidation, a series of organic compounds is obtained (*v.* Croconic acid, vol. ii. p. 275; Hexa-oxy-benzene, vol. iii. p. 678; Tetra-oxy-quinone, vol. iii. p. 771; Rhodizonic acid, this vol.).

Potassium, chloride of, KCl. Formula probably molecular, from analogy of KI. Melts at 734° (Carnelley, *C. J.* 33, 279). S.G. 1·9775 at 4° (Playfair a. Joule, *C. S. Mem.* 2, 401); 1·9453 at 15° (Stolba, *J. pr.* 97, 503); 1·612 at M.P. (Braun, *C. J.* [2] 13, 31); 1·87 *fused* (Quincke, *P.* 135, 642); *v.* also Spring (*B.* 16, 2721). S.H. 14° to 99° ·17295 (Regnault, *A. Ch.* [3] 1, 129; *v.* also Kopp, *T.* 155 [1] 71). Vol. at 40° = vol. at 0° (1 + ·00011408) (Fizeau, *C. R.* 64, 314). S. 32 at 10°, 33·4 at 15°, 34·7 at 20°, 37·4 at 30°, 40·1 at 40°, 42·8 at 50°, 45·5 at 60°, 48·3 at 70°, 51 at 80°, 53·8 at 90°, 56·6 at 100° (Mulder, *Scheikund. Verh.* 1864. 39); Coppet (*A. Ch.* [5] 30, 411) gives S. 28·51 + ·2837t°, where t° varies from −11° to 109°. S. at 0° in alcohol is given in following table (Gerardin, *A. Ch.* [4] 5, 139); where S.G. of alcohol is at 0°, and S + t° is solubility at t° (*cf.* Schiff, *A.* 126, 167):

Alcohol S.G.	S.	t°	Alcohol S.G.	S.	t°
·9904	23·2	·27	·9573	7·1	·162
·9848	19·4	·255	·9390	4·2	·125
·9793	15·7	·233	·8767	1·89	·061
·9726	11·9	·205			

Gerlach (*Fr.* 8, 281) gives the following data:

S.G. KClAq

1	per	cent.	1·0065	20	per	cent.	1·1861
5	„	„	1·0325	24	„	„	1·1657
10	„	„	1·0658	24·9	„	„	1·1723
15	„	„	1·1004				

H.F. [K,Cl] = 105,610; [K,Cl,Aq] 101,170 (*Th.* 3, 285). 30 parts KCl dissolved in 100 parts water at 13·2° lower the temperature to ·6°, *i.e.* through 12·6° (Rüdorff, *B.* 2, 68). Solution of 1 g. KCl in 100 g. water freezes at −·446°; saturated solution freezes at −10·9° (Rüdorff, *P.* 114, 63; 122, 337). Saturated solution boils at 108°.

Occurrence.—In small quantities in sea-water, and in some mineral springs. As chloride in *sylvine*; as double chloride, especially as *carnallite* KCl.$MgCl_2$.6aq. In crude pearl ash, in plant ash, and in kelp.

Formation.—1. By the direct union of the elements; K burns in Cl at the ordinary temperature.—2. By heating K in HCl gas.—3. By passing Cl over KOH or KI heated to redness.—4. By the action of HClAq on KOH or K_2CO_3.—5. By decomposing various metallic chlorides by fusion with K.

Preparation.—1. Commercial KCl is prepared chiefly from *carnallite*. The mineral is dissolved in warm water, heated by steam to c. 120°, and allowed to cool; at 60°–70°, $MgSO_4$.aq, $CaSO_4$, and NaCl separate, and on further cooling c. 70 p.c. of the KCl is obtained; the crystals of KCl are washed with a little cold water, to remove NaCl and $MgCl_2$, and a product containing c. 95 p.c. KCl is thus obtained (for details *v.* Dictionary of Applied Chemistry).—2. Pure KCl is prepared by neutralising pure HClAq by pure KOH or K_2CO_3, evaporating to the crystallising point, and recrystallising from water.

Properties.—White salt, crystallising in cubes. Saline taste. Unchanged in air. Decrepitates when heated; melts at c. 740°, and volatilises at a higher temperature. Fairly sol. water or aqueous alcohol; insol. absolute alcohol, or conc. HClAq; sol. in 20 p.c. $KC_2H_3O_2$Aq.

Reactions.—1. With *acids*, KCl generally gives K salt of the acid used and HCl.—2. Said to combine with *sulphuric anhydride*, and *chromic anhydride*, probably forming SO_2.Cl.OK and CrO_2.Cl.OK respectively (H. Rose, *P.* 38, 117).—3. Fused with *potassium*, in H, a blue substance is formed, supposed by H. Rose to be a subchloride (*P.* 120, 15). What is probably the same substance is formed during *electrolysis* of molten KCl (Bunsen a. Kirchoff, *P.* 113, 344). 4. For action of *water and oxygen*, in presence and absence of acids, *v.* Schulze, *J. pr.* [2] 21, 407.

Combinations. — 1. With *sulphuric* and *chromic anhydrides*, *v. Reactions*, No. 2.—2. With most *metallic chlorides*; some of the compounds are best regarded as K salts of metal-containing acids, *e.g.* $KAuCl_4$ (*v.* the different *metallic chlorides*). — 3. With *iodine trichloride*, to form KCl.ICl_3; prepared by mixing KClAq and ICl_3Aq, by passing Cl into warm KIAq containing HCl, or by dissolving 1 part KIO_3 in 8 parts HClAq of S.G. 1·176, at 40°–50°. Forms lustrous yellow prisms, smelling of Cl; on heating gives Cl, KCl, and ICl; with water forms KIO_3; ether dissolves out ICl_3 (Filhol, *J. Ph.* 25, 435, 506).—4. With *iodine monochloride*, to form KCl.ICl (Wells a. Wheeler, *Am. S.* [3] 43, 475).

Potassium, cyanide of; *v.* vol. ii. p. 346.

Potassium, chromicyanide of; chromisulphocyanide of; and chromocyanide of; *v.* vol. ii. p. 330.

Potassium, cobalti- and cobalto-cyanide of; *v.* vol. ii. p. 330.

Potassium, ferrate and ferrite of; *v.* vol. ii. p. 547.

Potassium, ferri- and ferro-cyanide of; *v.* vol. ii. pp. 339, 336.

Potassium, fluorides of. Two fluorides are known, KF, and KHF_2 or KF.HF.

Potassium fluoride KF. Formula probably molecular, from analogy of KI. Prepared by neutralising HFAq by K_2CO_3 in a dish of Ag or Pt, evaporating to dryness, and heating till HF ceases to be given off. According to Berzelius (*P.* 2, 218), KF is obtained in crystals by slowly evaporating an aqueous solution at 35°–40° in a very shallow dish. Deliquescent; fusible; solution has alkaline reaction to litmus, and etches glass. Guntz (*A. Ch.* [6] 3, 5) says KFAq is neutral, but the salt is decomposed in solution and becomes alkaline. Evaporation of a very conc. solution gives KF.$2H_2O$, according to H. Rose. S.G. 2·454 (Bödeker); 2·096 at 21·5° (Clarke, *Am. S.* [3] 13, 291). Combines with HF to form KF.HF (*v. infra*); with BF_3 to form KBF_4 (*v.* Potassium borofluoride, vol. i. p. 526); with SiF_4 to form K_2SiF_6 (*v.* p. 305); with B_2O_3 to form 2KF.B_2O_3, obtained by dissolving B_2O_3 in molten KF (Schiff, *A.* 228, 72); with TeF_4 to form KF.TeF_4, by evaporating TeO_3 in HFAq with addition of K_2CO_3 (Högborn, *Bl.* [2] 35, 60); and with many metallic fluorides.

Potassium-hydrogen fluoride KHF_2 or KF.HF. Prepared by dividing a quantity of HFAq into two equal parts, neutralising one, adding the other, and evaporating; also by evaporating KF in acetic acid. White cubes or four-sided tables; e. sol. water, almost insol. dil. HFAq. When heated gives HF, leaving KF. By electrolysis of HF containing KHF_2, F is obtained (*v.* Fluorine, vol. ii. p. 561). Moissan (*C. R.* 106, 547) says that two other compounds of KF and HF are obtained by dissolving dry KF in liquid HF, and cooling; to these compounds he gives the formulæ KF.2HF and KF.3HF. Guntz (*A. Ch.* [6] 3, 5) gives [HF,KF] = 21,100.

Potassium, haloid compounds of. The compounds KF, KCl, KBr, and KI are the chief halides of K; as KI has been gasified and the molecular weight corresponds with the simplest formula, it is probable that KX expresses the molecular composition of these halides. KI_3 also exists, but is decomposed by heat; and there are indications of the existence of KBr_3. KF combines with HF to form KHF_2, and, according to Moissan, also KF.2HF and KF.3HF.

Potassium, hydride of, K_2H. The absorption of H by heated K was observed by Gay-Lussac a. Thénard (*A. Ch.* 74, 203), and was confirmed by Jacquelain. Troost a. Hautefeuille (*A. Ch.* [5] 2, 273) found that the absorption of H by K begins at c. 200° and becomes rapid at 350°–400°; if the action continues for some time 126 vols. H are absorbed by 1 vol. K. The product is brittle, and much resembles Ag amalgam; it is fusible without change in H or *in vacuo*; takes fire in contact with air; heated *in vacuo*, dissociation begins at 200° (for vapour-pressures of H given off, *v.* Dissociation, vol. ii. p. 398). The formula K_2H requires 124·6 vols H to 1 vol. K.

Potassium, hydrosulphide of, KHS (*Potassium sulphydrate*). Gay-Lussac a. Thénard (*A. Ch.* 115, 165) obtained this compound by heating K in dry H_2S gas; it is more readily formed by heating K_2CO_3 to redness in H_2S (H_2O and CO_2 are given off) (Berzelius, *P.* 6, 438). By saturating KOHAq with H_2S, and evaporating the conc. solution over CaO or $CaCl_2$ *in vacuo*, Schöne (*P.* 131, 380) obtained lustrous, rhombohedral crystals of $2KHS.H_2O$; and by dehydrating this in a stream of dry H_2S, Sabatier (*A. Ch.* [5] 22, 5) obtained KHS as a yellow, amorphous solid. Prepared in the dry way, KHS appears reddish-black when molten, and white when cold; it crystallises in prisms; is very deliquescent, and reacts strongly alkaline; easily sol. in alcohol. Thomsen (*Th.* 3, 235) gives [K,S,H,Aq] = 65,140. KHSAq gives off H_2S at 70°, according to Drechsel (*J. pr.* [2] 4, 20). When a current of an inert gas is passed through KHSAq, H_2S is given off, and K_2SAq remains (Gernez, *C. R.* 64, 606). Electrolysis produces H and KOH at the negative pole, and H_2S at the positive (Bunge, *B.* 3, 911). KHSAq dissolves S with evolution of H_2S; it ppts. MnS, or PbS, from a neutral solution of a Mn or Pb salt, at the same time giving off H_2S. These reactions distinguish KHSAq from K_2SAq; the latter does not give off H_2S while dissolving S or ppg. MnS or PbS. KHSAq dissolves several sulphides of the less positive metals, *e.g.* Sb, As, Sn, forming K thiosalts.

Potassium, hydroxide of, KOH (*Caustic potash. Potassium*, or *potassic, hydrate*). S.G. 2·1 (Dalton); 2·044 (Filhol, *A. Ch.* [3] 21, 415). H.F. [K,O,H] = 103,170; [K,O,H,Aq] = 116,460 (*Th.* 3, 235).

Formation.—1. By the reaction between K and H_2O, or K_2O and H_2O, followed by evaporation.—2. By boiling K_2CO_3Aq with CaO.—3. By adding powdered K_2SO_4 to warm conc. BaOAq, evaporating, filtering, and again evaporating (Schubert, *J. pr.* 26, 117).—4. By heating KNO_3 with 2-3 parts thin copper turnings, to redness, in an iron, or copper, crucible, extracting with water when cold, filtering from CuO and Cu_2O, and evaporating (Wöhler, *A.* 87, 373).—5. By heating 1 part KNO_3 with 1 part Fe_2O_3, in a closed crucible of Cu, H being passed in; treating with water, and drawing off the clear liquid, and evaporating it (Schulze, *Z.* 1861. 109). Evaporation of KOHAq should be performed in vessels of polished iron, or, better, of silver.

Preparation.—1. A solution of pure K_2CO_3 in 10-12 parts water is boiled, in a dish of silver or polished iron, with milk of lime, added little by little, till a portion of the clear supernatant liquid gives no effervescence with an acid; rather more than half as much CaO is required as the weight of K_2CO_3 taken; large excess of CaO should be avoided; water should be added as the boiling proceeds, because if the quantity of water is less than c. 10 times the quantity of K_2CO_3 used the KOHAq begins to decompose the $CaCO_3$ formed, and the change of K_2CO_3 to KOH stops (Liebig, *A.* 1, 124). When the change is completed, the vessel is closed, and, after a few hours, the clear liquid is drawn off by a syphon; the liquid is then rapidly evaporated in an iron vessel, allowed to stand for an hour or two, the vessel being closed, syphoned off from any pp. that has formed, evaporated in a silver dish till the oily liquid thus produced begins to volatilise in white clouds, and cooled in an exsiccator. Impure KOH may be freed from all impurities, except KCl and traces of K_2CO_3 and $KC_2H_3O_2$, by dissolving in absolute alcohol, allowing to settle, draining off, and evaporating, at first on a water-bath, in a silver dish; the resinous matter which is produced is removed from the warm evaporated semi-solid mass, by a silver spatula, and the KOH is then poured out on to a plate of polished iron, or, better, of silver.

Graeger (*J. pr.* 96, 188) recommends to heat the K_2CO_3Aq used with Ag_2CO_3, to filter from AgCl and excess of Ag_2CO_3, to boil, in a silver dish, with pure CaO made by strongly heating pure $CaCO_3$, to filter the solution of KOH through pounded marble which has been washed with water till free from very fine particles, and to evaporate in a silver dish.—2. Water and benzene are placed in a silver dish, and small pieces of K, cut from the inside of a lump, are thrown in one by one; the K remains near the surface of separation of the two liquids, and reacts fairly slowly with the water. The benzene is removed by warming, and the aqueous solution of KOH is then evaporated to dryness.

Properties.—After fusion, KOH is a white, hard, brittle solid, often showing a fibrous texture. Melts below red heat, and volatilises at full redness in white pungent vapour. Very deliquescent; sol. water with production of much heat, [KOH,Aq] = 13,290 (*Th.* 3, 235). Easily sol. alcohol. Skey (*C. N.* 36, 48) says KOH is very sl. sol. ether. Absorbs CO_2 rapidly from the air, forming $KHCO_3$. KOH has a slight, but nauseous, odour, a strongly acrid taste, and acts as a powerful cautery towards both animal and vegetable matter. KOHAq should be kept in glass vessels free from Pb, as it corrodes lead-glass; it attacks vessels of glass or porcelain when heated in them. To keep KOHAq free from carbonate, it is advisable to store it in bottles fitted with corks carrying a syphon-tube, and a rather wide tube filled with a mixture c. equal parts CaO and Na_2SO_4, well rubbed together, dried over a flame, and passed through a sieve to remove fine powder; the air which enters through this mixture is quite free from CO_2.

KOHAq is strongly alkaline; the affinity of KOH in solution is large, about equal to that of NaOH and LiOH, and about 50 times greater than NH_3Aq (Ostwald). KOH saponifies ethereal salts, and ppts. most of the heavier metals as oxides or hydroxides from solutions of their salts.

The table on next page, given by Lunge, shows the composition of KOHAq of different S.G.

Expansion occurs when conc. KOHAq is diluted; Frankenheim (*J.* 1847-8. 69) gives $V = 1 + \cdot000415t + \cdot000000577t^2$ as representing the volume of KOHAq S.G. 1·2738 at 0°, between 13° and 100°.

Reactions.—1. According to Deville (*C. R.* 45, 857), KOH is decomposed to K, O, and H by *heating to white heat.*—2. Strongly heated with *non-volatile acidic anhydrides*, water and potass[illegible] salts are formed.—3. Heated with *potassium*, K_2O and H are formed; heated with *sodium* under a liquid free from O, an alloy of K and Na

S.G. KOHAq	Baumé	Twaddell	100 pts. by weight contain		1 cub. metre contains Kilos	
			K_2O	KOH	K_2O	KOH
1·007	1	1·4	0·7	0·9	7	9
1·014	2	2·8	1·4	1·7	14	17
1·022	3	4·4	2·2	2·6	22	26
1·029	4	5·8	2·9	3·5	30	36
1·037	5	7·4	3·8	4·5	39	46
1·045	6	9·0	4·7	5·6	49	58
1·052	7	10·4	5·4	6·4	57	67
1·060	8	12·0	6·2	7·4	66	78
1·067	9	13·4	6·9	8·2	74	88
1·075	10	15·0	7·7	9·2	83	99
1·083	11	16·6	8·5	10·1	29	109
1·091	12	18·2	9·2	10·9	100	119
1·100	13	20·0	10·1	12·0	111	132
1·108	14	21·6	10·8	12·9	119	143
1·116	15	23·2	11·6	13·8	129	153
1·125	16	25·0	12·4	14·8	140	167
1·134	17	26·8	13·2	15·7	150	178
1·142	18	28·4	13·9	16·5	159	188
1·152	19	30·4	14·8	17·6	170	203
1·162	20	32·4	15·6	18·6	181	216
1·171	21	34·2	16·4	19·5	192	228
1·180	22	36·0	17·2	20·5	203	242
1·190	23	38·0	18·0	21·4	214	255
1·200	24	40·0	18·8	22·4	226	269
1·210	25	42·0	19·6	23·3	237	282
1·220	26	44·0	20·3	24·2	248	295
1·231	27	46·2	21·1	25·1	260	309
1·241	28	48·2	21·9	26·1	272	324
1·252	29	50·4	22·7	27·0	284	338
1·263	30	52·6	23·5	28·0	297	353
1·274	31	54·8	24·2	28·9	308	368
1·285	32	57·0	25·0	29·8	321	385
1·297	33	59·4	25·8	30·7	335	398
1·308	34	61·6	26·7	41·8	349	416
1·320	35	64·0	27·5	32·7	363	432
1·332	36	66·4	28·3	33·7	377	449
1·345	37	69·0	29·3	34·9	394	469
1·357	38	71·4	30·2	35·9	410	487
1·370	39	74·0	31·0	36·9	425	506
1·383	40	76·6	31·8	37·8	440	522
1·397	41	79·4	32·7	38·9	457	543
1·410	42	82·0	33·5	39·9	472	563
1·424	43	84·8	34·4	40·9	490	582
1·438	44	87·6	35·4	42·1	509	605
1·453	45	90·6	36·5	43·4	530	631
1·468	46	93·6	37·5	44·6	549	655
1·483	47	96·6	38·5	45·8	571	679
1·498	48	99·6	39·6	47·1	593	706
1·514	49	102·8	40·6	48·3	615	731
1·530	50	106·0	41·5	49·4	635	756
1·546	51	109·2	42·5	50·6	655	779
1·563	52	112·6	43·6	51·9	681	811
1·580	53	116·0	44·7	53·2	706	840
1·597	54	119·4	45·8	54·5	731	870
1·615	55	123·0	47·0	55·9	759	905
1·634	56	126·8	48·3	57·5	789	940

is said to be formed (Williams, *Rép. Chim. pure*, 3, 177).—4. *Iron* decomposes KOH at white heat, forming Fe_2O_3, H, and K.—5. *Molten KOH acts generally as an oxidiser : e.g.* Fe, As, Sb, Pt, &c. form ferrate, arsenate, antimonate, and platinate of K; Cr_2O_3 forms K_2CrO_4, &c. Salts are generally decomposed by molten KOH, giving K salts, and setting free the bases.—6. KOHAq neutralises *acids*, forming salts.—7. KOHAq decomposes most *metallic salts in solution*, ppg. oxides or hydroxides of the metals.—8. According to Schöne (*A.* 193, 241), addition of *hydrogen peroxide* to KOHAq produces K_2O_4 (*v.* POTASSIUM TETROXIDE, p. 305).

Combinations.—1. With *carbon dioxide*, to form $KHCO_3$.—2. With *water*, to form hydrates. Pickering (*C. J.* 63, 890) obtained $KOH.H_2O$ freezing at 143°, $KOH.2H_2O$ freezing at 35·5°, and $KOH.4H_2O$ freezing −32·7° (*cf.* Walter, *P.* 39, 192; Schöne, *P.* 131, 147). P. (*l.c.*) gives full data for freezing points of KOHAq. Göttig (*B.* 20, 1094) described two hydrates, $2KOH.9H_2O$ and $2KOH.5H_2O$, obtained from an alcoholic solution of KOH containing some water; but in a later paper (*B.* 20, 1907) G. says that these hydrates contained alcohol besides water. 3. With *methyl alcohol*, to form 3KOH.5MeOH (Göttig, *B.* 20, 1832). 4. With *ethylic alcohol*, to form KOH.2EtOH (Engel, *C. R.* 103, 155); decomposed by heating to EtOK, EtOH, and H_2O.

Potassium, iodides of. Two iodides are known, KI and KI_3.

POTASSIUM IODIDE, KI. Mol. w. 165·57. Melts at 634° (Carnelley, *C. J.* 33, 279). S.G. 3·059 (Playfair a. Joule, *C. S. Mem.* 2, 401); 3·077 to 3·081 (Schröder, *P.* 106, 226); *fused* 2·497 (Quincke, *P.* 138, 141); *v.* also Spring (*B.* 16, 2724). V.D. 91·5 (Dewar a. Scott, *Pr.* 29, 206); 84·6 at above 1300°, in N (Mensching a. Meyer, *Z. P. C.* 1, 157). S.H. (20° to 99°) ·08191 (Regnault, *A. Ch.* [3] 1, 129). Vol. at 40° = vol. at 0° (1 + ·00012796) (Fizeau, *C. R.* 64, 314). S. 132·1 at 5°, 136·1 at 10°, 140·2 at 15°, 144·2 at 20°, 152·3 at 30°, 160 at 40°, 168 at 50°, 176 at 60°, 184 at 70°, 192 at 80°, 201 at 90°, 209 at 100°, 218 at 110° (Mulder, *Scheikund. Verhandel*, Rotterdam, 1864. 162). Coppet (*A. Ch.* [5] 30, 411) gives S. at $t° = 126·23 + ·8088t$, where t varies from −5·9° to 120°. S. in aqueous alcohol is given in following table (Gerardin, *A. Ch.* [4] 5, 139); the values hold for 0° to 18°:

S.G. alcohol	S.	S.G. alcohol	S.
·9904	130·5	·9528	76·9
·9851	119·4	·9390	66·4
·9726	100·1	·9088	48·2
·9665	89·9	·8464	11·4
		·8322	6·2

H.F. [K,I] = 80,130; [K,I,Aq] = 75,020 (*Th.* 3, 235).

Formation.—1. By the direct union of K and I.—2. By neutralising HIAq by K_2CO_3, and evaporating.—3. I is added to water and iron filings till the iron is almost wholly dissolved, the solution is filtered, and K_2CO_3 added so long as $FeCO_3$ ppts.; the liquid is filtered (if alkaline it is neutralised by HIAq) and evaporated, any Fe_2O_3 which separates being filtered off (Baup, *J. Ph.* 9, 37, 122).—4. By adding I to KOHAq, evaporating, heating with C, dissolving, filtering, and evaporating (*v. Preparation*).—5. BaI_2Aq is formed by the action of I and water on BaS, and is decomposed by K_2SO_4; $BaSO_4$ is filtered off, and the liquid is evaporated. Liebig (*A.* 121, 222) used CaI_2 in place of BaI_2 (*cf.* Pettenkofer, *A.* 121, 225).

Preparation.—Moderately, but not too, conc. KOHAq, quite free from K_2CO_3, is prepared from K_2CO_3Aq and CaO (*v.* Potassium hydroxide, *Preparation*, p. 302); I is added, little by little, to the slightly warm liquid till a slight yellow colour is produced; very finely powdered charcoal is now added, equal to c. $\frac{1}{10}$ of the weight of I used, the liquid is evaporated quite to dryness, the residue is powdered, and heated, in a closed crucible, to dull redness for some time ($6KOHAq + 6I = 5KIAq + KIO_3Aq + 3H_2O$; $KIO_3 + 3C = KI + 3CO$). The contents of the crucible, when cold, are extracted with water, the liquid is filtered, neutralised by HIAq if alkaline, and crystallised. Morse a. Burton (*Am.* 10, 321) recommend to remove traces of KIO_3 by boiling for some time with Zn amalgam and water, filtering, and crystallising; neither Zn nor Hg is found in the filtrate. The Zn amalgam is made by agitating zinc-dust with Hg in presence of tartaric acid solution, and washing with water.

Properties.—White cubes; non-deliquescent. Has a sharp taste. Solution in water is attended with fall of temperature; 140 pts. in 100 pts. water at 10·8° produce a fall to −11·7° (Rüdorff, *P.* 136, 276).

Reactions.—1. Unchanged in dry air, but decomposed in *ordinary air when exposed to sunlight* (*v.* Downes a. Blunt, *Pr.* 29, 319; Loew, *Fr.* 1870. 251). Air containing ozone also decomposes KI (Houzeau, *J.* 1858. 60).—2. *Heated in air* to 230°, some KIO_3 is formed.—3. *Heated in steam*, I is evolved (Petterson, *Fr.* 1870. 362) and HIAq formed (Schindler, *Mag. Pharm.* 31, 33).—4. Decomposed, with separation of I, and formation of KOH, by heating with *lead dioxide, manganese dioxide, arsenic oxide, antimonic oxide, chromium trioxide, hydrogen peroxide*, &c. (*v.* Weltzien, *A.* 138, 134).—5. *Chlorine* decomposes hot KI to KCl and I. KIAq with ClAq gives KClAq, and I; with excess of Cl, ICl_3 is formed and remains in solution, or combines with the KCl and separates as $KCl.ICl_3$, according to the quantity of water present. *Bromine* acts similarly to Cl.—6. *Nitrous acid solution* sets I free; KNO_2 and dil. HClAq act in the same way (*v.* Price, *C. J.* 4, 155).—7. *Conc. sulphuric acid*, or *nitric acid*, decomposes KI when heated with it, giving sulphate or nitrate of K, and I; with H_2SO_4, SO_2 and H_2S are also formed. Addition of conc. H_2SO_4 to KIAq, or evaporation with HNO_3Aq, sets I free. If KIAq contains KIO_3 a few drops of a dilute acid suffice to give free I ($5HIAq + HIO_3Aq = 3I_2 + 3H_2O$). *Aqua regia* sets I free from KIAq (for the delicacy of this reaction *v.* Harting, *J. pr.* 22, 46).—8. Heated with *sulphuric anhydride*, K_2SO_4, SO_2, and I are formed (H. Rose, 38, 121).—9. *Manganese dioxide and sulphuric acid* produce I, $MnSO_4$, and K_2SO_4 when heated with KI.—10. KI fused with *potassium-hydrogen sulphate* gives K_2SO_4 and I.—11. Fusion with *potassium chlorate* produces KIO_3.—12. Heating with *barium nitrate* forms KIO_3 and BaO_2 (Henry, *J. Ph.* 18, 345).—13. By heating with *ammonium chloride*, I, AmI, and KCl are formed.—14. *Conc. potassium ferricyanide solution* gives I and K_4FeCy_6Aq; on dilution the action is reversed (Mohr, *A.* 105, 57).—15. Heated with *potassium borate*, KIO_3 and a polyborate (? probably $K_2B_8O_{13}$) are formed (Schiff, *A.* 228, 72).

Combinations.—1. With most *iodides of less positive metals* (*v.* various *metallic iodides*). Several of the compounds produced are best regarded as K salts of metal-containing acids (*v.* Remsen, *Am.* 11, No. 5).—2. With *arsenious oxide* to form $KI.As_4O_6$ (Schiff, *A.* 228, 72).—3. With *potassium ferricyanide*, to form a very unstable compound, $KI.K_3FeCy_6$ (Preuss, *A.* 29, 323; Mohr, *A.* 105, 57; Blomstrand, *J. pr.* [2] 3, 207; Kern, *C. N.* 33, 184).

Potassium tri-iodide KI_3. Dark-blue, lustrous needles; almost black by reflected light; melts at 45°; S.G. 3·498 at c. 15°; by saturating KIAq with I, and evaporating over H_2SO_4 (Johnson, *C. J.* 31, 249). Very deliquescent; in a little water some I is deposited; sol. alcohol, in a very small quantity water, and in saturated solution of I in KIAq. Agitation with CS_2 of conc. KIAq saturated with I abstracts the dissolved I (Baudrimont, *C. R.* 51, 827). Jörgensen (*J. pr.* [2] 2, 347) found, however, that CS_2 did not remove the I from an alcoholic solution of KI containing excess of I in ratio KI:2I, and that alcoholic KI completely decolourised solutions of I in CS_2.

Potassium di-iodide ?KI_2. A solution of 3 pts. I in 4 pts. KI in water is said by Guyard (*Bl.* [2] 31, 297) to contain an unstable compound of this composition; with $Pb(NO_3)_2Aq$ or $Pb(C_2H_3O_2)_2Aq$, this solution gives an almost black pp., said by G. to be PbI_4.

Potassium, iodobromide of. The compound KBr.IBr may be called iodobromide of potassium; *v.* Potassium bromide, *Combinations*, p. 300.

Potassium, iodochlorides of. The compounds $KCl.ICl_3$ and KCl.ICl may be called iodochlorides of potassium; *v.* Potassium chloride, *Combinations* Nos. 3 and 4, p. 301.

Potassium, iridicyanide of; *v.* vol. ii. p. 332.

Potassium mangani- and mangano-cyanide of; *v.* vol. ii. p. 342.

Potassium, nitride of, K_3N. Formed by heating to redness KNH_2 (*v.* Potassium amide, p. 299) in absence of O. A dark-grey, almost black, solid. Sublimes partially at white heat. Takes fire in air, with evolution of N; reacts with water to give KOHAq and NH_3. K_3N is a conductor of electricity. Combines with S and P (Gay-Lussac a. Thénard, *A. Ch.* 65, 325).

Potassium, nitroprusside of; *v.* vol. ii. p. 341.

Potassium, osmocyanide of; *v.* vol. ii. p. 343.

Potassium, oxides of. Two oxides have been certainly isolated, K_2O and K_2O_4; there are indications of the existence of others.

Potassium oxide K_2O (*Potassium monoxide*). A mixture of K_2O and K_2O_4 is formed by burning K in air; when K is burnt in a stream of dry O only K_2O_4 is produced, but on strongly heating this product O is given off, and K_2O remains (Davy, *T.* 1808 [1] 5). K_2O is also formed by heating KOH and K in the ratio KOH : K; according to Beketoff (*Bl.* [2] 37, 491), K and KOH do not react. B. says that K_2O may be prepared by heating a mixture of K_2O_4 and K in a silver dish. To prepare pure K_2O Kühnemann (*C. C.* 1864. 491) recommends to lead air, freed from CO_2, over K heated just to fusion; the K spreads out into a thin layer which burns to K_2O. K_2O is a greyish, non-lustrous solid; S.G. 2·656 (Karsten, *S.* 65, 394); melts at full red-heat, and volatilises at a very high temperature. Thomsen (*Th.* 3, 235) gives $[K^2,O,Aq] = 165,460$. K_2O reacts with water to form KOHAq, with production of much heat. Von Schaffgotsch (*A.* 43, 17) says that $K_2O.Fe_2O_3$ is obtained, but not pure, by heating Fe_2O_3 with K_2CO_3.

POTASSIUM TETROXIDE K_2O_4 (*Potassium peroxide*). The formation of this compound by heating K in dry air or O was observed by Gay-Lussac a. Thénard (*A. Ch.* 65, 325). The preparation and properties of the compound were examined by Vernon Harcourt (*C. J.* 14, 267). Prepared by heating K till it melts, in a hard glass flask filled with N, then sending in a slow stream of dry air, and continuing to heat in the air-stream until the metal is completely changed to a yellowish amorphous solid, and heating this for some time in dry O. It is also formed by throwing small pieces of K into molten KNO_3 (Bolton, *C. N.* 52, 289). A mixture of K_2O_4 with $KOH.H_2O$ is said to be formed by mixing equivalents of KOH and H_2O_2 in Aq, and evaporating *in vacuo* (Schöne, *A.* 193, 241). K_2O_4 is an amorphous powder, having the colour of $PbCrO_4$. It begins to soften at 280°, and melts at red heat to a black liquid, which crystallises in leaflets on cooling. At white heat gives off O and leaves K_2O. Deliquesces in moist air, giving off O. In water forms KOHAq and H_2O_2Aq, and evolves O. Heated in H produces KOH and H_2O. K_2O_4 oxidises P, S, C, &c., and many metals to their highest oxides. Reacts with CO, when heated, giving K_2CO_3 and O. No action with N_2O; with NO forms KNO_2 and KNO_3, and gives off N oxides.

OXIDES OF POTASSIUM OTHER THAN K_2O AND K_2O_4. Harcourt (*l.c.*) asserted the existence of K_2O_2, obtained by oxidation of K. Lupton (*C. J.* 1876. [2] 565) thought that the oxides K_8O_5, K_4O_3, and K_6O_4 are formed by the action of air on K at c. 65°; these oxides may be regarded, according to L., as $3K_2O.K_2O_2$, $K_2O.K_2O_2$, and $2K_2O.K_2O_2$ respectively. The substance described as a sub-oxide, K_4O, is said by L. to be a mixture of K and K_2O. Schöne (*A.* 193, 241) obtained $K_2H_4O_6$, probably $K_2O_2.2H_2O_2$, by evaporating, *in vacuo*, at −10°, a mixture of 1 equiv. KOH and 2 equivs. H_2O_2 in Aq.

Potassium, phosphide of. K and P combine when heated under rock-oil, or in N, forming a dark-yellow solid (Magnus, *P.* 17, 517; Vigier, *A.* 122, 331). A compound, or compounds, of K and P seems also to be formed when K is heated in PH_3, and also when K is heated in P in a stream of H (H. Rose, *P.* 12, 547). The compound prepared by Rose was a crystalline, reddish, lustrous solid; decomposed by water, giving KH_2PO_2Aq and PH_3, and burning, when heated in air, to K phosphate.

Potassium, platinocyanide of, *and allied salts*; *v.* vol. ii. pp. 344–5.

Potassium, salts of. *Compounds formed by replacing H of acids by K.* The chief salts of K, besides the halides and sulphides, are *carbonates, chlorate and perchlorate, chromate and derivatives, iodate and periodates, nitrate and nitrite, phosphates and derivatives, silicates, sulphates and derivatives, sulphite, thiosulphate* (*v.* CARBONATES, PHOSPHATES, &c.).

Potassium, selenides of. Berzelius (*Lehrbuch*, 5th ed. 2, 222) investigated the conditions of combination of K and Se, without isolating and analysing any definite compounds. Se and K combine when melted together; a steel-grey solid sublimes, which dissolves in water with formation of a red liquid that decomposes in air with separation of Se, and gives off H_2Se with acids. Compounds of Se and K are also formed by reducing K_2SeO_4 or K_2SeO_3 by C or H at red heat (Wöhler a. Dean, *A.* 97, 5; Rathke, *A.* 152, 211). Mixtures of selenate and selenides of K are formed by fusing KOH or K_2CO_3 with Se. Boiling KOHAq dissolves Se, forming a brown liquid, from which a brown powder separates on evaporation, and which gives Se when heated with acids, or when diluted and allowed to stand in air.

Fabre (*C. R.* 102, 613) obtained $K_2Se.xH_2O$, $x = 9$, 14, and 19, by passing a rapid current of H_2Se into KOHAq of different concentrations; these *hydrates of potassium monoselenide* are all very easily decomposed. Fabre (*C. R.* 102, 703) gives the following thermal data: $[K^2,Se] = 98,340$ from solid elements; $[2KOHAq,H_2SeAq] = 7,520$; $[2KOHAq,H_2Se] = 16,920$; $[K^2Se,Aq] = 8,540$.

Potassium, selenocyanide of, *v.* vol. ii. p. 348.

Potassium, selenostannate of, K_2SnSe_3 3aq. Yellow, unstable crystals; by saturating K_2SeAq with $SnSe_2$ and evaporating *in vacuo* (Ditte, *C. R.* 95, 641).

Potassium, selenothiostannate of, K_2SnSe_2S 3aq. Yellow, octahedral crystals; by boiling K_2SAq with Sn and Se, and evaporating *in vacuo*. Sol. water, with red colour. Both solid and solution in water very readily undergo decomposition, with separation of Se (Ditte, *l.c.*).

Potassium, silicide of. By reducing SiO_2 by K, Berzelius obtained a brown solid, which reacted with water to give H, KOHAq, and SiO_2 (*Lehrbuch*, 5th ed. 2, 84).

Potassium, silicofluoride of, K_2SiF_6. Prepared by adding H_2SiF_6Aq to a fairly conc. solution of a K salt, washing, and drying. Small tesseral white crystals. Preis (*Listy Chem.* 13, 150; abstract in *C. J.* 58, 694) found hexagonal, and also regular, crystals of this salt, along with $CaSO_4$, in a basin wherein phosphoric acid had been prepared from *phosphorite*. K_2SiF_6 is isodimorphous with the ammonium salt. S.G. 2·665 at 17·5° (Stolba, *J. pr.* 97, 503). Easily sol. hot water, very sl. sol. cold water. Melts at low red heat, giving off SiF_4 and leaving KF (*v.* Bothe, *Hofman's Ber. über die Entwick. der Chem. Industrie*, 1, 318). Decomposed by conc. H_2SO_4, giving off SiF_4 and HF. Decomposed by boiling (not cold) solutions of alkali hydroxides or carbonates, with separation of gelatinous silicic acid and formation of KF.

Potassium, siliconitride of. The white, infusible solid, obtained by heating SiO_2 with KCN, is probably a compound of K, Si, and N (Balmain, *P. M.* October 1842).

Potassium, sulphides of. K and S combine when heated together, the K burning brilliantly. Five compounds of K and S are known: K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5. They are all sol. water, the polysulphides also in alcohol. K_2SAq is colourless; solutions of the others are coloured yellowish brown, the colour being deeper the greater the proportion of S. Solutions are decomposed by acids; K_2SAq with evolution of H_2S, the other solutions also with ppn. of S. Solutions decompose in air; K_2SAq to $K_2S_2O_3Aq$ and KOHAq, K_2S_2Aq to $K_2S_2O_3Aq$, and the others to $K_2S_2O_3Aq$ with separation of S. Solutions of the polysulphides react with K_2SO_3Aq to form K_2SAq and $K_2S_2O_3Aq$; these solutions are reduced to K_2SAq by shaking with Hg. With EtI or EtBr they form Et_2S_2, which dissolves the S set free; these solutions dialyse unchanged (Spring a. Demarteau, *Bl.* [3] 1, 311).

Potassium monosulphide K_2S. Formed by reducing dry K_2SO_4; by heating in H (Berzelius, *P.* 6, 438); by heating with C (Berthier, *A. Ch.* 22, 233; Bauer, *J. pr.* 75, 246; Wittstock, *P.* 55, 536). Not obtained free from polysulphides by these methods; if vessels of glass or porcelain are used the product contains SiO_2, as K_2S acts on silicates. The product of the foregoing reactions is a brown, crystalline, deliquescent solid; sol. in water, with production of much heat and formation of KSHAq and KOHAq; Thomsen (*Th.* 3, 235) gives $[K^2,S,Aq] = 113{,}300$. Sabatier (*A. Ch.* [5] 22, 5) says that K_2S has never been obtained pure. An aqueous solution of K_2S is prepared by saturating KOHAq with H_2S, and adding an equal quantity of the same KOHAq. By evaporating this solution *in vacuo* at a low temperature, the *pentahydrate* $K_2S.5H_2O$ is obtained in orthorhombic crystals, which lose $3H_2O$ by heating to 150°, out of air (Schöne, *P.* 131, 380; *cf.* Sabatier, *l.c.*). K_2SAq is colourless out of contact with air; it is very alkaline and caustic; in air it becomes yellow, H_2S is given off, and K_2CO_3Aq and $K_2S_2O_3Aq$ are formed. K_2SAq dissolves S, forming polysulphides; it dissolves Fe or Fe_2O_3, forming a green liquid.

Potassium disulphide K_2S_2. Formed by allowing an alcoholic solution of K_2S to stand in air till the surface is covered with a film of $K_2S_2O_2$, then pouring off, and evaporating *in vacuo* (Berzelius, *l.c.*). Also by heating 2 equivalents $KHSO_4$ with 7 or more equivalents C (Geiger). Berzelius obtained K_2S_2 by heating 4 equivalents K_2CO_3 with rather less than 7 equivalents S. A yellowish red, deliquescent solid; K_2S_2Aq is yellow; in air it oxidises to $K_2S_2O_3Aq$ without separation of S; acids give off H_2S and cause ppn. of S.

Potassium trisulphide K_2S_3. Formed by passing CS_2 over K_2CO_3 heated to redness (Berzelius, *l.c.*; *cf.* Schöne, *l.c.*). Also by heating 100 parts K_2CO_3 with 58·22 parts S to dull redness, till CO_2 ceases to be given off; the product contains some K_2SO_4. Also, with some S, by passing H_2S over strongly-heated K_2SO_4. By heating K_2S_4 to over 800°. A yellowish-brown solid, black when molten; not decomposed at 900°, gives off S at white heat (B.). Easily sol. water and alcohol; K_2S_3Aq in air gives $K_2S_2O_3Aq$ with separation of S; decomposed by acids, S separating and H_2S being evolved.

Potassium tetrasulphide K_2S_4. Formed by passing CS_2 over strongly-heated K_2SO_4 so long as CO_2 is produced. Also by melting K_2CO_3 with 1 to 2 parts S, heating till excess of S is removed, and then reducing K_2SO_4 formed by heating in H_2S. A red-brown, crystalline solid (B., *l.c.*; S., *l.c.*). Decomposed at 800°–900° to K_2S_3 and S. The *dihydrate* $K_2S_4.2H_2O$ is obtained by boiling K_2SAq with the proper quantity of S, and evaporating *in vacuo* (S., *l.c.*). Sabatier (*A. Ch.* [5] 22, 53) obtained the *octahydrate*, $K_2S_4.8H_2O$, by adding 90 p.c. alcohol to K_2S_4Aq, separating the brown oily liquid, and letting it crystallise.

Potassium pentasulphide K_2S_5. Formed by heating any of the lower sulphides with S until the excess is removed; Schöne (*l.c.*) says temperature should not exceed 600° (*v.* B., *l.c.*). A solution of K_2S_5, containing also $K_2S_2O_3$, is formed by heating K_2CO_3Aq with S (Fordos a. Gélis, *C. R.* 23, 211); or by digesting a solution of a lower sulphide with S (B., *l.c.*). A red, fusible solid; decomposed by heating in steam, giving K_2SO_4 and H_2S (Drechsel, *J. pr.* [2] 4, 20). Very sol. water, also in alcohol; K_2S_5Aq slowly decomposes in air, giving $K_2S_2O_3Aq$, K_2CO_3Aq, and S; acids evolve H_2S and separate S.

Liver of sulphur. This name is given to the brown solid obtained by heating S with K_2CO_3 in a closed vessel; it contains various sulphides of K, along with K_2SO_4, and generally some K_2CO_3.

Potassium, sulphydrate of; *v.* Potassium hydrosulphide, p. 302.

Potassium, sulphocyanide of; *v.* vol. ii. pp. 351–2.

Potassium, telluride of. Probably K_2Te. By heating together K and Te in H; also by heating a mixture of 100 pts. H_2TeO_3, 20 pts. KOH, and 10 pts. C. A brittle, crystalline, copper-coloured solid. Easily sol. water; exposed to air Te separates from the solution. HClAq evolves H_2Te (Davy; *v.* also Berzelius, *Lehrbuch* (5th ed.) 2, 247).

Potassium, tellurofluoride of, $KF.TeF_4$; *v.* Potassium fluoride, p. 301.

Potassium, thio-arsenates and thio-arsenites of; *v.* vol. i. pp. 317, 316.

Potassium, thiocarbonate of; *v.* vol. i. p. 703.

M. M. P. M.

PRASEODYMIUM. The constituent of didymium which yields green-coloured salts; *v.* Didymium, vol. ii. p. 383.

PREHNITENE *v.* *c*-Durene.

PREHNITIC ACID $C_{10}H_6O_8$ *i.e.* $C_6H_2(CO_2H)_4$[1:2:3:4]. Mol. w. 254. [237°–250°]. Formed by heating either of the tetrahydrides of pyromellitic acid with H_2SO_4 (Baeyer, *A.* 166, 325), and by the oxidation of *c*-durene and of *c*-tetra-ethyl-benzene (Töhl, *B.* 21, 907; Galle, *B.* 16, 1746; Jacobsen, *B.* 17, 2518). Crystallises from water in large prisms (containing 2aq) resembling the mineral prehnite. Converted by fusion into an anhydride $C_{10}H_4O_7$ [239°]. May be reduced to a viscid hydride.—KH_3A^{iv}aq.—$BaH_6A^{iv}_2$ 3aq.—BaH_2A^{iv} aq: needles.—Pb_2A^{iv}: small needles, insol. water.

Methyl ether Me_4A^{iv}. [104°–108°].

PREHNITOL *v.* *c*-Durenol.

PREHNOMALIC ACID $C_{10}H_8O_9$ *i.e.* $C_6H_3(OH)(CO_2H)_4$. *Oxy-prehnitic acid dihydride.* [210°]. A product of the action of H_2SO_4 on the tetrahydrides of mellitic acid (Baeyer, *A.* 166, 325; *B.* 4, 275). Needles, readily converted by heat into an anhydride $C_{20}H_{14}O_{17}$ [210°]. By heating with H_2SO_4, or by treatment with Br, it is converted into prehnitic acid.—Ag_4A^{iv}.

PRIMULA CAMPHOR $C_{11}H_{12}O_5$. [49°]. (above 200°). Contained in the root of *Primula* *veris* (Mutschler, *A.* 185, 222). Six-sided plates, v. sl. sol. water, v. sol. alcohol and ether. Smells like anise. $FeCl_3$ colours its aqueous solution violet. Yields salicylic acid on oxidation.

PRIMULINE BASE $C_{28}H_{18}N_4S_3$ *i.e.*
$C_6H_3Me<^{N}_{S}>C.C_6H_3<^{N}_{S}>C.C_6H_3<^{N}_{S}>C.C_6H_4.NH_2$.
Prepared by heating *p*-toluidine (2 mols.) with sulphur (4 or 5 atoms), H_2S being evolved (Green, *C. J.* 55, 234). Yellowish powder, nearly insol. all solvents. Not decomposed at 400°. Its salts are decomposed by water. The Na salt of its sulphonic acid (primuline), is taken up by unmordanted cotton. KOH at 260° yields amido-tolyl-mercaptan and *p*-amido-benzoic acid (Gattermann, *B.* 22, 425, 1066).

Dehydrothiotoluidine $C_{14}H_{12}SN_2$ *i.e.* $C_6H_3Me<^{N}_{S}>C.C_6H_4.NH_2$. [191°]. (434° at 766 mm.) (Pfitzinger a. Gattermann, *B.* 22, 1066). An intermediate body in the preparation of primuline. Formed, together with primuline base, by heating *p*-toluidine with S (Dahl & Co., *G. P.* 35790; Green, *C. J.* 55, 230). Got also by the action of HI and P upon primuline (Jacobsen, *B.* 22, 330). Yellowish iridescent needles (from isoamyl alcohol), v. sol. HOAc, sl. sol. hot alcohol, v. sl. sol. benzene, almost insol. boiling water. Its alcoholic solutions have violet-blue fluorescence. Ppd. by adding water to its solution in HClAq.

Reactions.—1. Yields *p*-toluidine on distillation with zinc-dust.—2. Yields primuline on heating with S.—3. Converted by diazotisation in boiling alcoholic solution into $C_6H_3Me<^{N}_{S}>CPh$ [123°].—4. When diazotised and boiled with water it gives $C_{14}H_{11}(OH)N_2S$ [256°], which gives $C_{14}H_{11}(OAc)N_2S$ [132°].—5. Fuming H_2SO_4 (containing 70 p.c. SO_3) forms, below 50°, a sulphonic acid $C_{14}H_{11}(SO_3H)SN_2$, which crystallises in yellow needles (containing aq), or orange plates (containing 2aq), sl. sol. hot water, and forms $NH_4A'aq$, sl. sol. hot water, $CuA'_2 2aq$, a reddish-brown pp., and AgA', a white pp.—6. MeI yields $C_{14}H_{10}(NMe_2)NS$ [197°] (434°), and $C_{14}H_{10}(NMe_3I)NS$, a bright-yellow powder, v. sol. water. MeOH and HCl at 150°–200° give $C_{14}H_{10}(NMe_3Cl)NS$, a yellow powder which forms $(C_{14}H_{10}NS.NMe_3Cl)_2PtCl_4$ [234°].

Acetyl derivative $C_{14}H_{11}AcN_2S$. [227°]. White plates or prisms, sl. sol. HOAc.

PROPACONIC ACID *v.* *Lactone* of Oxy-butylmaleïc acid.

PROPANE C_3H_8 *i.e.* $CH_3.CH_2.CH_3$. Mol. w. 44. (−·17°). S. (alcohol) 6. H.F.p. 35,110. H.F.v. 33,370 (Thomsen, *Th.* 4, 52). Occurs in the gases given off from the petroleum springs of the United States (Ronalds, *C. J.* 18, 54; Lefevre, *Z.* [2] 5, 185). Formed by the action of HI on propyl iodide, allyl iodide, isopropyl iodide, acetone, and glycerin (Berthelot, *Bl.* 7, 60; 9, 13, 184). Prepared by heating *n*-propyl iodide (9·6 pts.) with $AlCl_3$ (2·5 pts.) at 140° (Köhnlein, *B.* 16, 560), or by heating isopropyl iodide with zinc and HClAq (Schorlemmer, *A.* 150, 209). Gas. On compression with water at a low temperature it yields a hydrate, dissociating at 8·5° (Villard, *C. R.* 111, 302).

References.—Di-bromo-, Bromo-iodo-, Bromo-nitro-, Chloro-, Chloro-iodo-, Di-chloro-nitro-, Di-iodo, and Nitro- Propane.

PROPANE CARBOXYLIC ACID *v.* Butyric acid.

Propane dicarboxylic acid *v.* Glutaric, Pyrotartaric, and Ethyl-malonic acids.

Propane tricarboxylic acid $C_6H_8O_6$ *i.e.* $CH_3.CH(CO_2H).CH(CO_2H)_2$ (Bischoff, *B.* 13, 2164; 14, 614; 15, 1107; 17, 2783; 22, 3180; *A.* 214, 53). [146°]. Formed by saponifying the ether with dilute alcoholic potash. Crystalline mass, v. e. sol. water, alcohol, and ether. Splits up when heated alone, or with dilute HClAq, into CO_2 and pyrotartaric acid. Bromine forms bromopyrotartaric and bromocrotonic acids.—$Ba_3A'''_2$: bulky pp.

Methyl-di-ethyl ether $MeEt_2A'''$. (268°). S.G. ${}^{15}_{4}$ 1·078. Formed from methyl α-chloro-propionate and sodium malonic ether.

Ethyl ether Et_3A'''. (270·3° cor.). S.G. ${}^{20}_{4}$ 1·0698. $\mu_D = 1·4288$ at 20°. Formed from sodium malonic ether and α-bromo-propionic ether. Oil, miscible with alcohol and ether. NaOEt yields $C_3H_4Na(CO_2Na)(CO_2Et)_2$.

Propane tricarboxylic acid $CH_3.C(CO_2H)_2.CH_2.CO_2H$.

Methyl ether Me_3A'''. Oil (Barthe).

Ethyl ether Et_3A'''. (273·5° cor.). S.G. ${}^{15}_{4}$ 1·077. $\mu_D = 1·4311$ at 20°. Formed from sodium methyl-malonic ether and chloro-acetic ether, and also from sodium ethane tricarboxylic ether and MeI or MeCl (Bischoff a. Von Kuhlberg, *B.* 23, 635). Yields on saponification pyrotartaric and a little succinic acid.

Methyl ether of the mono-nitrile $CH_3.C(CN)(CO_2Me).CH_2.CO_2Me$. Formed from methyl cyanosuccinate, MeOH, and MeI at 70° (Barthe, *Bl.* [3] 1, 303; *C. R.* 108, 297; 112, 1013). Oil. The corresponding $CH_3.C(CN)(CO_2Et).CH_2.CO_2Et$ is also an oil (185° at 35 mm.).

Propane tricarboxylic acid $CO_2H.CH_2.CH_2.CH(CO_2H)_2$.

Ethyl ether Et_3A'''. (161° at 13 mm.). S.G. ${}^{20}_{4}$ 1·0808. Formed from sodium malonic ether and β-bromo-propionic ether (Emery, *B.* 24, 282). The free acid splits up into CO_2 and glutaric acid on boiling with HClAq.

Isomeride *v.* Tricarballylic acid.

Propane tetracarboxylic acid $CO_2H.CH_2.CH(CO_2H).CH(CO_2H)_2$.

Ethyl ether Et_4A^{iv} (204° at 18 mm.). S.G. ${}^{20}_{4}$ 1·1184. Formed from sodium malonic ether and chloro-succinic ether (Emery, *B.* 23, 3759). Oil, v. sol. alcohol and ether. The free acid splits up into CO_2 and tricarballylic acid.

Propane tetracarboxylic acid $(CO_2H)_2CH.CH_2.CH(CO_2H)_2$. *Dicarboxy-glutaric acid.* [170°]. An acid formed by the action of sodium amalgam on dicarboxyglutaconic ether $C_7H_2Et_4O_8$ in alkaline solution (Conrad a. Guthzeit, *A.* 222, 257). One of the products of the action of chloro-di-methyl oxide on sodium malonic ether (Kleber, *A.* 246, 106). Got also by boiling its ether with dilute alcoholic potash (Guthzeit a. Dressel, *B.* 21, 2234; 22, 1423; *A.* 256, 174). Crystalline powder (from ether), v. e. sol. water. At 180° it splits up into CO_2 and glutaric acid [98°].—Ba_2A^{iv} 2aq.—Ca_2A^{iv} 2aq.—Pb_2A^{iv} 2aq.

Ethyl ether Et_4A^{iv}. (235° at 30 mm.).

S.G. $\frac{12}{12}$ 1·116. Formed from sodium malonic ether by treatment with CH_2Cl_2 or CH_2I_2, and got also by reducing dicarboxy-glutaconic ether with zinc-dust and HOAc (W. H. Perkin, jun., *C. J.* 59, 993). Oil, with very bitter taste. NaOEt forms a di-sodium derivative, which reacts with EtI forming oily $C_{17}H_{28}O_8$ (c. 248° *in vacuo*).

Propyl-tri-ethyl ether Et_3PrA^{iv}. (195°–202° at 15 mm.). Formed from propyl triethyl dicarboxy-glutaconate, zinc-dust, and HOAc. Colourless oil.

Propane tetracarboxylic acid $CO_2H.CH_2.C(CO_2H)_2.CH_2.CO_2H$. [151°]. Got by saponifying its ether with alcoholic potash. Prisms (from water), v. sol. water, alcohol, and ether. At 170° it splits up into CO_2 and tricarballylic acid.—K_3HA^{iv} 2½aq (at 100°).—Zn_2A^{iv} 3aq (dried at 100°).—Pb_2A^{iv} aq.—Ag_4A^{iv}: insoluble pp.

Ethyl ether Et_4A^{iv}. (295° uncor.). S.G. $\frac{15}{15}$ 1·102. Formed from malonic ether, alcoholic NaOEt, and chloro-acetic ether, followed by a second dose of NaOEt and chloro-acetic ether (Bischoff, *B.* 13, 2163; *A.* 214, 61). Oil.

Ethyl ether of the mono-nitrile $CO_2Et.CH_2.C(CN)(CO_2Et).CH_2.CO_2Et$. [41°]. (200°–215° at 10 mm.). Formed from sodium cyano-succinic ether and chloro-acetic ether (Haller a. Barthe, *C. R.* 106, 1413). White crystals, sol. alcohol and ether.

Methyl ether of the mono-nitrile $CO_2Me.CH_2.C(CN)(CO_2Me).CH_2.CO_2Me$. [47°]. Prepared in like manner (Barthe, *C. R.* 111, 844). Prisms, insol. water and alkalis.

Propane pentacarboxylic acid $CH(CO_2H)_2.C(CO_2H)_2.CH_2.CO_2H$. [151°]. Got by saponifying its ether. Spherical aggregates (from ether).—K_5A^{v} 4aq.—$Ba_5A^{v}_2$ 4aq: crystalline pp.

Ethyl ether Et_5A^{v}. (275°–280° at 188 mm.). S.G. $\frac{15}{15}$ 1·121 (Bischoff, *B.* 15, 1107; 21, 2113). Formed from sodium-malonic ether and $CCl(CO_2Et)_2.CH_2.CO_2Et$. Formed also from sodium ethane tricarboxylic ether and chloro-acetic ether. Oil.

Reference.—OXYPROPANE TRICARBOXYLIC ACID.

PROPANE PHOSPHONIC ACID $C_3H_7.PO(OH)_2$. [60°–70°]. Prepared by oxidation of propyl-phosphine with fuming HNO_3 (Hofmann, *B.* 6, 304). Wax-like mass, sol. water.

PROPANE SULPHONIC ACID $CH_3.CH_2.CH_2.SO_3H$. Formed by oxidation of propyl mercaptan with nitric acid (S.G. 1·3) (Spring a. Winssinger, *Bl.* [2] 48, 110). ICl_3 at 160° forms chloro-propane sulphonic acid, CCl_4, and C_2Cl_6.

Propane sulphonic acid $(CH_3)_2.CH.SO_3H$. [below 100°]. Formed by oxidising isopropyl mercaptan with HNO_3. Obtained also from acetone by successive treatment with P_2S_5 and HNO_3 (Claus, *B.* 5, 660; 8, 533; Spring, *Bl.* [2] 40, 66). Crystalline. Its salts are v. e. sol. water.

Propane disulphonic acid $CH_2(SO_3H).CH_2.CH_2(SO_3H)$. Formed by boiling trimethylene bromide with a saturated solution of ammonium sulphite (Monari, *B.* 18, 1345). Deliquescent needles, v. sol. water and alcohol.—Na_2A'' 4½aq.—BaA'' 2aq: very soluble needles.

Propane disulphonic acid $CH_3.CH(SO_3H).CH_2(SO_3H)$. Formed in like manner from propylene bromide (M.).—Na_2A''aq.—BaA'': sparingly soluble crystals.

Propane disulphonic acid $C_3H_6(SO_3H)_2$. Got from butyramide and fuming H_2SO_4 (Buckton a. Hofmann, *A.* 100, 153), and also by heating butyric acid with $ClSO_3H$ at 140° (Baumstark, *A.* 140, 83).—BaA''.—PbA'': crystalline.

Propane trisulphonic acid $CH_2(SO_3H).CH(SO_3H).CH_2(SO_3H)$. Got by boiling *s*-tri-chloro-propane with aqueous K_2SO_3 (Schäuffelin, *A.* 148, 117).—$Ba_3A'''_2$: crystalline powder, sl. sol. water.

References.—CHLORO- and OXY-PROPANE SULPHONIC ACID.

DIPROPARGYL C_6H_6 *i.e.* $CH{\vdots}C.CH_2.CH_2.C{\vdots}CH$. *Hexunene.* (85°). S.G. $\frac{18}{}$ ·81. H.F.p. −96,040. H.F.v. −97,200 (Thomsen, *Th.*). Formed by distilling diallyl tetrabromide with solid KOH, and boiling the resulting di-bromo-diallyl with alcoholic potash (Henry, *B.* 6, 956; 7, 21; 14, 399; 17, 1132). Limpid, highly refractive oil, v. sol. ether. Burns with smoky flame. Combines with explosive violence with bromine, forming $C_6H_6Br_4$, a thick liquid S.G. $\frac{12}{}$ 2·464, from which, by further action of Br, crystalline $C_6H_6Br_8$ [141°] can be obtained. Iodine in KI forms dipropargyl tetraiodide $C_6H_6I_4$ [113°] crystallising from CS_2 in prisms. Dipropargyl gives with ammoniacal cuprous chloride a yellow pp. $Cu_2C_6H_4$ 2aq, which explodes at about 100°. Aqueous $AgNO_3$ ppts. $Ag_2C_6H_4$ 2aq, which explodes below 100°. Dipropargyl is very easily polymerised, forming a resin.

PROPARGYL ALCOHOL C_3H_4O *i.e.* $CH{\vdots}C.CH_2OH$. Mol. w. 56. (115°). V.D. 1·88 (calc. 1·93). S.G. $\frac{20}{4}$ ·9715. $\mu_\beta = 1·437$. $R_\infty = 24·01$ (Brühl). H.F.p. −3,500. H.F.v. −4,370 (Thomsen, *Th.*). Formed by boiling bromo-allyl alcohol with KOHAq (Henry, *B.* 5, 274, 449, 569; 6, 728; 7, 20, 761). Formed also from propargylamine oxalate, $NaNO_2$, and HCl (Paal a. Hempel, *B.* 24, 3039). Colourless liquid of peculiar odour, sol. water.

Reactions.—1. Ammoniacal Cu_2Cl_2 ppts. canary-yellow $Cu_2(C_3H_3O)_2$ which explodes when heated, and is decomposed by dilute acids with reproduction of propargyl alcohol.—2. Ammoniacal $AgNO_3$ ppts. white AgC_3H_3O.—3. Anhydrous BaO forms $Ba(C_3H_3O)_2C_3H_4O$, crystallising in small plates.—4. On heating with solid KOH it yields formic acid and acetylene.—5. HBr forms bromo-allyl alcohol.—6. HNO_3 yields CO_2 and oxalic acid.

Acetyl derivative $C_3H_3.OAc$. (125°). S.G. $\frac{20}{4}$ 1·0052. $\mu_\beta = 1·427$. $R_\infty = 39·71$ (Brühl). Got from the alcohol and AcCl.

Methyl ether C_3H_3OMe. (62°). S.G. $\frac{12·5}{}$ ·83. H.F.p. −10,910. H.F.v. −12,360 (Thomsen, *Th.*). Formed by boiling *s*-tri-bromo-propane with KOH dissolved in MeOH (Liebermann, *A.* 135, 287) and by boiling the dibromide of methyl allyl oxide with alcoholic potash (Henry). Ammoniacal $AgNO_3$ ppts. lemon-yellow $C_3H_2Ag.OMe$, whence I in KI forms oily $C_3H_2I.OMe$ [12°].

Ethyl ether C_3H_3OEt. (81°–85°). S.G. $\frac{20}{4}$ ·8326. $\mu_\beta = 1·4096$. $R_\infty = 39·5$ (Brühl). This body is formed by the action of alcoholic potash on $CH_2Br.CHBr.CH_2Br$, on $CH_3.CBr_2.CH_2Br$,

on dichloropropylene, or on ethyl bromo-allyl oxide (Liebermann, *A.* 135, 278; 158, 230; Henry, *B.* 5, 274; Baeyer, *A.* 138, 196). Mobile liquid, with penetrating odour, v. sl. sol. water, miscible with alcohol. Combines with Br, forming $C_3H_3Br_2.OEt$. Boiling very dilute (1 p.c.) H_2SO_4 splits it up into alcohol and propargyl alcohol. Sodium forms C_3H_2NaOEt. Alcoholic silver nitrate forms crystalline $(C_3H_2Ag.OEt)_2AgNO_3$ converted by ammonia into amorphous C_3H_2AgOEt, whence I in KI forms crystalline C_3H_2IOEt and oily $C_3H_2I_3OEt$. An ammoniacal solution of AgCl added to an alcoholic solution of C_3H_3OEt ppts. white $(C_3H_2AgOEt)_2AgCl$. Ammoniacal Cu_2Cl_2 gives yellow amorphous C_3H_2CuOEt.

Isoamyl ether $C_3H_3OC_5H_{11}$. (140°-145°).

PROPARGYLAMINE $C_3H_3NH_2$. Formed by the action of NaOEt on bromo-allyl-amine and on di-bromo-propyl-amine (Paal a. Hermann, *B.* 22, 3080). The free base has not been isolated. —$B'H_2C_2O_4$. [143°]. Large tables (from water), sl. sol. alcohol. Gives a white pp. with ammoniacal $AgNO_3$.—$B'C_6H_2(NO_2)_3OH$. [189°]. Large red plates or tables.—B'HCl.—B'HBr. [130°-171°].—B'HI. [205°]. White plates, v. e. sol. water.

PROPARGYL-ISOAMYL-AMINE $C_8H_{15}N$ *i.e.* $C_3H_3.NHC_5H_{11}$. Formed from di-bromo-isoamyl-amine and NaOEt (Paal a. Hermann, *B.* 22, 3084). Liquid.—$B'H_2C_2O_4$ aq. [204°]. White needles (from water).—B'HBr. [186°]. Pearly plates.

PROPARGYL BROMIDE $CH:C.CH_2Br$. (89°). S.G. ^{11} 1·59. Formed from propargyl alcohol and PBr_3 (Henry, *B.* 6, 728). Liquid.

Propargyl tribromide *v.* Tri-bromo-propylene.

PROPARGYL-ISOBUTYL-AMINE $C_7H_{13}N$ *i.e.* $CH:C.CH_2.NH.CH_2Pr$. (135°). Formed from di-bromo-propyl-isobutyl-amine and NaOEt (Paal a. Heupel, *B.* 24, 3045). Liquid, miscible with water.—B'HCl. [148°].—$B'_2H_2PtCl_6$. [172°].—$B'H_2C_2O_4$. [210°]. Needles and plates, m. sol. cold water.

PROPARGYL CHLORIDE C_3H_3Cl. (65°). S.G. ^{5} 1·045. Formed from propargyl alcohol and PCl_3 (Henry, *B.* 8, 398). Mobile oil.

PROPARGYLIC ACID is Propiolic acid.

PROPARGYL IODIDE $CH:C.CH_2I$. (c. 115°). S.G. ^{0} 2·018. Formed from propargyl bromide and NaI in alcohol (Henry, *B.* 17, 1132). Yellowish liquid. Iodine forms $CHI:CI.CH_2I$. [41°].

PROPARGYL-PROPYL-AMINE $C_6H_{11}N$ *i.e.* $C_3H_3.NH.C_3H_7$. The salt B'HBr [180°] is got from propyl bromide and propargylamine (Paal a. Hermann, *B.* 22, 3084).

PROPARGYL SULPHOCYANIDE C_3H_3SCN. Formed from propargyl bromide and potassium sulphocyanide (Henry, *B.* 6, 729). Oil, smelling like mustard. Decomposed by heat.

PROPARGYL-DI-THIO-CARBAMIC ACID $CH:C.CH_2.NH.CS_2H$. [115°]. Formed by boiling propargylamine with CS_2 and alcohol (Paal a. Heupel, *B.* 24, 3041). Needles (from dilute alcohol) or plates (from benzene-ligroïn).

PROPENYL-*o*-AMIDO-PHENOL CARBOXYLIC ETHER $C_6H_4<^{O}_{NH}>CMe.CH_2.CO_2Et$. **[108°]. Formed by heating a mixture of *o*-amidophenol and acetoacetic ether (Hantzsch, *B.* 16, 1948). Flat prisms, readily resolved into the parent substances by dilute acids, alkalis, or even boiling water.**

PROPENYL-*o*-AMIDO-PHENYL MERCAPTAN C_9H_9NS *i.e.* $C_6H_4<^{N}_{S}>CEt$. (252°). Formed by heating *o*-amido-phenyl mercaptan with propionyl chloride at 160° (Hofmann, *B.* 13, 21). Heavy oil.—$B'_2H_2PtCl_6$: large prisms.

PROPENYLAMINE $CH_3.CH:CH.NH_2$. Formed by the action of baryta on *β*-bromo-propylamine (Hirsch, *B.* 23, 968). Does not decolourise bromine water.—$B'_3H_3I_3 2BiI_3$: six-sided plates.

PROPENYL-BENZENE SULPHONIC ACID $CH_2:CMe.C_6H_4.SO_3H$. The salts of this acid are formed by heating the dry salts of the acid $CMe_2(OH).C_6H_4.SO_3H$ (R. Meyer, *A.* 219, 302).

Amide $C_9H_9SO_2NH_2$. [152°].

***o*-PROPENYL-BENZOIC ACID** $CH_2:CMe.C_6H_4.CO_2H$. [61°]. Formed from di-methyl-phthalide and KCy at 260° (Wislicenus, *A.* 248, 64). Needles (from water).

***p*-Propenyl-benzoic acid** $CH_2.CMe.C_6H_4.CO_2H$. [161°]. Formed by heating $(CH_3)_2.C(OH).C_6H_4.CO_2H$ with dilute HCl on a water bath (R. Meyer a. J. Rosicki, *B.* 11, 1791; *A.* 219, 270). White satiny plates (from 1 pt. alcohol and 1 pt. water) or slender needles (from water). Sl. sol. hot water, v. e. sol. alcohol and ether. Sodium amalgam reduces it to cuminic acid.

Salts.—NH_4A'.—BaA'_2 aq.—CuA'_2 7aq.—AgA': amorphous pp.

Methyl ether.—MeA' [53°]. (254° cor.). V.D. 6·09. Insol. water.

Isopropenyl-benzoic acid $C_3H_5.C_6H_4.CO_2H$ [255°-260°]. By boiling oxy-propyl-benzoic acid $(CH_3)_2C(OH).C_6H_4.CO_2H$ with fuming HCl (R. Meyer, *B.* 12, 1076; *A.* 219, 281). Minute needles grouped in stars (from alcohol). Insol. water. Does not decolourise bromine, and is not reduced by sodium amalgam, but is converted by HI into cuminic acid. Hence it would appear to be a polymeride of propenyl-benzoic acid, not containing a C:C group.

Salts.—NH_4A'aq. Sl. sol. water.—BaA'_2aq.—$CaA'_2 1\frac{1}{2}$aq.—CuA'_2.—AgA': pp., insol. water.

Methyl ether MeA'. [83°]. Decomposed by heat.

References.—Amido-, Nitro-, and Oxy- Propenyl-benzoic acid.

PROPENYL BROMIDE *v.* Bromo-propylene.

PROPENYL CARBINOL *v.* Butenyl alcohol.

PROPENYL-TRICARBOXYLIC ACID *v.* Propanetricarboxylic acid.

PROPENYL CHLORIDE *v.* Chloro-propylene.

PROPENYL-PHENOL. *Methyl derivative v.* Anethol.

PROPENYL-ISOPROPYL BENZENE $C_{12}H_{16}$ *i.e.* $Pr.C_6H_4.CH:CHMe$. (230°). S.G. ^{15} ·890. Got by boiling $Pr.C_6H_4.CH_2.CBrMe.CO_2H$ with Na_2CO_3Aq (Perkin, *C. J.* 1877, ii. 660). *Dibromide* $C_{12}H_{16}Br_2$ [59°].

PROPENYL-SALICYLIC ACID *v.* Oxy-propenyl-benzoic acid.

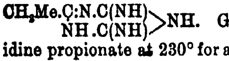
PROPEPTONE *v.* Proteïds.

PROPHETIN $C_{22}H_{36}O_7$. **A bitter resin got from the fruit of *Cucumis prophetarum*, split up**

by boiling dilute HClAq into glucose and prophetein $C_{20}H_{30}O_4$ (Walz, *J.* 1859, 566).

PROPINENE *v.* ALLYLENE.

PROPINENE DIPHTHALIDE $C_{19}H_{12}O_4$ *i.e.* $C_6H_4\!<\!\begin{smallmatrix}\text{—C:CMe.CH:C—}\\ \text{CO.O}\qquad\quad\text{O.CO}\end{smallmatrix}\!>\!C_6H_4$. Formed by heating phthalic anhydride (3 pts.) with pyrotartaric acid (3 pts.) and sodium acetate (1 pt.) at 240°–290° (Roser, *B.* 17, 2776). Fine yellow needles, not melted at 280°.

PROPIO-GUANAMINE $C_5H_9N_5$ *i.e.*  $\begin{matrix}CH_2Me.C{:}N.C(NH)\\ NH.C(NH)\end{matrix}\!>\!NH$. Got by heating guanidine propionate at 230° for an hour (Haaf, *J. pr.* [2] 43, 78). Granules (from NaOHAq) or dimetric prisms (from water).

PROPIO-HOMO-FERULIC ACID *v.* DI-OXY-PHENYL-CROTONIC ACID.

PROPIOLIC ACID $C_3H_2O_2$ *i.e.* $CH{:}C.CO_2H$. *Propargylic acid.* [6°]. (c. 144°). Formed by boiling the acid K salt of acetylene dicarboxylic acid with water (Bandrowski, *B.* 13, 2340). Liquid, solidifying at about 4°. Smells like acetic acid. Turns brown in air. Sol. water, alcohol, and ether. Reduces $HgCl_2$, $AgNO_3$, and $PtCl_4$.

Reactions.—1. Ammoniacal $AgNO_3$ gives a white crystalline explosive pp.—2. Ammoniacal Cu_2Cl_2 gives a green amorphous explosive pp., turning brown.—3. *Sodium-amalgam* reduces it to propionic acid.—4. Combines with HCl, forming β-chloro-acrylic acid. HBr and HI act in like manner.—5. Br forms di-bromo-acrylic acid [85°].—6. I forms $CHI{:}CI.CO_2H$ [104°] (Bruck, *B.* 24, 4120).

Salt.—KA′ aq. Transparent prisms, v. sol. water, deflagrating at 105°.

Ethyl ether EtA′. (119°). V.D. 3·47. Liquid, smelling like horse-radish. Oxidised by alkaline K_3FeCy_6 to diacetylene dicarboxylic acid (Baeyer, *B.* 18, 677, 2269).

Reference. — BROMO- and IODO- PROPIOLIC ACID.

PROPIONAMIDE *v.* *Amide* of PROPIONIC ACID.

PROPIONAMIDINE $C_3H_8N_2$ *i.e.* $CEt(NH).NH_2$. The hydrochloride is formed by leading HCl into a solution of propionitrile in isobutyl alcohol, and heating the product with alcoholic NH_3 (Pinner a. Klein, *B.* 11, 1484; 17, 176; 18, 2845). Very unstable oil, sl. sol. ether. On heating with NaOAc and Ac_2O it yields a base $C_8H_{13}N_3$ [204°].—B′HCl. [129°]. Needles, insol. ether.—$B'_2H_2PtCl_6$. [200°].—$B'HNO_3$. [116°]. Crystals (from alcohol), v. sol. water (C. Lossen, *A.* 265, 167).

Reference.—OXY-PROPIONAMIDINE.

PROPIONE *v.* DI-ETHYL KETONE.

PROPIONIC ACID $C_3H_6O_2$ *i.e.* $CH_3.CH_2.CO_2H$. *Metacetonic acid.* Mol. w. 74. [−23°] (Pettersson, *J. pr.* [2] 24, 295). (140·7° cor.) (Zander). S.G. $\frac{20}{4}$ ·9946 (B.); $\frac{15}{15}$ ·9983; $\frac{25}{25}$ ·9896 (Perkin). M.M. 3·462 at 20°. $\mu_\beta = 1{\cdot}391$. $R_\infty = 28{\cdot}01$ (Brühl). S.V. 85·3. C.E. (0°–10°) ·00106. H.F.p. 109,450. H.F.v. 107,710 (Thomsen, *Th.*). S.H. ·440 at 0° (R. Schiff, *A.* 234, 300). Critical temperature 340° (Pawlewski, *B.* 16, 2634). Occurs in the fruit of *Gingko biloba* (Béchamp, *A.* 130, 364), in suint (Buisine, *Bl.* [2] 48, 639), and in wood vinegar (Anderson, *C. N.* 14, 257; Barré, *Z.* [2] 5, 445).

Formation.—1. By oxidation of metacetone with chromic acid (Gottlieb, *A.* 52, 121).—2. By potash-fusion from sugar, starch, mannite, and angelic acid (G.).—3. By reduction of acrylic acid (Linnemann, *A.* 125, 317), of lactic acid (Lautemann, *A.* 113, 217), and of pyruvic acid (Wislicenus, *A.* 126, 229).—4. By heating potassium oxalate with dry NaOEt (Van't Hoff, *B.* 6, 1107).—5. By heating NaOEt with CO at 180° (Fröhlich, *A.* 202, 290; *cf.* Hagemann, *B.* 4, 877).—6. From $ZnEt_2$, sodium, and CO_2 (Wanklyn, *A.* 107, 125).—7. Together with di-ethyl ketone, by heating $ZnEt_2$ with CO_2 at 160° (Schmitt, *J. pr.* [2] 42, 568).—8. By the action of sunlight on a solution of succinic acid containing a uranium salt (Seekamp, *A.* 133, 253). 9. By heating barium succinate with NaOMe for 8 hours at 300° (Mai, *B.* 22, 2133).—10. Among the products of destructive distillation of colophony (Renard, *C. R.* 103, 157).

Preparation.—1. By oxidation of *n*-propyl alcohol (Pierre a. Puchot, *A. Ch.* [4] 28, 75).—2. By saponification of the nitrile (Linnemann, *A.* 148, 251; Beckurts a. Otto, *B.* 10, 262).—3. By heating lactic acid with HIAq (Freund, *J. pr.* [2] 5, 446).

Properties.—Liquid, miscible with water, alcohol, ether, benzene, and ligroïn. Separated from its aqueous solution by $CaCl_2$, but not by NaCl and Na_2SO_4. Heated in a sealed tube with ICl_3 it gives C_2Cl_6, CO_2, and HCl (Krafft, *B.* 9, 1085). On boiling the dry acid with Br and P for some time the product is α-bromo-propionic acid (Volhard, *A.* 242, 141).

Salts.—NH_4A'.—$(NH_4)HA'_2$ (Sestini, *Z.* 1871, 34).—NaA′. S. 99 at 15°; 187 at 100° (R.). S. (alcohol) 2·4 at 20°, 3 at 100°.—NaA′aq.—KA′aq: deliquescent plates (Renard, *C. R.* 104, 913). S. (of KA′) 178 at 16°; 309 at 100°.—KHA'_2.—LiA′ aq.—CaA'_2 aq. S. 54 at 17° (L.); 41 at 0°; 39 at 80° (K.). Needles, insol. alcohol.—$Ca_2HA'_5$ 5aq.—BaA'_2 aq. S. 60 at 17° (Linnemann, *A.* 160, 220); 48 at 0°; 68 at 80° (von Krasnicki, *M.* 8, 605).—BaA'_2 6aq.—$BaHA'_3$ 3aq (Mixter, *Am.* 8, 343).—$SrHA'_3$ 3½aq: long thin crystals. [67°–75°].—$SrA'_2$6aq. Crystals.—$Ba_5Mg_4A'_{18}$ 12aq (Fitz, *B.* 13, 1312; 14, 1085).—$Mg_4Pb_5A'_{18}$ 12aq.—$Ca_4Pb_5A'_{18}$ 12aq: monometric crystals.—$BaCa_2A'_6$: monometric octahedra.—$SrCa_2A'_6$.—MgA'_2 aq.—$Ba_6A'_{10}Ac_2$ (Fitz, *B.* 11, 1897).—PbA'_2. [100°]. Crystalline mass.—$Pb_7A'_6O_4$. S. c. 11 at 14°.—$Pb_2A'_2O$. S. 8·8 at 20°; 6·3 at 85°.—CuA'_2aq: green prisms.—$Cu_2A'_2O$ aq—×CdA'_2. V. e. sol. water.—ZnA'_2 aq: needles. S. (of ZnA'_2) 32 at 15°.—HgA'_2. [110°]. S. 19·2 at 15°.—$Hg_2A'_2$. [225°]. S. 1·4 in the cold.—NiA'_2 2aq.—CoA'_2 3aq.—FeA'_2: pale-green crystals.—$Fe_2A'_6$.—$Al_2A'_4O$: white pp.—$Cr_2A'_4O$.—AgA′. Crystals. S. ·9 at 18.

Methyl ether MeA′. (80°). S.G. $\frac{0}{4}$ ·9373 (Elsässer, *A.* 218, 313); $\frac{0}{0}$ ·9403 (Gartenmeister). C.E. (0°–10°) ·001296. $\mu_D = 1{\cdot}3812$. H.F.p. 107,330. H.F.v. 105,010 (Thomsen, *Th.*). S.V. 104·6.

Ethyl ether EtA′. Mol. w. 102. (99° cor.). S.G. $\frac{0}{4}$ ·9124 (E.); $\frac{15}{15}$ ·8958; $\frac{25}{25}$ ·8868. M.M. 5·452 at 15·7° (Perkin). C.E. (0°–10°) ·001215. S.V. 127·7 (R. Schiff, *A.* 220, 110). Formed from AgA′ and EtI and also by distilling the acid with alcohol and H_2SO_4. Oil.

Propyl ether PrA'. (122° cor.). S.G. $\frac{0}{4}$ ·9619 (Elsässer, *A.* 218, 321); $\frac{15}{15}$ ·8868; $\frac{25}{25}$ ·8781 (Perkin, *C. J.* 45, 497); $\frac{0}{0}$ ·9023 (Gartenmeister). M.M. 6·429 at 21·3°. C.E. (0°–10°) ·001052. S.V. 150.

Isopropyl ether PrA'. (110° cor.). S.G. ^{0} ·8931 (Pribram a. Handl, *M.* 2, 687); $\frac{15}{15}$ ·8717; $\frac{25}{25}$ ·8626. M.M. 6·595 at 14°.

n Butyl ether C_4H_9A'. (145°). S.G. $\frac{0}{0}$ ·8953. S.V. 173·2. C.E. (0°–10°) ·00106 (Gartenmeister, *A.* 233, 265).

Isobutyl ether $PrCH_2$A'. (137°). S.G. $\frac{0}{4}$ ·8876. C.E. (0°–10°) ·001015 (E.). S.V. 174 (R. Schiff, *A.* 220, 332).

Isoamyl ether C_5H_{11}A'. Mol. w. 144. (160°). S.G. $\frac{0}{4}$ ·8877 (Elsässer, *A.* 218, 330). C.E. (0°–10°) ·00099. S.V. 197 (Schiff); 195 (E.).

Heptyl ether C_7H_{15}A'. (208°). S.G. $\frac{0}{0}$ ·8847. C.E. (0°–10°) ·00096. S.V. 247·1 (Gartenmeister).

Octyl ether C_8H_{17}A'. (226°). S.G. $\frac{0}{0}$ ·8833. C.E. (0°–10°) ·00093. S.V. 270·5 (Gartenmeister).

Ethylene ether $C_2H_4A'_2$. (211° cor.). S.G. $\frac{15}{17}$ 1·0544 (Perkin, *C. J.* 45, 505).

Phenyl ether PhA'. (200° i.V.) at 744 mm.

Chloride C_2H_5.COCl. (80°). S.G. $\frac{20}{4}$ 1·0646 (Brühl, *A.* 203, 14; *cf.* Sestini, *Bl.* [2] 11, 470). $\mu_\beta = 1{\cdot}4107$. $R_\infty = 34{\cdot}12$. $ZnMe_2$, followed by water, forms methyl ethyl ketone and oily $C_8H_{14}O$ (168°). S.G. ^{0} ·877 (Pawloff, *A.* 188, 138).

Bromide C_3H_5OBr. (104° i.V.). S.G. ^{25} 1·52 (Lobry de Bruyn, *R. T. C.* 3, 389).

Iodide C_3H_5OI. (128°).

Anhydride $(C_3H_5O)_2O$. Mol. w. 130. (162°) at 708 mm. (L.); (165°) (Limpricht a. Uslar, *A.* 94, 322); (167°) (Kahlbaum, *B.* 16, 2481); (169°) (Perkin, *C. J.* 28, 10). Formed by the action of $Pb(NO_3)_2$ (also of nitrates of other heavy metals) upon propionyl chloride; $PbCl_2$ is formed, and N_2O_4 and oxygen evolved; the yield is 77 p.c. of theoretical (Lachowicz, *B.* 18, 2991). Reacts with hydroxylamine hydrochloride, forming $CH_3.CH_2$.C(OH):NOH [85°] (Miolati, *B.* 25, 700).

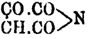
Amide C_3H_7NO, *i.e.* $C_2H_5.CO.NH_2$. Mol. w. 73. [79°]. (213°). H.C.p. 436,000. H.C.v. 435,600. H.F. 88,400 (Berthelot, *C. R.* 111, 145; *A. Ch.* [6] 22, 20; *Bl.* [3] 4, 229). Formed from propionic ether and NH_3 (Dumas, *C. R.* 25, 657; Sestini, *Cimento*, 4, 21; L. Meyer, *B.* 22, 24). Prepared by heating ammonium propionate at 230° under pressure; the yield being 55 p.c. of the theoretical amount (Hofmann, *B.* 15, 981). Got also by heating propionic acid (46 g.) with ammonium sulphocyanide (18 g.) for 4 days, and distilling the product (J. Schulze, *J. pr.* [2] 27, 517).—B'_2HCl. Needles, v. e. sol. water, v. sl. sol. ether.—$Hg(NH.C_3H_5O)_2$. Large dimetric plates, sl. sol. cold water.

Bromo-amide $C_3H_5O.NHBr$. [80°]. Formed from propionamide, bromine, and KOHAq (Hofmann, *B.* 15, 753). Colourless needles, sol. alcohol. Converted by hot KOHAq into ethylamine.—$C_3H_5O.NNaBr_2$. [c. 100°]. Needles.

Acetyl-amide C_3H_5O.NHAc. [82°]. (230°–240°). Formed from propionamidine hydrochloride, NaOAc, and Ac_2O, a compound $C_6H_{12}N_2$ [204°] being formed at the same time (Pinner, *B.* 22, 1604).

Imide $(C_3H_5O)_2NH$. [154°] (Otto a. Tröger, *B.* 23, 759). (210°–220°). *Formation.*—1. By heating the amide in a current of HCl.—2. By heating the amide with the chloride and $AlCl_3$.—3. By the action of $AlCl_3$ at 100° on a mixture of propionitrile with AcCl or propionyl chloride.—4. By heating propionic acid with propionitrile for some hours at 200°. *Properties.*—Rectangular tables or silky needles, sl. sol. cold water. May be sublimed.

Anilide C_3H_5ONHPh. [105°]. S. ·42 at 24°. Formed by heating the amide with aniline (Kelbe, *B.* 16, 1200). Plates, sol. ether. With oxalic ether, benzene, and NaOEt it forms



$\begin{matrix}\text{CO.CO}\\ \text{MeCH.CO}\end{matrix}\!>\!\text{NPh}$ [192°] (Wislicenus a. Sattler, *B.* 24, 1256).

Methyl-anilide C_3H_5O.NPhMe. [58·5°]. Formed from the anilide and MeI (Norton a. Allen, *B.* 18, 1998).

Ethyl-p-toluide $C_3H_5O.NHC_6H_4Me$. (c. 270°). From the chloride and ethyl-toluidine (Norton a. Livermore, *B.* 20, 2271).

Nitrile C_3H_5N, *i.e.* Et.CN. *Propionitrile. Ethyl cyanide.* (97°). S.G. $\frac{4}{4}$ ·7998; $\frac{25}{25}$ ·7815 (Perkin, *C. J.* 55, 701); $\frac{0}{4}$ ·8010 (Thorpe). C.E. (0°–10°) ·00125; (0°–100°) ·00148. M.M. 3·331. μ_D 1·3659 at 24° (Gladstone, *C. J.* 59, 290). H.F.p. −9,670 (Thomsen, *Th.*); +8,700 (from diamond) (Berthelot, *C. R.* 108, 1219). H.F.v. −10,830. H.C. 446,700 (Berthelot); 471,450 (Thomsen, *Th.* 4, 129). S.V. 78·4. *Formation.*—1. By distilling dry KCy with $KEtSO_4$ or $Ba(EtSO_4)_2$ (Pelouze, *A.* 10, 249).—2. By boiling KCy with EtI and alcohol (Williamson, *P. M.* [4] 6, 205; Buckton a. Hofmann, *C. J.* 9, 250; Rossi, *A.* 159, 79).—3. From the amide and P_2O_5 (Dumas, *A.* 64, 334).—4. From $ZnEt_2$ and cyanogen or CyCl (Gal. *Z.* 1868, 252; Frankland a. Graham, *C. J.* 37, 740).—5. By the action of Ac_2O on the oxim of propionic aldehyde in the cold (Dollfus, *B.* 25, 1915). *Preparation.*—The nitrile cannot be freed from alcohol by distillation, since the compound $C_3H_5N3HOEt$ boils constantly at 79°, and is not decomposed by water or $CaCl_2$. It is best, therefore, to prepare it from the amide. *Properties.*—Colourless liquid, v. sol. water, but separates on addition of NaCl or $CaCl_2$. Miscible with alcohol and ether. Combines with metallic chlorides, yielding $(C_3H_5N)SbCl_5$, $C_3H_5NAuCl_3$, $C_3H_5NPtCl_4$, $(C_3H_5N)_2SnCl_4$, and $(C_3H_5N)_2TiCl_4$ (Henke, *A.* 106, 280). Forms also $(C_3H_5N)_4FeCy_2$ 6aq, $(C_3H_5N)_4FeCy_2Et_2Cl_2$ 6aq (Buff, *A.* 91, 253), and $(EtCy)_2PtCy_2$ 2aq (Than, *A.* 107, 315). *Reactions.*—1. *Potash* forms propionic acid. Dilute H_2SO_4 acts in like manner. 2. Dry *chlorine* forms $CH_3.CCl_2.CN$ (Otto, *A.* 116, 195).—3. *Bromine* forms $C_3H_5NBr_2$ [64°], converted by water into $(C_3H_4BrO)_2NH$ (Engler, *A.* 142, 65).—4. Dry HCl slowly forms C_3H_6NCl [121°] (Gautier, *A.* 142, 289), while HBr gives $C_3H_7NBr_2$ [50°–55°] (Engler, *A.* 149, 307). HI below 0° forms $EtCI_2NH_2$ crystallising in plates (Biltz, *B.* 25, 2542).—5. *Sodium* converts it on heating into the polymeric cyanethine (*q. v.*). Sodium added to its solution in dry ether gives off H and ethane, and forms a product which is left when the ether is evaporated as a white powder (Et.C(NH).CMeNa.CN ?). This powder is converted by water into $C_8H_{10}N_2$ [48°] (258° uncor.), and by HClAq into C_6H_9NO or C_2H_5.CO.CHMeCN (193·5°). The white powder treated with MeI yields $C_7H_{12}N_2$ [43°] (262°), whence HClAq forms liquid $C_7H_{11}NO$ (175°), S.G. $\frac{0}{4}$ ·945, mol. w. 125 (obs.). EtI and HClAq acting on the white powder yield $C_8H_{13}NO$ (195°), S.G. $\frac{0}{4}$ ·943 (E. von Meyer, *J. pr.* [2] 38, 336; Hanriot a. Bouveault, *C. R.* 108, 1171; *Bl.* [3] 1, 551). The compounds $C_7H_{11}NO$ and $C_8H_{13}NO$ are converted by heating with HClAq in sealed tubes into ethyl isopropyl ketone and ethyl butyl ketone respectively.—6. A mixture of propionitrile and benzonitrile in ethereal solution is converted by Na, followed by water, into CPh(NH).CHMe.CN [97°], whence warm dilute HClAq forms oily C_6H_5.CO.CHMe.CN (E. von Meyer, *J. pr.* [2] 39, 189).—7. *Zinc* and HClAq yield propylamine together with smaller quantities of di- and tripropylamine (Pisanello, *G.* 16, 446).—Ac_2O at 200° forms $C_7H_{14}N_2O_2$ [68°] (220°) (Gautier, *Z.* 1869, 127).

References.—Amido-, Bromo-, Bromo-nitro-, Chloro-, Chloro-bromo-, Iodo-, Nitro-, and Oxy-amido-propionic acid and propionitrile.

PROPIONIC ALDEHYDE C_3H_6O *i.e.* $CH_3.CH_2$.CHO. Mol. w. 58. (48°). S.G. $\frac{15}{15}$ ·8065; $\frac{25}{25}$ ·7966 (Perkin, *C. J.* 45, 476); $\frac{20}{4}$ ·8066 (Brühl, *A.* 203, 13). S. 16 at 20°. MM. 3·332 at 13·6°. μ_β 1·368. R_∞ = 25·42. S.V. 75·4. H.F.p. 55,240. H.F.v. 53,790 (Thomsen). Formed by oxidation of propyl alcohol (Michaelson, *A.* 134, 69; Chancel, *A.* 151, 301; Lieben a. Zeisel, *M.* 4, 14) and by distilling calcium formate with calcium propionate (Rossi, *C. R.* 70, 129). Pungent liquid, sol. water. Readily oxidised by air. Reduces ammoniacal $AgNO_3$, forming a mirror. Readily dissolves in aqueous $NaHSO_3$. Decomposed by hot KOHAq. Coloured brownish-red by alkaline sodium nitroprusside, the colour being destroyed by HOAc (Von Bitto, *A.* 267, 376).

Reactions.—1. Reduced in aqueous solution by sodium-amalgam to *n*-propyl alcohol.—2. H_2S passed into its aqueous solution, acidified by HCl, forms oily $(C_3H_6S)C_3H_6O$ (Alexejeff, *B.* 10, 1739).—3. Dry *ammonia* passed into propionic aldehyde dissolved in ligroïn cooled by a freezing mixture forms a white flocculent pp. of $C_3H_6(OH)NH_2$, which readily deliquesces, forming $C_{15}H_{19}N_3$ [74°], crystallising in triclinic tables, $a:b:c$ = 1:1·185:·801, insol. water, sol. alcohol and ether (Waage, *M.* 4, 708).—4. PH_3 and HCl form $(CH_3.CH_2.CHO)_4PH_4Cl$ [128°], while PH_3 and HBr give $(C_3H_6O)_4PH_4Br$ [106°]. These compounds are decomposed by water (Messinger a. Engels, *B.* 21, 331). PH_4I at 0° forms, in like manner, $(C_3H_6O)_4PH_4I$ [96°] (Girard, *A. Ch.* [6] 2, 24).—5. *Mercaptan* and $ZnCl_2$ give $CH_3.CH_2.CH(SEt)_2$ (198°) (Fromm, *A.* 253, 150). 6. *Propyl alcohol* and HOAc at 100° form $CHEt(OPr)_2$ (166° cor.) (Schudel, *M.* 5, 247).

Oxim C_2H_5.CH:NOH. (131°). Formed from the aldehyde and aqueous hydroxylamine (Petraczek, *B.* 15, 2784). Liquid, sol. water. It is a *syn*-oxim, because it is converted by Ac_2O and ether in the cold into propionitrile (Dollfus, *A.* 25, 1915).

Phenyl-hydrazide CHEt:N_2HPh (152° *in vacuo*) (Bischoff, *B.* 23, 1916).

References.—Bromo-, Chloro-, Iodo-, and Oxy- Propionic aldehyde.

PROPIONIC IMIDO-ETHYL ETHER C_2H_5.C(NH).OEt. The hydrochloride, B'HCl, formed by passing gaseous HCl into a mixture of propionitrile and alcohol diluted with ether (⅓ vol.), crystallises in prisms, decomposing at about 92° into EtCl and propionamide (Pinner, *B.* 16, 1654).

PROPIONITRILE *v.* *Nitrile* of Propionic acid.

PROPIONYL-ACETOPHENONE *v.* Phenyl-methylene-ethyl-diketone.

PROPIONYL-BENZOIC ACID *v.* Phenyl ethyl ketone carboxylic acid.

PROPIONYL BROMIDE *v.* *Bromide* of Propionic acid.

PROPIONYL-BUTYRIC ACID $C_2H_5.CO.CMe_2.CO_2H$.

Methyl ether MeA'. (188° uncor.). Formed by the action of MeOH and HCl on the nitrile $C_2H_5.CO.CMe_2$.CN (175°), which is got by the action of cold HCl upon $C_2H_5.C(NH).CMe_2$.CN [43°] which is made by the action of MeI on the product of the action of Na on propionitrile (Bouveault, *C. R.* 111, 531). Liquid.

PROPIONYL CHLORIDE *v.* *Chloride* of Propionic acid.

PROPIONYL CYANIDE C_4H_5NO *i.e.* $CH_3.CH_2$.CO.CN. (109°). Prepared by heating propionyl chloride (12 g.) with silver cyanide (8 g.) in closed tubes for 1 hour at 100°. The product is fractionally distilled (Claisen a. Moritz, *C. J.* 37, 692). HCl converts it into ethyl-glyoxylic acid (*q. v.*).

Di-propionyl di-cyanide $(Et.CO)_2C_2N_2$. [59°]. (208°). V.D. 5·6 (calc. 5·7). Obtained in the preparation of the preceding (C. a. M.) and by the action of AgCy on propionyl bromide (Lobry de Bruyn, *R. T. C.* 3, 390). Prisms, sl. sol. water, sol. alcohol and ether.

PROPIONYL-CYANO-ACETIC ETHER *v.* Cyano-acetic acid.

PROPIONYL-MALONIC ETHER $C_{10}H_{16}O_5$ *i.e.* $C_2H_5.CO.CH(CO_2Et)_2$. (239°–242° uncor.). Formed by the action of propionyl chloride upon sodio-malonic ether (Lang, *B.* 20, 1326). Colourless liquid.

PROPIONYL-PHENOL *v.* Oxy-phenyl ethyl ketone.

α-PROPIONYL-PROPIONIC ACID $C_6H_{10}O_3$ *i.e.* $CH_3.CH_2.CO.CHMe.CO_2H$.

Methyl ether $C_2H_5.CO.CHMe.CO_2Me$ or $C_2H_5.C(OH):CMe.CO_2Me$. (187° cor.). S.G. $\frac{20}{}$ 1·07. Formed by the action of Na on methyl propionate (Pingel, *A.* 245, 84). Colourless liquid with aromatic odour. Converted by ammonia into $C_7H_{13}NO_2$ and a hygroscopic substance $C_{12}H_{12}N_2O_4$ (?) [82°]. Aniline forms oxy-methyl-ethyl-quinoline [295°] (Bouveault, *C. R.* 111, 41). NaOHAq yields a mixture of di-ethyl ketone and methyl ethyl ketone. NaOEt followed by alkyl iodides yields the alkyl derivatives: $C_7H_{11}MeO_3$ or $CEt(OMe):CMe.CO_2Me$ [194°], $C_7H_{11}EtO_3$ (208°), $C_7H_{11}PrO_3$ (220°), and $C_7H_{11}(CH_2Pr)O_3$ (231°), all being liquid.

Ethyl ether EtA'. (199°). S.G. $\frac{0}{4}$ ·995; $\frac{15}{4}$ ·983. Formed by digesting propionic ether in Et_2O with Na (Oppenheim a. Hellon, *B.* 10, 699; Israel, *A.* 231, 197). Gives no colour with $FeCl_3$. Ammonia forms $C_8H_{15}NO_2$ (195°), insol.

water, and a hygroscopic substance [75°]. NaOHAq forms di-ethyl ketone. NaOEt and EtI yield propionic ether and $CH_3.CHEt.CO_2H$ (Geuther, *A.* 239. 386). Na followed by EtI added to the solution in benzene forms $C_2H_5.C(OEt):CMe.CO_2Et$ (206°), S.G. ^{15} ·966. Reduced by HI and P to $CHMePr.CO_2H$ (193°). Nitrous acid yields $CH_3.C(NOH).CO_2Et$ [94°] (Hantzsch a. Wohlbrück, *B.* 20, 1320).

Amide $C_3H_5O.CHMe.CO.NH_2$. [153°]. Formed by adding water to the product of the action of $AlCl_3$ on a mixture of propionyl chloride and propionitrile (Otto a. Tröger, *B.* 22, 1455). Needles, sl. sol. cold water.

Nitrile $C_2H_5.CO.CHMe.CN$. (c. 188°). Formed by the action of cold conc. HClAq on the product of the action of Na on propionitrile (Meyer, *J. pr.* [2] 38, 339). Oil. Converted by ammonia into the imide [45°]. Hydroxylamine forms the oxim $C_2H_5.C(NOH).CHMe.CN$ [44°] (180° at 200 mm.) (Hanriot, *C. R.* 112, 796). Aniline yields amido-methyl-ethyl-quinoline (Hanriot a. Bouveault, *Bl.* [3] 1, 552).

Propionyl-propionic acid $CH_3.CH_2.CO.CH_2.CH_2.CO_2H$. [33°]. A product of the action of boiling water on di-bromo-hexoic acid (from hydrosorbic acid and Br) (Fittig, *A.* 268, 69). Crystalline, v. e. sol. water, alcohol, and ether.—$CaA'_2 1\frac{1}{2}aq$: plates.—AgA'.

PROPIONYL - PROPIONIC ALDEHYDE $C_2H_5.CO.CHMe.CHO$. [c. 40°]. (165°). Formed by adding a well-cooled mixture of formic ether (11 g.) and di-ethyl ketone (13 g.) to NaOEt (10·5 g.) suspended in dry ether (10 g.). After 12 hours the product is acidified and distilled under 50 mm. pressure (Claisen a. Meyerowitz, *B.* 22, 3273). Crystals, v. sol. water. Deliquesces and turns brown in air. NH_3 forms deliquescent crystals of $(C_6H_{10}O_2)NH_3$. $Cu(OAc)_2$ added to its alcoholic solution forms $Cu(C_6H_9O_2)_2$ [168°]. Phenyl-hydrazine produces $C_{12}H_{14}N_2$ (283°).

PROPIOPHENONE *v.* PHENYL ETHYL KETONE.

PROPYL. The radicle C_3H_7. *n*-Propyl $CH_3.CH_2.CH_2$ changes in some reactions to isopropyl $(CH_3)_2CH$ and *vice versâ*.

Pr changes to Pr: 1. When cumyl alcohol is reduced to *n*-cymene by boiling with zinc-dust (Kraut, *A.* 192, 225; Jacobsen, *B.* 12, 431). — 2. When cumyl chloride is reduced to *n*-cymene by zinc and HCl (*J.* 1879, 369). — 3. When nitro-cymylene chloride is reduced to *n*-cymidine by boiling with zinc and HCl (Widman, *B.* 15, 166; 19, 245).—4. When isopropyl-cinnamic acid is reduced by sodium-amalgam to *n*-cumyl-propionic acid.—5. When *o*-amido-isopropyl-cinnamic acid is reduced by sodium-amalgam to (*B.* 5)-*n*-propyl-(*Py.* 3)-oxy-quinoline dihydride.

Pr changes to Pr: 1. When *n*-cymene is oxidised to cuminic acid—(*a*) by passing through the organism, (*b*) by air and gaseous NaOH (*B.* 5, 749; 12, 512; 11, 369; 14, 1144).—2. When *n*-cymene sulphonic acid is oxidised to oxy-isopropyl-sulpho-benzoic acid by alkaline $KMnO_4$ (Meyer a. Boner, *B.* 14, 1136, 2391; *A.* 220, 6).—3. When *n*-cymene is oxidised to oxyisopropyl-benzoic acid by alkaline $KMnO_4$.—4. When thymol is oxidised by KOH fusion to the oxy-cuminic acid, which is obtained from *m*-nitro-cuminic acid by reduction and diazotisation (Barth, *B.* 11, 1571).—5. When carvacrol (which contains *n*-propyl, since by distillation with P_2S_5 it gives *n*-cymene) is oxidised by KOH fusion to the oxy-cuminic acid [93°], which is obtained from *o*-amido-cuminic acid by diazotisation (*B.* 6, 936; 9, 1061).—6. Since cuminol is always accompanied in plants by *n*-cymene, it is probably produced by oxidation of the latter.—7. When *n*-propyl bromide is boiled with $AlBr_3$ (Gustavson, *C. J.* 44, 565).

From the above may be deduced the general law: *When a propyl group in a benzene derivative occurs in the para- position to* Me, CHO, *or* CO_2H, *it is predisposed to be* NORMAL *by* Me, ISO *by* CHO *or* CO_2H (Widman, *B.* 19, 251, 273, 2769, 2781; *cf.* Fileti, *G.* 16, 300, 497).

Dipropyl *v.* HEXANE.

DI-PROPYL-ACETAL *v.* ALDEHYDE.

PROPYL ACETATE *v. Acetyl derivative* of PROPYL ALCOHOL.

PROPYL-ACETIC ACID *v.* VALERIC ACID.

Di-propyl-acetic acid *v.* OCTOIC ACID.

PROPYL-ACETOACETIC ETHER *v.* vol. i. p. 23.

DI-PROPYL-ACETONE *v.* METHYL HEPTYL KETONE.

PROPYL-ACETYLENE *v.* PENTINENE.

DI-PROPYL-ACRYLIC ACID *v.* ENNENOIC ACID.

***n*-PROPYL ALCOHOL** C_3H_8O *i.e.* $CH_3.CH_2.CH_2OH$. Mol. w. 60. (97·4° i.V.). S.G. $\frac{0}{0}$ ·8177 (Zander, *A.* 224, 79); $\frac{15}{15}$ ·8088; $\frac{25}{25}$ ·8025 (Perkin); $\frac{20}{4}$ ·8044 (Brühl, *A.* 203, 268). C.E. (0°-10°) ·00082. M.M. 3·77 at 15·6°. μ_β 1·3901. R_∞ 28·0. H.F.p. 82,000 (Berthelot); 65,690 (Thomsen). S.V. 81·3 (R. Schiff, *A.* 220, 101). S.H. ·670 (Diaconoff, *Bl.* [2] 38, 172). Occurs in fusel oil, especially in that of wine (Chancel, *C. R.* 37, 410; 68, 659, 726; Pierre a. Puchot, *C. R.* 66, 302; 70, 406; Linnemann, *A.* 160, 195; Fittig, *Z.* [2] 4, 44; Ekman, *Chem. Zeit.* 12, 564). Thus 40 g. of it were found in 100 litres of old cognac (Ordonneau, *C. R.* 102, 217; Clandon a. Morin, *C. R.* 104, 1187; 105, 1019). A litre of potato-fusel oil was found to contain 30 c.c. of *n*-propyl alcohol, 150 c.c. of isopropyl alcohol, 115 c.c. of butyl alcohols, 335 c.c. of amyl alcohols, 125 c.c. of water, and 245 c.c. of other bodies (Rabuteau, *C. R.* 87, 501). Propyl alcohol also occurs, together with isopropyl alcohol, among the products of the lactic and butyric fermentation of sugar (Bouchardat, *C. R.* 78, 1145; Meyer a. Forster, *B.* 9, 535), and in the fermentation of glycerin (Fitz, *B.* 13, 36, 1311).

Formation.—1. By reducing propionic anhydride with sodium-amalgam (Linnemann, *A.* 148, 251; 160, 231; 161, 18).—2. By adding sodium-amalgam and dilute H_2SO_4 to a solution of propionic aldehyde (1 pt.) in water (18 pts.) (Rossi, *C. R.* 70, 129).—3. By heating allyl alcohol with KOH (Tollens, *Z.* [2] 7, 242).

Properties.—Liquid with alcoholic odour, miscible with water, but separated from the solution by $CaCl_2$. Does not yield isopropyl alcohol when heated in sealed tubes (Aronstein, *R. T. C.* 1, 134). When propyl alcohol (71·46 c.c.) is mixed with water (28·54 c.c.), contraction (1·85 c.c.) is observed (Ramsay a. Young, *C. J. Proc.* 4, 101).

Reactions.—1. *Chromic acid* oxidises it to propionic aldehyde and acid.—2. HBr and H_2SO_4 give propyl bromide, propylene bromide, and $C_3H_5Br_3$ (Niemilovitch, *M.* 10, 820).—3. I and KOHAq form iodoform (Lieben, *A. Suppl.* 7, 230).—4. Fused $ZnCl_2$ forms propylene, isobutyl alcohol, $CH_2{:}CMe_2$, and CHMe:CHMe (Le Bel a. Greene, *C. R.* 89, 413).—5. *Phosphoplatinous chloride* followed by water forms crystalline $P(OPr)_3PtCl_2$ (Pomey, *C. R.* 104, 364).—6. *Calcium chloride* yields $(C_3H_8O)_3CaCl_2$ crystallising in needles (Göttig, *B.* 23, 181).

Metallic derivatives. KOPr (De Forcrand, *C. R.* 104, 68).—NaOPr2HOPr (Fröhlich, *A.* 202, 295). $Ba_2(OPr)_2(OH)_2$. Formed by heating propyl alcohol with BaO under pressure (Destrem, *A. Ch.* [5] 27, 32). Yields propylene, methane, and hydrogen when heated. The corresponding lime compound yields di-ethyl ketone when heated.—$Al(OPr)_3$. [c. 60°]. S.G. ^{4} 1·026. Formed in small quantity from propyl alcohol, AlI_3, and Al (Gladstone a. Tribe, *C. J.* 39, 6). Isopropyl alcohol does not react in this way.

Acetyl derivative PrOAc. *Propyl acetate.* (102°). S. 1·5 at 16° (Linnemann, *A.* 161, 30). S.G. $\frac{0}{4}$ ·9091 (E.); $\frac{20}{4}$ ·8856 (Brühl); $\frac{0}{0}$ ·9093 (Gartenmeister); $\frac{15}{15}$ ·8933; $\frac{25}{25}$ ·8840 (Perkin, *C. J.* 45, 421). C.E. (0°–10°) ·001197 (Elsässer, *A.* 218, 320). S.V. 128·3. μ_β 1·3890. R_∞ 43·11. M.M. 5·487 at 15·2°. Liquid. Not changed into isopropyl acetate by heating in a sealed tube (Aronstein, *R. T. C.* 1, 134).

Benzoyl derivative BzOPr. (230° cor.). S.G. ^{18} 1·032 (Linnemann).

Isopropyl alcohol $(CH_3)_2CH.OH$. (83° cor.). S.G. $\frac{0}{0}$ ·7996 (Zander); $\frac{15}{15}$ ·7914; $\frac{25}{25}$ ·7845 (Perkin); $\frac{20}{4}$ ·7887 (Brühl, *A.* 203, 12). μ_β = 1·3821. R_∞ 27·99. M.M. 4·019 at 17·9°. S.V. 81·7 (R. Schiff, *A.* 220, 331); 82·8 (Zander). C.E. (0°–10°) ·00108. H.F.p. 71,000. H.F.v. 68,970 (Thomsen, *Th.*).

Formation.—1. By distilling $PrO.SO_3H$ (made from propylene and H_2SO_4) with water (Berthelot, *J.* 1855, 611).—2. By reducing acetone or propylene oxide with sodium-amalgam (Friedel, *A.* 124, 327; Linnemann, *A.* 140, 178).—3. By heating a solution of *n*-propylamine nitrite (Linnemann, *A.* 161, 43; *B.* 10, 1111; Meyer, *B.* 9, 535).—4. By the action of sodium-amalgam on $(CH_2Cl)_2CH.OH$ dissolved in wet ether (Buff, *Z.* [2] 4, 124).—5. From $CH_2I.CH_2OH$ by successive treatment with $ZnMe_2$ and water (Butlerow a. Ossokin, *A.* 145, 257).

Preparation.—1. *Acetone* (1 vol.) is diluted with water (5 vols.) and sodium-amalgam is slowly added. The liquid is distilled and the process repeated upon the distillate (Linnemann, *A.* 136, 87).—2. By boiling isopropyl iodide (1 pt.) with water (10 pts.) and $Pb(OH)_2$ (Flavitzky, *A.* 175, 380).—3. By heating isopropyl iodide (1 pt.) with water (20 pts.) at 100° for 40 hours (Niederist, *A.* 186, 391).

Properties.—Liquid with peculiar odour, not solid at −20°. Inactive to light. Miscible with water, yielding on distillation the hydrate $(C_3H_8O)_3 2aq$ (80°), S.G. ^{15} ·832. When K_2CO_3 is added to an aqueous solution of the alcohol a hydrate $(C_3H_8O)_2aq$ separates (Erlenmeyer, *A.* 126, 307). After drying over $CuSO_4$ the hydrate $(C_3H_8O)_3aq$ (81°) S.G. ^{15} ·800 is left. Dilute CrO_3 forms acetone. *Bromine* forms acetone and PrBr.

Acetyl derivative PrOAc. *Isopropyl acetate.* (91°). S.G. ^{0} ·917 (Friedel, *A.* 124, 327; Pribram a. Handl, *M.* 2, 686).

Benzoyl derivative PrOBz. (218°) (Silva, *Bl.* [2] 12, 225). Liquid. Split up by distillation into benzoic acid and propylene (Linnemann, *A.* 161, 51).

References.—Bromo-, Chloro-, Chloro-iodo-, and Iodo- Propyl alcohol.

PROPYL ALDEHYDE *v.* Propionic aldehyde.

PROPYL-DI-ALLYL-CARBINOL *v.* Decinyl alcohol.

PROPYLAMIDOACETIC ACID $NHPr.CH_2.CO_2H$. Formed from $CH_2Br.CO_2Et$ and NH_2Pr (Chancel, *Bl.* [3] 7, 409; *C. R.* 114, 756). Needles, v. sol. water and alcohol, insol. ether.—$(HA')_2H_2PtCl_6$ aq.—$CuA'_2 2aq$: crystals, v. sol. water and alcohol.

PROPYL-AMIDO-ISOPROPYL ALCOHOL $C_6H_{15}NO$ *i.e.* $CH_3.CH(OH).CH_2.NHC_3H_7$. Formed by heating allyl-propyl-amine with H_2SO_4 (3½ pts.) at 135° (Liebermann a. Paal, *B.* 16, 532).—$B'_2H_2PtCl_6 2aq$: nodules (from water).

Di-propyl-amido-isopropyl alcohol $CH_3.CH(OH).CH_2.N(C_3H_7)_2$. Formed in like manner from allyl-di-propylamine.—$B'_2H_2PtCl_6$.

***n*-PROPYLAMINE** C_3H_9N *i.e.* $CH_3.CH_2.CH_2.NH_2$. Mol. w. 59. (49°). S.G. $\frac{15}{15}$ ·7222; $\frac{25}{25}$ ·7144. H.F.p. 22,760. H.F.v. 20,420 (Thomsen, *Th.*). S.V. 85·6. M.M. 4·564 (Perkin, *C. J.* 55, 693). μ_D = 1·3873 (Gladstone, *C. J.* 59, 290).

Formation.—1. By reduction of propionitrile. Using 36 g. of propionitrile, 500 g. alcohol, 200 g. water, zinc, and 500 g. of 20 p.c. HClAq, the yield is 9 g. (Mendius, *A.* 121, 129; Linnemann, *A.* 161, 44).—2. From *n*-propyl iodide by successive treatment with silver cyanate and KOHAq (Silva, *Z.* [2] 5, 638).—3. By heating *n*-propyl iodide with alcoholic NH_3, and distilling the product with potash. The fraction boiling below 78° is mixed with alcohol and oxalic ether, and the di-propyl-oxamide [161·5°] thus formed distilled with alcoholic potash (Vincent, *C. R.* 103, 208). *n*-Propyl iodide heated with conc. NH_3Aq for 13 hours at 100°–150° forms propylamine hydriodide and NPr_4I (Malbot, *A. Ch.* [6] 13, 480, 546).—4. When *n*-propyl chloride is heated with aqueous ammonia in equimolecular proportions at 140°–165°, one-fifth of the product is *n*-propylamine and is nearly all contained in the lower layer. The upper layer consists of free di- and tri- propyl-amines, water, and alcohol (Malbot, *C. R.* 104, 998).—5. By heating *n*-propyl nitrate with alcoholic NH_3 at 100° (Wallach, *A.* 214, 311).

Preparation.—1. A mixture of equimolecular quantities of bromine and butyramide is run into an excess of a 10 p.c. solution of KOH at 60° and the propylamine distilled off; the yield is 80–90 p.c. (Hofmann, *B.* 15, 769). It may be dried over CaO and afterwards over Na.—2. PrCl (1 mol.) heated with aqueous NH_3 (1 mol.), and enough alcohol to effect solution, in sealed tubes at 110° forms 45 p.c. propylamine, 35 p.c. dipropylamine, and 20 p.c. tri-propyl-amine (Chancel, *Bl.* [3] 7, 405). The product is neutralised with HCl, the alcohol distilled off, cooled, filtered from separated NH_4Cl, the syrup mixed with NaOH, distilled, and fractionated.

The bases may be further purified by means of their oxalates.

Properties.—Mobile liquid with ammoniacal smell; mixes with water, becoming hot. When wet it boils at 78°–82°. Its aqueous solution ppts. salts of Cu and Fe, the pp. not dissolving in excess, but with $AgNO_3$ it gives a pp. sol. excess.

Reactions.—1. *Chromic acid* yields propionic acid (Chapman a. Thorpe, *A.* 142, 176).—2. *Nitrous acid* forms *n*- and iso- propyl alcohols and propylene (Meyer a. Forster, *B.* 9, 535).—3. *Benzoic aldehyde* forms $C_6H_5.CH:NPr$ (210°) (Zaunschirm, *A.* 245, 282).—4. *Oxalic ether* added to a mixture of equal volumes of propylamine and water forms CONHPr.CONHPr and $CO_2H.CONHPr$ [110°], which yields CaA'_2 2aq. S. 1·38 at 17°.

Salts.—B'HCl. [158°] (Topsoë, *J.* 1883, 621).—$B'HHg_2Cl_5$.—$B'HHg_5Cl_{11}$.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$. Monoclinic crystals.—**Oxalate.** $NH_2Pr\ C_2H_2O_4$ ½aq. Plates. S. 14·8 at 18°; S. (alcohol) ·6 at 18°.—**Picrate** [135°].

Nitramine $CH_3.CH_2.CH_2.NH.NO_2$. (129° at 40 mm.). S.G. ^{15} 1·102. Formed by heating $PrN(NO_2).CO_2Et$ in a current of dry NH_3, and decomposing the product with dilute H_2SO_4 (Thomas, *R. T. C.* 9, 75). Liquid, crystallising at −23°. Decomposes at 142°. Sl. sol. water; decomposes carbonates.—$PrNK.NO_2$. Formed by dissolving the nitramine in alcoholic potash and ppg. with ether. Small pearly plates, forming an alkaline solution in water.—$PrNAg.NO_2$. Slender needles, blackening in light. AcCl yields N_2O.

Isopropylamine $(CH_3)_2CH.NH_2$. (32°). S.G. ^{15} ·690.

Formation.—1. By the action of HClAq on isopropyl-carbamine (Siersch, *A.* 148, 263; Gautier, *C. R.* 67, 723).—2. By running a mixture of bromine (1 mol.) and isobutyramide (1 mol.) into an excess of a 10 p.c. solution of KOH at 60°; the yield being 65 p.c. (Hofmann, *B.* 15, 768).—3. By reducing acetoxim dissolved in alcohol with sodium-amalgam and HOAc at 40° (Goldschmidt, *B.* 20, 728).—4. By heating isopropyl iodide with conc. NH_3Aq (Malbot, *C. R.* 111, 650; *cf.* Jahn, *M.* 3, 166).

Preparation.—By reduction of a solution of acetone-phenyl-hydrazide (1 pt.) in 96 p.c. alcohol (10 pts.) by means of acetic acid (2½ pts.) and sufficient ·67 p.c. sodium-amalgam, the temperature being kept below 25°; the yield is 70 p.c. of the theoretical (Tafel, *B.* 19, 1926).

Properties.—Mobile liquid, with ammoniacal smell, miscible with water. Converted by nitrous acid into isopropyl alcohol.

Salts.—B'HCl. [140°]. Deliquescent cubes.—$B'_2H_2PtCl_6$: orange plates, m. sol. Aq.

Nitramine $PrNH.NO_2$. [−4°]. (91°). S.G. ^{15} 1·098. Formed from $PrN(NO_2).CO_2Et$ by successive treatment with dry NH_3 and dilute H_2SO_4 (Thomas, *R. T. C.* 9, 78). Needles.—$PrNK.NO_2$. Slender hygroscopic needles.—$PrNAg.NO_2$. Thin plates. Converted by PrI into $PrNPr.NO_2$ (67° at 10 mm.).

Di-*n*-propylamine Pr_2NH. (110°) (P. a. C.); (98°) (V.). S.G. $\frac{15}{15}$ ·7480; $\frac{25}{25}$ ·7857 (Perkin, *C. J.* 55, 698). M.M. 7, 549. $\mu_\gamma = 1·4083$ (Gladstone, *C. J.* 59, 290). A product of the action of alcoholic NH_3 on PrI at 100° (Vincent, *C. R.* 103, 208; *Bl.* [2] 46, 287) or of aqueous NH_3 on PrCl at 190° (Malbot, *C. R.* 105, 575). Purified by means of its nitrosamine. Liquid with ammoniacal smell, sl. sol. water. The pps. that it forms with salts of Ag and Al are sol. excess; those with salts of Cu and Zn are insol. excess.

Salts.—$B'H_2C_2O_4$. Flat needles. S. 5 at 17°. S. (alcohol) ·33 at 18° (Chancel, *Bl.* [3] 7, 406). **Picrate.** [75°]. S. 2·2 at 19°. Melts under water at 45°.

Nitrosamine $Pr_2N.NO$. (206°). S.G. $\frac{0}{0}$ ·931. Liquid smelling like hay. Decomposed by HClAq, with formation of dipropylamine.

Nitramine $Pr_2N.NO_2$. A liquid, got from $PrNK.NO_2$ and PrBr (Thomas, *R. T. C.* 9, 79).

Di-isopropylamine Pr_2NH. (84°). S.G. ^{22} ·722. A product of the action of alcoholic NH_3 on PrI at 100° (Van der Zande, *R. T. C.* 8, 202; *cf.* Siersch, *Z.* [2] 5, 145). Liquid with very ammoniacal odour, miscible with water.—$B'HNO_3$. [138°].—$B'_2H_2PtCl_6$: orange tables.

Nitrosamine $Pr_2N.NO$. [46°]. (195°).

Nitramine $Pr_2N.NO_2$. (56° at 10 mm.). Formed from $PrNAg.NO_2$ and PrI (Thomas, *R. T. C.* 9, 82). Liquid.

Tri-*n*-propylamine Pr_3N. (157°). S.G. $\frac{0}{0}$ ·770; $\frac{15}{15}$ ·760; $\frac{25}{25}$ ·751 (Perkin). S.V. 222·1 (Zander, *A.* 214, 171). M.M. 11·664. $\mu_D = 1·4171$ (Gladstone, *C. J.* 59, 290). C.E. (0°–10°) ·00105. A product of the action of PrI on alcoholic NH_3 (V.). It is the chief product got by heating PrCl with conc. NH_3Aq (Malbot, *A. Ch.* [6] 13, 480, 546). Purified by means of its picrate (Chancel, *Bl.* [3] 7, 407). Liquid with faintly ammoniacal odour, almost insol. water.—**Picrate.** S. ·3 at 18°; S. (94 p.c. alcohol) 4·4 at 19°.

Propylo-iodide Pr_4NI. The chief product of the action of PrI on NH_3Aq at 150°–190°. Prisms. Yields $(Pr_4NCl)_2PtCl_4$ and deliquescent Pr_4NOH, which is decomposed by heat into Pr_3N, propylene, and water (Roemer, *B.* 6, 784).

References.—BROMO-, CHLORO-, CHLORO-IODO-, and OXY- PROPYLAMINE.

PROPYL-ISOAMYL-GLYOXALINE $C_6H_9(C_5H_{11})N_2$. *Oxalisoamyl-butyline.* (251°). S.G. ^{18} ·920. Formed from propyl-glyoxaline and $C_5H_{11}I$ (Rieger, *M.* 9, 609).

PROPYL ISOAMYL OXIDE $Pr.O.C_5H_{11}$. (125°–130°) (Chancel, *A.* 151, 305).

PROPYL-ANILINE $C_9H_{13}N$ *i.e.* PhNHPr. (222° i.V.) (Pictet a. Crépieux, *B.* 21, 1111). S.G. $\frac{18}{4}$ ·949. Formed by heating aniline with PrBr (Claus a. Roques, *B.* 16, 909; Wacker, *A.* 243, 290). Liquid. **Salts.**—*B'HCl. [150°].—*$B'_2H_2C_2O_4$. [152°]. Large tables, v. sol. water.

Formyl derivative PhNPr(CHO). (269° i.V.). S.G. $\frac{16}{4}$ 1·044. Got from formanilide and *n*-propyl bromide.

Acetyl derivative PhNPrAc. [48°]. (269° i.V.). Hexagonal plates (from ligroïn).

Nitrosamine. Yellow oil.

Isopropyl-aniline PhNHPr (213° i.V.). Liquid. Yields an oily nitrosamine.—$B'_2H_2PtCl_6$. Red prisms (P. a. C.).

Formyl derivative PhNPr.NO. (264° i.V.). Formed from formanilide and PrBr.

Acetyl derivative PhNPrAc. [39°]. (265° i.V.). Transparent leaflets (from ligroïn).

Di-*n*-propyl-aniline NPhPr$_2$. (245° i.V.): S.G. $\frac{0}{0}$ ·9240. S.V. 243·1 (Zander, *A.* 214, 168). C.E. (0°-10°) ·00081. Formed from aniline and PrI (Lippmann a. Fleissner, *M.* 3, 711).—B$'_2$H$_2$PtCl$_6$. Decomposed by water.

Di-isopropyl-aniline NPhPr$_2$. (220° i.V.). S.G. $\frac{0}{0}$ ·9338. S.V. 235·4 (Zander). C.E. (0°-10°) ·00087.

References.—Nitro- and Nitroso- Propyl-aniline.

DI-PROPYL-ANTHRACENE DIHYDRIDE $C_{20}H_{24}$ *i.e.* $C_6H_4<\substack{CPr_2\\CH_2}>C_6H_4$. Formed from di-propyl-anthrone, HI, and P at 140°-170° (Hallgarten, *B.* 22, 1070). Plates, getting soft at 47°.

Di-isopropyl-anthracene dihydride $C_6H_3Pr<\substack{CH_2\\CH_2}>C_6H_3Pr$. [90°]. (above 360°). Formed by boiling $C_6H_4Pr.CH_2Cl$ alone or with $ZnCl_2$ (Errera, *G.* 14, 280). Amorphous yellow powder, insol. alcohol, sol. ether. Its solutions are red with green fluorescence.

PROPYL-ANTHRANOL. *Propyl derivative.* $C_{20}H_{22}O$ *i.e.* $C_6H_4<\substack{CPr\\C(OPr)}>C_6H_4$. [72°]. Formed by boiling anthranol with KOHAq and PrI (Hallgarten, *B.* 22, 1070). Needles, sol. ether and alcohol, insol. alkalis. Chromic acid solution converts it in the cold into propyl-oxanthranol $C_{17}H_{16}O_2$ [164°], v. sol. benzene.

DI-PROPYL-ANTHRONE $C_{20}H_{22}O$ *i.e.* $C_6H_4<\substack{CO\\CPr_2}>C_6H_4$. [124°]. Formed, together with the preceding body, by boiling anthranol (5 g.) with KOH (5 g.), water (25 c.c.), and PrI (13 g.) (Hallgarten, *B.* 22, 1069). Trimetric crystals, sol. hot alcohol. CrO_3 in HOAc oxidises it to anthraquinone.

TRI-PROPYL-ARSINE *v.* vol. i. p. 319.

PROPYL-BENZENE *v.* Cumene.

Di-*n*-propyl-benzene $C_6H_4Pr_2$[1:4]. (219°). Formed from *p*-di-bromo-benzene, *n*-propyl bromide, and Na (Körner, *B.* 11, 1863; *A.* 216, 223). Formed also, together with the *m*-isomeride, by the action of $AlCl_3$ and HCl on *n*-cumene (Heise a. Töhl, *A.* 270, 165). Liquid, volatile with steam. Bromine forms $C_6H_2Br_2Pr_2$ [48°].

***n*-iso-Di-propyl-benzene** C_6H_4PrPr[1:4]. (212° cor.). S.G. ^{0} ·8713. Formed from $C_6H_4Pr.CH_2Cl$ and $ZnEt_2$ (Paterno a. Spica, *B.* 10, 1746) and from PrBr, *p*-bromo-cumene, and Na. Formed also, together with the *m*- isomeride, by the action of $AlCl_3$ at −2° on a mixture of *n*-cumene and PrBr (Heise, *B.* 24, 772).

***m*-Di-isopropyl-benzene** $C_6H_4Pr_2$[1:3]. (204°). Formed, together with the *p*- isomeride, by the action of propyl or isopropyl chloride on benzene in presence of $AlCl_3$ (Silva, *Bl.* [2] 43, 320; Uhlhorn, *B.* 23, 3142) and by the action of $AlCl_3$ and HCl at 100° on cumene (H. a. T.). Yields isophthalic acid on oxidation.

***p*-Di-isopropyl-benzene** $C_6H_4Pr_2$[1:4]. (c. 202°). Formed as above. Yields terephthalic acid on oxidation.

PROPYL-BENZENE SULPHONIC ACID *v.* Cumene sulphonic acid.

***p*-Di-*n*-propyl-benzene sulphonic acid** $C_6H_3Pr_2.SO_3H$. [62°]. Formed from di-propyl-benzene and fuming H_2SO_4 (Körner, *B.* 11, 1865; *A.* 216, 224; Remsen, *Am.* 5, 162). Deliquescent needles, with pearly lustre.—NaA′4aq.—KA′4aq.—BaA$'_2$ ½aq.—BaA$'_2$ 2aq.—CaA$'_2$ 9aq.—PbA$'_2$ aq.

Amide $C_6H_3Pr_2.SO_2NH_2$. [103°]. Hexagonal crystals (from alcohol), sl. sol. hot water.

***n*-iso-Di-propyl-benzene sulphonic acid** [1:4:*x*] $C_6H_3PrPr.SO_3H$. [60°]. Needles (Heise, *B.* 24, 771).—BaA$'_2$ *x*aq.—PbA$'_2$ aq: minute needles, m. sol. cold water.—PbA$'_2$ 8aq: needles.

Amide. [96°]. Needles.

***m*-Di-isopropyl benzene sulphonic acid** $C_6H_3Pr_2.SO_3H$ [1:3:*x*]. Formed by shaking with H_2SO_4 (1½ pts.) the fraction (200°-210°) got by the action of $AlCl_3$ on a mixture of PrCl and benzene, and separated from the accompanying *p*-di-isopropyl-benzene sulphonic acid by means of its Ba salt (Uhlhorn, *B.* 23, 3142).—BaA$'_2$ 2aq: needles, sl. sol. water.—CuA$'_2$ 4½aq.—MgA$'_2$ 4aq.

Amide $C_6H_3Pr_2.SO_2NH_2$. [145°].

***p*-Di-isopropyl-benzene sulphonic acid** $C_6H_3Pr_2(SO_3H)$ [1:4:2]. Formed as above.—BaA$'_2$: nodules, v. sol. water.—CuA$'_2$ 6½aq.

Amide $C_6H_3Pr_2.SO_2NH_2$. [102°].

***m*-Di-*n*-propyl-benzene disulphonic acid** $C_6H_2Pr_2(SO_3H)_2$. Deliquescent tables (Heise).—K$_2$A″ *x*aq.—BaA″ 1½aq: tables, v. sol. water.—PbA″ 1½aq: tables, v. e. sol. warm water.

Amide. [195°]. Needles.

PROPYL-BENZOIC ACID *v.* Cuminic acid.

PROPYL-BENZOYL-ACETIC ACID *v.* Benzoyl-acetic acid and Phenyl butyl ketone carboxylic acid.

PROPYL-BENZYL- *v.* Cuminyl-.

***n*-PROPYL BORATE** $(PrO)_3B$. (172°-175°). S.G. ^{16} ·867 (Cahours, *C. R.* 76, 1383).

Isopropyl borate $(PrO)_3B$. (140° cor.). Formed by heating B_2O_3 with isopropyl alcohol at 120° (Councler, *J. pr.* [2] 18, 389). Mobile oil, slowly saponified by water.

***n*-PROPYL BROMIDE** PrBr. (71°). S.G. $\frac{0}{0}$ 1·3835 (Zander, *A.* 214, 159); $\frac{20}{4}$ 1·3520 (Brühl, *A.* 203, 13); $\frac{15}{15}$ 1·3611; $\frac{25}{25}$ 1·3474 (Perkin). C.E. (0°-10°) ·00123. $\mu_\beta = 1·4406$. $R_\infty = 38·20$. S.V. 97. M.M. 6·885 at 19·2°. H.F.p. 30,850. H.F.v. 29,110 (Thomsen, *Th.*). Formed from *n*-propyl alcohol and HBr (Linnemann, *A.* 161, 40; Pierre a. Puchot, *J. Ph.* [4] 13, 9). When heated in sealed tubes at 280° it partially changes to isopropyl bromide (Aronstein, *R. T. C.* 1, 134). When heated for a short time with $AlBr_3$ it is completely changed to isopropyl bromide (Kekulé a. Schrötter, *B.* 12, 2279; Gustavson, *J. R.* 15, 61). Bromine forms propylene bromide.—$C_3H_7Br(H_2S)_2$ 23aq (De Forcrand, *A. Ch.* [5] 28, 35).

Isopropyl bromide PrBr. (60°). S.G. $\frac{0}{0}$ 1·3397 (Z.); $\frac{20}{4}$ 1·3097 (B.); $\frac{15}{15}$ 1·3198; $\frac{25}{25}$ 1·3052 (Perkin). C.E. (0°-10°) ·00127. $\mu_\beta = 1·4317$. R_∞ 38·58 (Brühl). M.M. 7·003 at 17·1°. S.V. 99.

Formation.—1. From isopropyl alcohol and HBr at 150° (Linnemann, *A.* 136, 41).—2. From *n*-propyl bromide and $AlBr_3$.—3. From propylene bromide and HI (Linnemann, *A.* 161, 57).

Preparation.—By adding bromine (65 g.) gradually to PrI (100 g.) in the cold; the yield being 45 g. (R. Meyer, *J. pr.* [2] 34, 105).

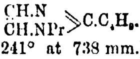
Properties.—Liquid, not attacked by Cl.

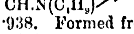
ISOPROPYL-BUTENYL-BENZENE *v.* Butenyl-cumene.

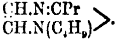
***n*-PROPYL-ISOBUTYL-AMINE** $C_7H_{17}N$ *i.e.* $PrNH.C_4H_9$. (124°). Formed by reducing isobutyl-propargyl-amine in alcoholic solution with

sodium (Paal a. Heupel, *B.* 24, 3048).—$B'HCl$. [185°].—$B'H_2C_2O_4$. [224°]. Needles.

ISOPROPYL-BUTYL-AMINE DICARBOXYLIC ACID $C_9H_{17}NO_4$ *i.e.* $CO_2H.CMe_2.NH.CMe_2.CH_2.CO_2H$. A product of the oxidation of triacetonamine with chromic acid mixture (Heintz, *A.* 198, 69). Crystalline grains, m. sol. hot water. Yields amido-isobutyric acid when heated. — $H_2A''HCl$. — $KHA''2aq$. — $Zn(HA'')_2\,6aq$. — $ZnA''aq$. — $CuA''aq$.—$AgHA''$.—$Ag_2A''HNO_3aq$: grains.

PROPYL-ISOBUTYL-GLYOXALINE $C_{10}H_{18}N_2$ *i.e.*  $\begin{matrix}CH.N\\CH.NPr\end{matrix}\!\!>C.C_4H_9$. *Oxal-propyl-iso-amyline.* (241° at 738 mm.). S.G. $^{\underline{18}}$ ·915. Formed from isobutyl-glyoxaline and PrBr (Radziszewski a. Szul, *B.* 17, 1295). Liquid.—$B'_2H_2PtCl_6$: minute orange prisms.

Propyl-butyl-glyoxaline  $\begin{matrix}CH.N{:}CPr\\CH.N(C_4H_9)\end{matrix}\!\!>$. (243°) at 728 mm. S.G. $^{\underline{12}}$ ·938. Formed from propyl-glyoxaline and butyl iodide. Oxidised by H_2O_2 to butyl-oxamide [198°] (Rieger, *M.* 9, 609). —$B'HZnCl_3$.—$B'_2H_2CdCl_4$.—$B'_2H_2PtCl_6$.

Propyl-isobutyl-glyoxaline  $\begin{matrix}CH.N{:}CPr\\CH.N(C_4H_9)\end{matrix}\!\!>$. (232°) at 736 mm. S.G. $^{\underline{13}}$ ·940. Formed from propyl-glyoxaline and isobutyl iodide (Rieger).

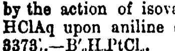
PROPYL ISOBUTYL KETONE $Pr.CO.C_4H_9$. (155°) at 750 mm. S.G. $\frac{0}{0}$ ·831. Formed from isovaleryl chloride and $ZnPr_2$ (Wagner, *J. R.* 16, 668). Liquid.

Isopropyl isobutyl ketone $Pr.CO.CH_2Pr$. (160°). S.G. $^{\underline{14}}$ ·865. Formed by oxidising *sec*-octyl alcohol with cold dilute $K_2Cr_2O_7$ and H_2SO_4 (Williams, *C. J.* 35, 130). Liquid, not solid at −17°. Does not form a crystalline compound with $NaHSO_3$.

PROPYL-ISOBUTYL-MALONIC ACID $C_4H_9.CPr(CO_2H)_2$. [129°]. This appears to be the composition of the acid got by saponifying $C_4H_9.C(C_3H_5)(CO_2Et)_2$ (249°), which is got from malonic ether, isobutyl iodide, allyl iodide, and NaOEt (Ballo, *B.* 14, 335).

PROPYL BUTYL OXIDE $Pr.O.C_4H_9$. (117°). S.G. $\frac{0}{0}$ ·7773. C.E. (0°–10°) ·00124. S.V. 174·4 (Dobriner, *A.* 243, 7).

ISOPROPYL-ISOBUTYL-PHOSPHINE $PHPr.CH_2Pr$. (140°). Formed from isopropyl-phosphine and isobutyl iodide at 130° (Hofmann, *B.* 6, 300).

ISOPROPYL-ISOBUTYL-QUINOLINE  $C_6H_4\!<\!\begin{matrix}CH{:}CPr\\N{=}C.CH_2Pr\end{matrix}$. (296°) at 710 mm. Formed by the action of isovaleric aldehyde and conc. HClAq upon aniline (Spady, *B.* 17, 1718; 18, 3373).—$B'_2H_2PtCl_6$. Yellow needles, sl. sol. water.—$B'C_6H_2(NO_2)_3OH$. Large yellow plates. — $B'HCl\,aq$. — $B'HNO_3\,aq$. — $B'H_2SO_4$. — $B'H_2Cr_2O_7$: orange needles, sol. hot water.

Methylo-iodide $B'MeI\,aq$. Yellow needles, v. sol. alcohol.—$B'_2Me_2PtCl_6$: yellowish-red triclinic prisms.

PROPYL-TRICARBALLYLIC ACID $CHPr(CO_2H).CH(CO_2H).CH_2.CO_2H$. [152°]. Formed by saponifying its ether, which is made by the action of fumaric ether on sodium propyl-malonic ether (Auwers, *B.* 24, 311, 2898). Prisms (containing $x$aq), v. e. sol. ether.

Ethyl ether Et_3A'''. (206° at 16 mm.). S.G. $\frac{19}{4}$ 1·092.

Isopropyl-tricarballylic acid $CHPr(CO_2H).CH(CO_2H).CH_2.CO_2H$. [162°]. Prepared in like manner from isopropyl-malonic ether. Plates or prisms, v. sl. sol. ligroïn.

Ethyl ether Et_3A'''. (206° at 20 mm.). S.G. $\frac{19}{4}$ 1·085.

PROPYL CARBAMATE $NH_2.CO.OPr$. [52°]. (195°). Formed by heating urea with propyl alcohol (Cahours, *C. R.* 76, 1387). Formed also from $Cl.CO_2Pr$ and NH_3 (Roemer, *B.* 6, 1102). Prisms, v. e. sol. water and alcohol.

Isopropyl carbamate $NH_2.CO.OPr$. [87°]. Formed from $Cl.CO_2Pr$ and dry NH_3 (Spica a. Varda, *G.* 17, 165). Hygroscopic needles.

ISOPROPYL-CARBAMINE PrNC. (87°). S.G. ^{9} ·760. Formed from isopropyl iodide and AgCy (Gautier, *C. R.* 67, 723; *A.* 149, 155). HClAq forms isopropyl-formamide.

PROPYL-CARBAMIC ACID $NHPr.CO_2H$.

Methyl ether MeA′. (180° at 755 mm.). S.G. $^{\underline{15}}$ ·992. Liquid (Thomas, *R. T. C.* 9, 71). The nitramine $NPr(NO_2).CO_2Me$. S.G. ^{15} 1·187 is made from $NAgPr(NO_2)$ and $Cl.CO_2Me$.

Ethyl ether EtA′. (186°). Formed from propylamine and chloro-formic ether (Schreiner, *J. pr.* [2] 21, 125).

Isopropyl-carbamic acid $NHPr.CO_2H$.

Methyl ether MeA′. (165·5°). S.G. ^{15} ·981. Liquid. The nitramine $NPr(NO_2).CO_2Me$ S.G. $^{\underline{15}}$ 1·159 is also liquid.

PROPYL-CARBINOL *v.* Butyl alcohol.

Di-propyl-carbinol *v.* Heptyl alcohol.

DI-PROPYL-CARBOBENZONIC ACIDS $C_{20}H_{22}O_2$. Two acids of this formula [139°] and [90°] are formed by heating phenyl benzyl ketone with *n*-propyl alcohol and KOH (Zagumenny, *A.* 184, 166). The acid [139°] forms a di-nitro- derivative [176°].

PROPYL CARBONATE $CO(OPr)_2$. (168° cor.). S.G. $^{\underline{17}}$ ·949 (Roese, *A.* 205, 230).

Propyl orthocarbonate $C(OPr)_4$. (224° cor.). S.G. ^{8} ·911. Formed from NaOPr and chloropicrin (Roese, *A.* 205, 253).

***n*-PROPYL CHLORIDE** PrCl. Mol. w. 78½. (46° i.V.). S.G. $\frac{0}{0}$ ·9123 (Zander, *A.* 214, 156); $\frac{20}{4}$ ·8898 (Brühl, *A.* 200, 179), $\frac{15}{15}$ ·8930; $\frac{25}{25}$ ·8813 (Perkin). M.M. 5·056 at 16°. $\mu_\beta = 1{\cdot}3934$. $R_\infty = 33{\cdot}36$. S.V. 91·6. H.F.p. 37,760. H.F.v. 36,020. C.E. (0°–10°) ·00137. Formed by the action of chlorine on propane and on PrI. Prepared by saturating *n*-propyl alcohol with gaseous HCl, and heating at 125° with conc. HClAq (Malbot, *Bl.* [3] 2, 136; *cf.* Pierre a. Puchot, *A. Ch.* [4] 20, 234). Acts with extreme slowness on alcoholic NH_3 (Vincent, *Bl.* [2] 45, 504). Not changed to PrCl by heating in sealed tubes (Aronstein, *R. T. C.* 1, 134).—$PrCl(H_2S)_2\,23aq$ (De Forcrand, *A. Ch.* [5] 28, 34).

Isopropyl chloride PrCl. (36°). S.G. $\frac{0}{0}$ ·8825 (Z.); $\frac{15}{15}$ ·8688; $\frac{25}{25}$ ·8575 (P.). M.M. 5·159 at 17·2°. S.V. 94. C.E. (0°–10°) ·00142. Formed from isopropyl alcohol and HCl. Chlorine converts it into $CH_3.CCl_2.CH_3$ and $CH_3.CHCl.CH_2Cl$. Partially converted into NH_2Pr by heating with conc. NH_3Aq at 140° (Malbot, *C. R.* 111, 650).

ISOPROPYL CINNAMIC ACID *v.* Cumyl-acrylic acid.

References.—Amido-, Chloro-, and Nitro-Propyl-cinnamic acids.

PROPYL-*m*-CRESOL $C_6H_3MePr.OH$. (230°–235° at 734 mm.). Formed, together with its propyl ether and di-propyl-*m*-cresol, by heating *m*-cresol with propyl alcohol and $MgCl_2$ (Mazzara, *G.* 12, 187, 332). Liquid, sl. sol. water, sol. alcohol and ether. Not solid at −15°. Not coloured by $FeCl_3$. Yields a crystalline nitroso-derivative [140°].

Methyl ether MeA′. (226°) at 740 mm.

Propyl ether PrA′. (235°-240°).

Acetyl derivative AcA′. (240°) at 743 mm.

Isopropyl-*m*-cresol C_6H_3PrMe.OH. (238°). Formed in like manner by heating *m*-cresol with isopropyl alcohol and $MgCl_2$ (Mazzara, *G.* 12, 505). Oil. Yields C_6H_2(NO)PrMe.OH [167°].

Methyl ether MeA′. (215°-220°).

Isopropyl ether PrA′. (230°-235°).

Isomeride *v.* THYMOL.

Propyl-*o*-cresol *v.* CARVACROL and CYMENOL.

Isopropyl-cresol C_6H_3PrMe.OH. (229° cor.). S.G. $\frac{0}{}$ 1·0012. Formed by potash-fusion from the *m*-isocymene derived from camphor (Spica, *G.* 12, 552). Not coloured by $FeCl_3$.

Ethyl ether EtA′. (228° cor.).

Di-propyl-*m*-cresol $C_6H_2Pr_2$Me.OH. (250°). Formed as above. Liquid, yielding a liquid acetyl derivative (255°-260°).

Di-isopropyl-*m*-cresol $C_6H_2Pr_2$Me(OH). (251°). Formed at the same time as isopropyl-*m*-cresol (M.). Liquid smelling like phenol, sl. sol. water, insol. dilute potash.

Methyl ether MeA′. (243°).

Acetyl derivative AcA′. (255°-260°).

ISOPROPYL-CUMIDINE C_6H_4Pr.NHPr. (245°-250°). A product of the action of aniline and $ZnCl_2$ on isopropyl alcohol (Louis, *B.* 16, 111). Liquid. Forms a granular picrate.

ISOPROPYL CYANATE *v.* vol. ii. p. 315.

PROPYL CYANIDE *v.* *Nitrile* of BUTYRIC ACID.

PROPYLENE C_3H_6. Mol. w. 42. S. ·44 at 0°; ·22 at 20° (von Than, *A.* 123, 187). S. (alcohol) 13. S. (H_2SO_4) 200 (Berthelot). H.F.p. 8,220. H.F.v. 2,060 (Thomsen, *Th.*).

Formation.—1. By passing fusel oil, valeric acid, or light petroleum through a red-hot tube (J. W. Reynolds, *A.* 77, 118; Prunier, *J.* 1873, 347).—2. By distilling calcium oxalate with KOAc (Dusart, *A.* 97, 127).—3. By the action of mercury (containing a trace of zinc) and fuming HClAq on allyl iodide (Berthelot a. De Luca, *A.* 92, 306).—4. Mixed with H ($\frac{1}{8}$ vol.), by reducing allyl iodide in alcoholic solution with granulated zinc and HClAq (Tollens a. Henninger, *A.* 156, 156).—5. From allyl iodide and HI (Butlerow, *A.* 145, 271).—6. A product of the action of $ZnEt_2$ on CCl_4 (Rieth a. Beilstein, *A.* 124, 242) on allyl iodide (Wurtz, *Bl.* 5, 51) and on $CHBr_3$ (Beilstein, *Bl.* [2] 2, 51).—7. By boiling *n*- or iso-propyl iodide with alcoholic potash (Freund, *M.* 3, 633; Erlenmeyer, *A.* 139, 228).—8. Together with other hydrocarbons, by treating propylene bromide with water and sodium-amalgam or with zinc and HClAq (Prunier, *C. R.* 76, 98).—9. By heating CCl_2Me_2 or CBr_2Me_2 with Na at 140° (Friedel a. Ladenburg, *Z.* 1868, 48; Reboul, *A. Ch.* [5] 14, 488).—10. Together with cresol, by heating thymol with P_2O_5 (Engelhardt a. Latschinoff, *Z.* 1869, 616).—11. In the manufacture of oil-gas (Armstrong, *C. J.* 49, 74).—12. Together with ethylene, by heating allyl alcohol with P_2O_5 (Béhal, *A. Ch.* [6] 16, 360).—13. By heating $N(C_3H_7)_3$ with C_3H_7Cl at 190° (Malbot, *A. Ch.* [6] 13, 546).

Preparation.—1. By dropping propyl alcohol on strongly-heated $ZnCl_2$ (Le Bel a. Greene, *Am.* 2, 23).—2. By passing gaseous HI into allyl iodide, PrI being also formed (Malbot, *C. R.* 107, 114; *Bl.* [2] 50, 449).—3. By pouring an alcoholic solution of allyl iodide on zinc (Gladstone a. Tribe, *B.* 6, 1550; Niederist, *A.* 196, 358).—4. By dropping propyl alcohol (4 pts.) on P_2O_5 (3 pts.) (Beilstein, *B.* 15, 1498).—5. By mixing isopropyl alcohol (200 g.) with $ZnCl_2$ (650 g.) and heating after twenty-four hours (Friedel a. Silva, *J.* 1873, 322).

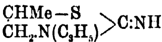
Properties.—Colourless gas, liquefied by a pressure of eight atmospheres (Moltschanoffsky, *J. R.* 21, 31). Unites with Cl and Br. Its solution in H_2SO_4 yields isopropyl alcohol on distilling with water. Cuprous chloride in HClAq absorbs it somewhat. HClAq heated with propylene for seventy hours at 100° forms isopropyl chloride (Berthelot, *A.* 104, 184); HBr and HI act in like manner. Dilute CrO_3 forms acetone acetic acid and CO_2 (Berthelot, *A.* 150, 373). Alkaline $KMnO_4$ forms formic and acetic acids (Truchot, *C. R.* 63, 274). KCl added to a solution of propylene in $PtCl_2$ and HClAq ppts. $C_3H_6PtCl_2KCl$ aq (Birnbaum, *A.* 145, 72).

Di-propylene *v.* HEXYLENE.

References. — BROMO-, DI-BROMO-IODO-, CHLORO-, CHLORO-IODO-, DI-CHLORO-NITRO-, and IODO- PROPYLENE.

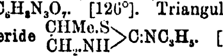
PROPYLENE-ACETOACETIC ACID *v.* ACETO-ACETIC ACID and METHYL TRIMETHYLENYLMETHYL KETONE CARBOXYLIC ACID.

PROPYLENE-ALLYL-ψ-THIO-UREA



$\left.\begin{matrix}\text{CHMe}-\text{S}\\ \text{CH}_2.\text{N}(\text{C}_3\text{H}_5)\end{matrix}\right>$C:NH. Formed from propylene-ψ-thio-urea and allyl iodide (Hirsch, *B.* 23, 973). Oil.—$B'C_6H_3N_3O_7$. [126°]. Triangular prisms.

Isomeride



$\left.\begin{matrix}\text{CHMe.S}\\ \text{CH}_2.\text{NH}\end{matrix}\right>$C:$NC_3H_5$. [56°]. Got from β-bromo-propyl-amine and mustard oil. Prisms (from ligroïn).—$B'C_6H_3N_3O_7$. [130°].—$B'C_3H_5$NCS. [52°]. White prisms.

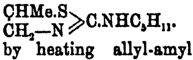
PROPYLENE-DIAMINE $C_3H_{10}N_2$ *i.e.* $CH_3.CH(NH_2).CH_2.NH_2$. (119°). S.G. $\frac{15}{}$ ·878. Formed by heating propylene bromide with alcoholic ammonia at 100°-150° (Hofmann, *B.* 6, 308; Strache, *B.* 21, 2358). Hygroscopic liquid, fuming in the air. Yields a hydrate $(C_3H_{10}N_2)_2$ aq, boiling at the same temperature as the base, and dehydrated by Na. Benzoic aldehyde forms oily $C_3H_6(N:CHPh)_2$, decomposed by HCl into the parent substances. Acetoacetic ether forms oily $C_3H_6(NH.CMe:CH.CO_2Et)_2$.

Salts.—$B''H_2Cl_2$. [220°]. Very hygroscopic needles.—$B''H_2PtCl_6$. Small four-sided tables.

Acetyl derivative $C_3H_6(NHAc)_2$. [139°]. Needles, v. e. sol. water and alcohol.

Benzoyl derivative $C_3H_8Bz_2N_2$. [193°].

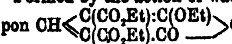
PROPYLENE-AMYL-ψ-THIO-UREA



$\left.\begin{matrix}\text{CHMe.S}\\ \text{CH}_2-\text{N}\end{matrix}\right>$$C.NHC_5H_{11}$. [32°]. (267°). Formed by heating allyl-amyl-thio-urea with conc. HClAq at 100° (Avenarius, *B.* 24, 264).

PROPYLENE BROMIDE *v.* DI-BROMO-PROPANE.

PROPYLENE TRICARBOXYLIC ACID. *Ethyl ether* $CO_2Et.CH:CH.CH(CO_2Et)_2$. (171°

at 15 mm.). Formed by the action of water or of NaOHAq upon  $CH\begin{cases}C(CO_2Et):C(OEt)\\C(CO_2Et).CO\end{cases}O$ [94°], which is got by distilling di-carboxy-glutaconic ether *in vacuo* (Guthzeit a. Dressel, *B.* 22, 1425). It is identical with iso-aconitic ether.

Isomeride *v.* ACONITIC ACID.

Propylene tetra-carboxylic acid $(CO_2H)_2CH.C(CO_2H):CH.CO_2H$. [192°]. Got by saponifying its ether. Colourless crystals (containing 2aq). Gives off CO_2 at 180°.

Salts.—Na_3HA^{iv} 8aq. — Ba_2A^{iv} $1\frac{1}{2}$aq. — Ca_2A^{iv} $3\frac{1}{2}$aq.

Ethyl ether Et_4A^{iv}. (220°-230° at 40 mm.). Formed from sodium-malonic ether and bromo-maleïc ether (Schacherl, *A.* 229, 91).

Isomerides.—DICARBOXY-GLUTACONIC ACID and TRIMETHYLENE TETRACARBOXYLIC ACID.

PROPYLENE CHLORHYDRIN *v.* CHLORO-PROPYL ALCOHOL.

PROPYLENE CHLORIDE *v.* DICHLORO-PROPANE.

PROPYLENE CHLOROBROMIDE *v.* CHLORO-BROMO-PROPANE.

PROPYLENE GLYCOL $C_3H_8O_2$ *i.e.* $C_3H_6(OH)_2$. *Di-oxy-propane.* Mol. w. 76. (189°). S.G. $\frac{0}{0}$ 1·0527 (Z.). C.E. (0°-10°) ·00069. S. (ether) 11. S.V. 85·2 (Zander, *A.* 214, 177).

Formation.—1. By saponifying its acetyl-derivative (Wurtz, *A. Ch.* [3] 55, 438).—2. By reduction of $CH_2Cl.CH(OH).CH_2OH$ by sodium-amalgam (Lourenço, *C. R.* 52, 1043).—3. By heating propylene bromide with PbO and much water at 150° (Eltekoff, *J. R.* 10, 210).—4. By boiling propylene bromide with aqueous K_2CO_3 for some days (Hartmann, *J. pr.* [2] 16, 383).—5. By boiling propylene bromide (1 pt.) with water (36 pts.), the yield being 43 p.c. (Niederist, *A.* 196, 359).—6. By the action of the copper-zinc couple and some HClAq on the product of the action of AcBr on glycerin (Hanriot, *C. R.* 86, 1139).—7. By treating allyl alcohol with dilute H_2SO_4 (20 p.c.) or HCl (10 p.c.) (Solonina, *Bl.* [2] 46, 816).

Preparation.—Glycerin (1,300 g.) is distilled with NaOH (550 g.) and the aqueous layer concentrated and distilled; the yield is 140 g. (Belohoubek, *B.* 12, 1872; Morley a. Green, *C. J.* 47, 182).

Properties. — Liquid, with sweet taste; miscible with water and alcohol.

Reactions.— 1. *Water* containing a trace of HCl forms propionic aldehyde at 215° (Linnemann, *A.* 192, 61). It also yields propionic aldehyde on heating with $ZnCl_2$ (Flavitzky, *B.* 11, 1256).—2. Conc. HIAq forms isopropyl iodide (Wurtz, *A. Suppl.* 1, 381).—3. PCl_5 forms di-chloro-propane.—4. KOH at 250° forms oxalic acid and H.—5. *Chromic acid mixture* forms acetic acid (Flavitzky, *B.* 11, 1256).—6. Oxidised by *platinum black* and air to lactic acid.—7. *Glyceryl trimetric* forms, at 100°, oily $CH_3.CH(O.NO).CH_2.O.NO$ (109°), S.G. ^{2} 1·44, which explodes in sunlight (Bertoni, *C. C.* 1887, 85).

Acetyl derivative $C_7H_{12}O_4$ *i.e.* $C_3H_6(OAc)_2$. *Propylene acetate.* (186°). S.G. ^{2} 1·109. S. 11. Formed by heating $C_3H_6Br_2$ with AgOAc and HOAc (Wurtz, *A.* 105, 202). Neutral liquid.

Mono-benzoyl derivative $CH_3.CH(OBz).CH_2OH$. Formed from the amine $CH_3.CH(OBz).CH_2NH_2$ and HNO_2 (Gabriel a. Heymann, *B.* 23, 2501). Oil.

Di-benzoyl derivative $CH_3.CH(OBz).CH_2OBz$. (240° at 13 mm.). Liquid (Friedel a. Silva, *C. R.* 73, 1379).

Di-nitrate $C_3H_6(O.NO_2)_2$. S.G. ^{5} 1·335. Formed by dropping propylene oxide into strongly-cooled fuming HNO_3 (Henry, *A. Ch.* [4] 27, 261). Oil.

Chlorhydrin *v.* CHLORO-PROPYL ALCOHOL.

Bromhydrin *v.* BROMO-PROPYL ALCOHOL.

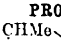
Iodhydrin $C_3H_6I(OH)$. (105° at 60 mm.). Formed from propylene oxide and HI (Markownikoff, *Z.* 1870, 423). Liquid.

Active propylene glycol $C_3H_6(OH)_2$. $a_D = -4° 35'$ to $-1° 15'$ in a 22 mm. tube. Formed, together with propionic and lactic acids, by allowing *Bacterium termo* to breed in ordinary inactive propylene glycol (Le Bel, *C. R.* 92, 532). Yields active propylene oxide (35°) $a_D = +1° 10'$ in a 22 mm. tube.

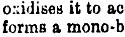
***n*-Propylene glycol** *v.* TRI-METHYLENE GLYCOL.

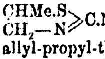
PROPYLENE IODIDE *v.* DI-IODO-PROPANE.

PROPYLENE MERCAPTAN $C_3H_6(SH)_2$. (152° *in vacuo*). Formed by reducing propylene sulphocyanide with Zn and HClAq (Hagelberg, *B.* 23, 1087).

PROPYLENE OXIDE C_3H_6O *i.e.*  $\begin{matrix}CHMe\\CH_2\end{matrix}\!>\!O$. Mol. w. 58. (35°). S.G. ^{0} ·859. V.D. 2·0. Formed by warming propylene chlorohydrin with KOHAq (Oser, *Bl.* 1860, 237; Morley, *B.* 15, 179). Dried over KOH. Neutral liquid, smelling like acetone. Miscible with water, alcohol, and ether. Reduced by sodium-amalgam to isopropyl alcohol. Yields acetic acid when oxidised by moist Ag_2O (Linnemann, *M.* 6, 369)

PROPYLENE-OXIDE CARBOXYLIC ACID *v.* METHYL-GLYCIDIC ACID.

PROPYLENE PHENYL ETHYL KETATE  $\begin{matrix}CHMe.O\\CH_2-O\end{matrix}\!>\!CPhEt$. (235° cor.). S.G. ^{22} ·988. Formed by dropping $C_3H_5Cl.OBz$ into a mixture of $ZnEt_2$ and toluene, and then adding water (Morley a. Green, *C. J.* 47, 134; *B.* 17, 3015). Oil, with pleasant odour; sol. ether. Not attacked by alcoholic potash, by AcCl, by Na, by hydroxylamine, by phenyl-hydrazine, or by HClAq at 155°. HI at 200° yields PrI and phenyl ethyl ketone. By dissolving in H_2SO_4 and pouring into water, it is split up into propylene glycol and $C_6H_5.CO.C_2H_5$. Nitric acid oxidises it to acetic and benzoic acids. Bromine forms a mono-bromo- derivative (230°).

PROPYLENE - PROPYL - ψ - THIO - UREA  $\begin{matrix}CHMe.S\\CH_2-N\end{matrix}\!\geqslant\!C.NHPr$. [237°]. Formed by heating allyl-propyl-thio-urea with conc. HClAq at 100° (Avenarius, *B.* 24, 264). Oil.—Picrate [126°].

PROPYLENE SULPHIDE C_3H_6S. Formed from $C_3H_6Br_2$ and alcoholic Na_2S (Husemann, *A.* 126, 296). Amorphous powder.

PROPYLENE SULPHOCYANIDE $C_5H_6N_2S_2$ *i.e.* $CH_3.CH(SCy).CH_2(SCy)$. Formed by heating $C_3H_6Br_2$ with potassium sulphocyanide and alcohol at 100° (Hagelberg, B. 23, 1086). Insol. water, sol. alcohol and ether.

PROPYLENE DISULPHONIC ACID v. Propane disulphonic acid.

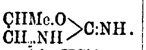
PROPYLENE SULPHONIC ACID $CH_2:CH.CH_2.SO_3H$. Formed by boiling allyl iodide with conc. K_2SO_3Aq (Von Rad, *A.* 161, 218).—KA'. Crystalline solid.—$(KA')_7K_8I_6$.—$(KA')_3K_2I_2$. White solid.

PROPYLENE TRI-THIO-CARBONATE $C_3H_6:CS_3$. S.G. ^{20} 1·31. Formed from $C_3H_6Br_2$ and Na_2CS_3 (Husemann, *A.* 126, 269). Thick liquid, of disagreeable smell.

PROPYLENE-ψ-THIO-UREA $C_4H_8N_2S$ *i.e.*

$\begin{matrix} CHMe.S \\ CH_2.NH \end{matrix}\!\!>\!C:NH$. *Imido-methyl-thiazole tetrahydride.* Formed by heating allyl-thio-urea with HClAq (S.G. 1·17) under pressure at 100° (Gabriel, *B.* 22, 2985). Formed also from β-bromo-propyl-amine hydrobromide and potassium sulphocyanide (Hirsch, *B.* 23, 965). Liquid. — $B'_2H_2PtCl_6$. [212°]. — $B'HAuCl_4$. — $B'C_6H_3N_3O_7$. [200°]. — Methylo-iodide [172°]. Colourless prisms.

PROPYLENE ψ-UREA



$\begin{matrix} CHMe.O \\ CH_2.NH \end{matrix}\!\!>\!C:NH$.

Formed by heating allyl-urea with HClAq at 100° (Gabriel, *B.* 22, 2990), and by heating β-bromo-propyl-amine hydrobromide with potassium cyanate at 100° (Hirsch, *B.* 23, 966).—$B'C_6H_3N_3O_7$. [186°]. Needles.—$B'_2H_2PtCl_6$.

PROPYL ETHER v. Di-propyl oxide.

PROPYL-ETHYLENE v. Amylene.

PROPYL-EUGENOL v. Eugenol.

PROPYL FLUORIDE PrF. (2°). V.D. 2·161 at 20° (calc. 2·175). S. 1 at 15°. Formed by gently warming AgF with PrI (Meslans, *C. R.* 108, 352). Gas, with ethereal odour and hot, sweet taste. Has no action on glass when dry. V. sol. alcohol, ether, and benzene.

Isopropyl fluoride PrF. (−5°). S. 1·5 at 15°. S. (alcohol) 29 at 16°. V.D. 2·171. Formed from AgF and PrI. Gas, not affected by KOHAq at 100°. Br at 30° forms a liquid (143°), while chlorine forms a liquid (105°).

ISOPROPYL-FORMAMIDE v. *Formamide* in article on Formic acid.

DI-PROPYL-FURFURANE $C_4H_2Pr_2O$. (120°). One of the products of the distillation of sodium citrate with lime (Bischoff, *B.* 23, 1918).

DI-PROPYL-GLUTARIC ACID $C_{11}H_{20}O_4$ *i.e.* $(CO_2H.CH.Pr)_2CH_2$. [89°]. Formed by heating $((CO_2H)_2.CPr)_2CH_2$ above 170° (Dressel, *A.* 256, 190). Needles, v. sl. sol. water, v. sol. ether.

PROPYL-GLYCOL v. Propylene glycol.

PROPYL-GLYOXAL. *Mono-oxim.* $C_3H_7.CO.CH:NOH$. [51°]. Formed from methyl propyl ketone, amyl nitrite, and HCl or NaOEt (Claisen a. Manasse, *B.* 22, 528). Pearly plates.

Di-oxim Pr.C(NOH).CH(NOH). [168°].

Di-phenyl-di-hydrazide $PrC(N_2HPh).CH(N_2HPh)$. [163°]. Needles.

PROPYL-GLYOXALINE $C_6H_{10}N_2$ (219°–223°). S.G. ^{12} ·267. Formed by heating glyoxaline with PrBr (Wallach, *B.* 15, 650; 16, 534; *A.* 214, 321). Liquid, miscible with water. $HgCl_2$ added to its aqueous solution gives a pp. sol. HClAq.—$B'_2H_2PtCl_6$. Crystals, sol. hot water.

Propyl-glyoxaline

$\begin{matrix} CH.N \\ CH.NH \end{matrix}\!\!>\!CPr$. (267°).

Formed from glyoxal, *n*-butyric aldehyde and NH_3 (Rieger, *M.* 9, 603). Oil. — $B'_2H_2C_2O_4$. [192°].—$B'_2H_2C_2O_4$ 2aq: [161°]; plates or needles. —$B'_2H_2PtCl_6$: yellow prisms.

Isopropyl-glyoxaline. *Glyoxal-isobutyline.* [129°]. (c. 250°). Formed from glyoxal and isobutyric aldehyde-ammonia (Radziszewski, *B.* 16, 747). Needles, sol. alcohol, benzene, and hot water.—B'HCl. [105°] (Rieger).—B'HBr. [222°].—$B'H_2C_2O_4$. [195°].

Di-propyl-glyoxaline $C_6H_9PrN_2$. (227°). S.G. ^{19} ·939. Formed by heating propyl-glyoxaline with PrI (Rieger, *M.* 9, 607).

***n*-PROPYL-GLYOXYLIC ACID** $Pr.CO.CO_2H$. (180°–185°) at 760 mm.; (115°) at 84 mm. Got by the action of HCl on the nitrile (133°–137°) which is made from AgCy and butyryl chloride (E. Moritz, *C. J.* 39, 16). Liquid.

Amide $C_4H_7O.CONH_2$. [106°]. Formed from the nitrile and conc. HClAq.

Oxim $PrC(NOH).CO_2H$. [144°]. Formed by the action of alcoholic soda and $NaNO_2$ on propyl-acetoacetic ether (Fürth, *B.* 16, 2180). Small needles, v. sol. alcohol, sl. sol. water.

Isopropyl-glyoxylic acid $^{\times}Pr.CO.CO_2H$. A mixture (93° at 45 mm.) of this acid with isobutyric acid is got by the action of HCl on di-isobutyryl dicyanide (Moritz, *C. J.* 39, 14).

Amide $^{\times}Pr.CO.CONH_2$. [126°].

PROPYL HEPTYL KETONE $C_3H_7.CO.C_7H_{15}$. [12°]. (222°). S.G. ^{20} ·828. Formed by distilling calcium butyrate (Limpricht, *A.* 108, 185).

PROPYL HEPTYL OXIDE $PrOC_7H_{15}$. (188°). S.G. $\frac{0}{0}$ ·7987. S.V. 245·6. C.E. (0°–10°) ·00099 (Dobriner, *A.* 243, 7).

DI-ISO-PROPYL-HEXINYL DIKETONE $Pr.CO.C_3H_5:C_3H_5.CO.Pr$. *Di-isobutyrone.* (c. 266°). Formed by the action of sodium on isobutyric ether (Bruggemann, *A.* 246, 151).

PROPYL-HEXYL-CARBINOL v. Decyl alcohol.

PROPYL-HEXYL-GLYOXALINE $C_9H_{15}PrN_2$. *Oxalpropylœnanthyline.* (286°). S.G. ^{17} ·919. Formed from hexyl-glyoxaline and PrBr (Karez, *M.* 8, 222). Oil.

PROPYL HEXYL KETONE $Pr.CO.C_6H_{13}$. [−9·5°]. (207°]. S.G. $\frac{21}{0}$ ·824. Formed by oxidation of the corresponding alcohol (Wagner, *J. pr.* [2] 44, 271). Needles. Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to heptoic and propionic acids.

Isopropyl hexyl ketone $Pr.CO.C_6H_{13}$. (200°–210°). S.G. ^{17} ·841. Formed by distilling calcium isobutyrate with calcium heptoate (Fuchs, *J. R.* 7, 334). Yields acetone, HOAc, and heptoic acid on oxidation.

PROPYL HYPOPHOSPHATE $Pr_4P_2O_6$. S.G. ^{15} 1·134. Formed from $Ag_4P_2O_6$ and PrI (twice the calculated quantity) at 120° (Sänger, *A.* 232, 12). Oil. Decomposed by hot water.

Propyl-hypophosphate of barium $PrBaHP_2O_6$ 6aq. Needles.

PROPYLIDENE-ACETIC ACID v. Pentenoic acid.

ISOPROPYLIDENE-AMIDO-PHENOL $CMe_2:N.C_6H_4.OH$. [158°]. Formed from *p*-amidophenol, acetone, and HOAc (Haegele, *B.* 25, 2755). Colourless plates.

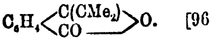
ISO-PROPYLIDENE-ANILINE $C_6H_5N:CMe_2$. (228°). V.D. 66·4 (calc. 66·5). From acetone and aniline in presence of dehydrating agents (Engler a. Heine, *B.* 6, 638; Riehm, *A.* 238, 10). Liquid; rapidly turning brown in air. Its salts

are v. sol. water and alcohol.—$B'_2H_2SO_4$: decomposes at 235°.

PROPYLIDENE CHLORIDE *v.* DI-CHLORO-PROPANE.

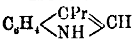
PROPYLIDENE - HYDRAZIDO - BENZENE *p*-SULPHONIC ACID $CMe_2:N.NH.C_6H_4.SO_3H$. Got from *p*-hydrazido-benzene sulphonic acid (phenyl-hydrazine *p*-sulphonic acid) and acetone (Pfülf, *A.* 239, 216). Plates, m. sol. hot water.

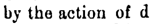
ISO-PROPYLIDENE HYDRAZINE $CMe_2:N.NH_2$. (125°). Formed from acetone and hydrazine hydrate (Curtius, *J. pr.* [2] 44, 543). Mobile liquid decomposing when kept, with evolution of N and NH_3.

ISO-PROPYLIDENE-PHTHALIDE $C_{11}H_{10}O_2$ *i.e.*  $C_6H_4<\substack{C(CMe_2)\\CO}>O$. [96°]. Formed by heating phthalic anhydride with NaOAc and isobutyric acid or pyrotartaric acid (Gabriel a. Michael, *B.* 11, 1683; Roser, *B.* 17, 2776). Needles, sl. sol. hot water. Converted by boiling alkalis into $Pr.CO.C_6H_4.CO_2H$.

DI-ISO-PROPYLIDENE DISULPHONE *v.* TETRA-METHYL-DI-METHYLENE DISULPHONE.

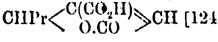
ISOPROPYLIDENE - DI - THIO - DIGLYCOLLIC ACID $CMe_2(S.CH_2.CO_2H)_2$. [127°]. Formed from thioglycollic acid, acetone, and $ZnCl_2$ (Bongartz, *B.* 21, 482). Crystals (from chloroform).

ISOPROPYL INDOLE $C_{11}H_{13}N$ *i.e.*  $C_6H_4<\substack{CPr\\NH}>CH$. (288°). Formed by heating the phenyl-hydrazide of isovaleric aldehyde with $ZnCl_2$ at 180° (Trenkler, *A.* 248, 106). Oil, solidifies by cold. Yields a dihydride (c. 260°) and a picrate [99°] crystallising in red needles.

Di-isopropyl-indole $C_{14}H_{19}N$ *i.e.*  $\substack{CPr:CH.C.CPr\\CH:CH.C.NH}>CH$. [65°]. (295°–300°). Formed by the action of dilute H_2SO_4 on isopropyl-pyrrole in the cold (Dennstedt, *B.* 21, 3430). Needles (from dilute alcohol). Colours acidified pinewood red. Yields a picrate [115°] and an acetyl derivative [186°]. Benzoic aldehyde and $ZnCl_2$ form $C_{45}H_{42}N_2$ [c. 164°].

***n*-PROPYL IODIDE** C_3H_7I. (102·5°) (Brown, *Pr.* 26, 238). S.G. $\frac{0}{0}$ 1·7829 (Dobriner, *A.* 243, 24); $\frac{10}{10}$ 1·7673; $\frac{15}{15}$ 1·7585 (Perkin); $\frac{20}{4}$ 1·7427 (Brühl, *A.* 203, 15). C.E. (0°–10°) ·00105. μ_β 1·5157. R_∞ 47·05. M.M. 11·08 at 18°. S.V. 106·9. Formed from propyl alcohol (60 g.), iodine (127 g.), and red P (10 g.), the yield being 90 p.c. of the theoretical amount (Chancel, *Bl.* [2] 39, 648; *cf.* Linnemann, *A.* 160, 240). Oil.

Isopropyl iodide PrI. (89°). S.G. $\frac{20}{4}$ 1·7033 (Brühl); $\frac{15}{15}$ 1·7163; $\frac{25}{25}$ 1·7005 (Perkin). M.M. 11·182 at 26°. μ_β 1·5108. R_∞ 47·48. S.V. 108·3. Formed by the action of HI on isopropyl alcohol, propylene glycol, glycerin, allyl iodide, or propylene (Linnemann, *A.* 161, 26; Wurtz, *A. Suppl.* 1, 381; Erlenmeyer, *A.* 126, 305; 139, 228; Maxwell Simpson, *A.* 129, 127; Berthelot, *A.* 104, 184; Butlerow, *A.* 145, 275). Prepared by distilling glycerin (200 g.) with I (300 g.), water (160 g.), and clear phosphorus (55 g. added slowly) in a current of CO_2 (Markownikoff, *A.* 138, 364; R. Meyer, *J. pr.* [2] 34, 98). Obtained also by saturating allyl iodide with HI and heating in sealed tubes at 100° (Malbot, *C. R.* 107, 114; *Bl.* [2] 50, 449; *A. Ch.* [6] 19, 352). Oil, converted by Br into PrBr. The copper-zinc couple decomposes it at 50°, giving off gases (Gladstone a. Tribe, *C. J.* 26, 969).

PROPYL-ITACONIC ACID $C_8H_{12}O_4$ *i.e.* $CO_2H.CH_2.C(CO_2H):CHPr$. [159°]. Formed by heating propyl-paraconic ether with alcoholic NaOEt, and saponifying the product (Fittig, *A.* 256, 106; *cf.* Schmidt, *A.* 255, 83). Tufts of prisms, insol. chloroform, v. sol. ether. Reduced by sodium-amalgam to butyl-succinic acid [81°]. Bromine, followed by hot water, gives rise to  $CHPr<\substack{C(CO_2H)\\O.CO}>CH$ [124°].—BaA″.

DI-PROPYL-KETINE *v.* DI-METHYL-DI-PROPYL-PYRAZINE.

DI-PROPYL KETONE $C_7H_{14}O$ *i.e.* $COPr_2$. *Butyrone.* Mol. w. 114. (145°). S.G. $\frac{15}{15}$ ·8217; $\frac{25}{25}$ ·8145. H.C. 1,053,064 (Louguinine, *Bl.* [2] 41, 389). Prepared by distilling calcium butyrate alone or mixed with $CaCO_3$ (Chancel, *A.* 52, 295; Kurtz, *A.* 161, 205; Schmidt, *B.* 5, 597). Formed also from $ZnPr_2$ and butyryl chloride, by the oxidation of di-propyl-carbinol (Schtscherbakoff, *J. R.* 13, 346), and by heating butyryl chloride (1 mol.) with $FeCl_3$ (1 mol.) at 50° (Hamonet, *Bl.* [2] 50, 355). Got also by heating butyric anhydride with sodium butyrate at 180° (Perkin, *C. J.* 49, 325). It is also one of the products formed by the action of sodium on butyric ether (Brüggemann, *A.* 246, 140). Oil, sol. alcohol. Does not combine with $NaHSO_3$ or NH_3. Chromic acid yields propionic and butyric acids. Treatment with Zn and EtI followed by water gives ethyl-di-propyl-carbinol; while Zn, MeI, and water give methyl-di-ethyl-carbinol (A. Saytzeff, *J. pr.* [2] 31, 320). Sodium-amalgam forms sec-heptyl alcohol and a pinacone $C_{14}H_{30}O_2$ [68°] (c. 260°). PCl_5 yields $C_7H_{14}Cl_2$ (181°) and $C_7H_{13}Cl$ (141°) (Tavildaroff, *B.* 9, 1442). Gives on chlorination, when cooled by ice and salt, the compound Pr.CO.CHCl.Et (c. 175°) converted by NH_3 into tetra-propyl-pyrazine (Vladesco, *Bl.* [3] 6, 835). P_2O_5 forms $(C_7H_{12})_x$ (200°–250°) (Tavildaroff, *B.* 9, 1442).

Oxim $Pr_2C:NOH$. (190°–195°) (Meyer a. Warrington, *B.* 20, 501). Yields an acetyl derivative.

Di-isopropyl-ketone Pr_2CO. (124° cor.). S.G. $\frac{0}{4}$ ·8230; $\frac{20}{4}$ ·8063 (Poletaeff, *J. R.* 20, 672). H.C. 1,044,559 (L.). R_∞ 33·46. Formed by distilling calcium isobutyrate (Popoff, *B.* 6, 1255; Münde, *B.* 7, 1370; *A.* 180, 327). Formed also by heating tetra-methyl-phloroglucin with HClAq at 200° (Spitzer, *M.* 11, 288). Oil, with ethereal odour, miscible with alcohol and ether. Does not unite with $NaHSO_3$. Reduces ammoniacal $AgNO_3$. Yields isobutyric and acetic acids and CO_2 on oxidation, and sec-heptyl alcohol (c. 140° cor.) on reduction.

Oxim $Pr_2C:NOH$. [8°]. (c. 183°). Liquid, converted by AcCl into $Pr_2C:NOAc$, which on heating produces PrCO.NHPr (M. a. W.).

Dipropyl-diketone *v.* DIBUTYRYL.

Reference.—CHLORO-DI-ISOPROPYL-KETONE.

PROPYL-LUPETIDINE *v.* DI-METHYL-PROPYL-PYRIDINE HEXAHYDRIDE.

PROPYL-LUTIDINE *v.* DI-METHYL-PROPYL-PYRIDINE.

PROPYL-MALONIC ACID $C_6H_{10}O_4$ *i.e.* $CHPr(CO_2H)$ Mol. w. 146. [84°] (S.); [96°]

(F.). H.C.p. 675,000. H.C.v. 674,700. H.F. 234,000 (Stohmann, *J. pr.* [2] 40, 211).

Ethyl ether Et_2A''. (222°) (Fürth, *M.* 9, 809). S.G. $\frac{15}{15}$ ·9931; $\frac{25}{25}$ ·9854. M.M. 10·367 at 18° (Perkin, *C. J.* 45, 514). Formed from malonic ether, PrI, and zinc or NaOEt.

Isopropyl-malonic acid $CPrH(CO_2H)_2$. [87°]. H.C.v. 674,900. H.C.p. 675,200. H.F. 233,800 (Stohmann). Formed by saponifying its ether, which is made from sodium-malonic ether and PrI (Conrad a. Bischoff, *B.* 13, 595; *A.* 204, 144). Prisms, sol. water, alcohol, and ether. Yields iso-valeric acid at 180°.—Ag_2A''.

Ethyl ether Et_2A''. (214°). S.G. $\frac{20}{15}$ ·997 (C. a. B.); $\frac{15}{15}$ ·9927; $\frac{25}{25}$ ·9852 (Perkin). M.M. 10·482 at 17°.

References.—Di-bromo- and Oxy- propyl-malonic acid.

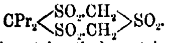
ISOPROPYL-MALONIC ALDEHYDE NITRILE PrCH(CN).CHO. (137°). V.D. 3·83 (calc. 3·87). S.G. ^{15} ·911. Formed by heating iodo-isovaleric aldehyde with KCy or AgCy (Chautard, *A. Ch.* [6] 16, 188). Oil which reduces Fehling's solution. Miscible with alcohol and ether.

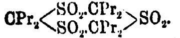
***n*-PROPYL MERCAPTAN** PrSH. Mol. w. 76. (68°) (Roemer, *B.* 6, 784; Schatzmann, *A.* 261, 7). Formed from PrBr and alcoholic KSH. Oil, smelling like mercaptan. $Hg(SPr)_2$.

Isopropyl mercaptan PrSH. (57°-60°) (Henry, *B.* 2, 495; Claus, *B.* 5, 659; 8, 532). Formed from PrI and alcoholic KSH. $Hg(SPr)_2$: white plates (from alcohol).

PROPYL-METHANE is Butane.

Di-propyl-methane *v.* Heptane.

DI-PROPYL-TRIMETHYLENE TRISULPHONE  $CPr_2{<}\begin{matrix}SO_2.CH_2\\SO_2.CH_2\end{matrix}{>}SO_2$. [297°]. Formed from sodium trimethylene trisulphone and PrI in alcohol (Camps, *B.* 25, 244). Slender needles, m. sol. boiling alcohol.

Hexa-propyl-trimethylene trisulphone  $CPr_2{<}\begin{matrix}SO_2.CPr_2\\SO_2.CPr_2\end{matrix}{>}SO_2$. [133°]. Formed from the trisulphone, PrI, and alcoholic NaOH (Camps). Prisms.

ISO-PROPYL-NAPHTHALENE $C_{13}H_{14}$ *i.e.* $C_{10}H_7Pr$. (265°). V.D. 5·85. Formed by heating naphthalene with PrBr and $AlCl_3$ (Roux, *Bl.* [2] 41, 379; *A. Ch.* [6] 12, 289). Oil, sol. alcohol and benzene. Yields (*β*)-naphthoic acid on oxidation.—$B'C_6H_3N_3O_7$. [90°]. Lemon-yellow needles.

PROPYL NITRATE $PrNO_3$. (110·5°) (Perkin, *C. J.* 55, 683). S.G. $\frac{15}{15}$ 1·0631; $\frac{25}{25}$ 1·0531. M.M. 4·085. Formed by distilling *n*-propyl alcohol with HNO_3 and a little urea (Wallach a. Schulze, *B.* 14, 420). Forms with anthracene $C_{14}H_{10}PrNO_3$ [92°] crystallising in four-sided prisms (Perkin, jun. a. Mackenzie, *C. J.* 61, 866).

Isopropyl nitrate $PrNO_3$. (102°). S.G. ^{2} 1·054 (Silva, *A.* 154, 256).

Reference.—Chloro-isopropyl nitrate.

PROPYL NITRITE PrO.NO. (43°-46°) (Cahours, *C. R.* 77, 749); (53°-60°) (Pribram a. Handl, *M.* 2, 655). S.G. ^{21} ·935 (C.); $\frac{0}{0}$ ·998 (P. a. H.). Formed by passing nitrous acid gas into *n*-propyl alcohol.

Isopropyl nitrite $PrNO_2$. (44°). S.G. ^{2} ·856; ^{25} ·844 (Silva, *Bl.* [2] 12, 227; Kissel, *J. R.* 1882, 226).

PROPYL ψ-NITROLE $C_3H_6N_2O_3$ *i.e.* $CH_3.C(NO_2)(NO).CH_3$. Mol. w. 118. [70°] (Bewad, *B.* 24, 976). Formed by adding KNO_2 and dilute H_2SO_4 to an alkaline solution of iso-nitro-propane $CHMe_2.NO_2$ (V. Meyer a. Locher, *B.* 7, 670; *A.* 175, 120). Monoclinic crystals, insol. water and alkalis. Forms a blue liquid when fused. Its solutions in alcohol and chloroform are blue.

PROPYL-NITROLIC ACID $C_3H_6N_2O_3$ *i.e.* $CH_3.CH_2.CH(NO_2)NO$ or $CH_3.CH_2.C(NO_2)$:NOH. [60°]. Formed by adding potassium nitrite and dilute H_2SO_4 to an alkaline solution of nitro-propane $CH_3.CH_2.CH_2.NO_2$. Formed also from $Et.CBr_2.NO_2$ and hydroxylamine (V. Meyer, *B.* 7, 670; 9, 395). Prisms, with sweet taste, v. sol. water, alcohol, and ether. Alkalis form a deep-red solution. Conc. H_2SO_4 forms propionic acid and N_2O.

PROPYL OCTYL OXIDE $Pr.O.C_8H_{17}$. (207°). S.G. $\frac{0}{0}$ ·8039. C.E. (0°-10°). ·00101. S.V. 272·4 (Dobriner, *A.* 243, 7).

DI-PROPYL OXIDE Pr_2O. *Propyl ether.* (90·7° i.V.). S.G. $\frac{0}{0}$ ·7633 (Zander, *A.* 214, 163). C.E. (0°-10°) ·00125 (Dobriner, *A.* 243, 20). S.V. 150·9. Formed from PrI and KOPr (Chancel, *A.* 151, 304). Got also from PrI and Ag_2O (Linnemann, *A.* 161, 37) and by heating *n*-propyl alcohol with H_2SO_4 at 135° (Norton a. Prescott, *Am.* 6, 243).

Di-isopropyl oxide Pr_2O. (68·8° i.V.). S.G. $\frac{0}{0}$ ·7435. C.E. (0°-10°) ·00130. S.V. 151·6 (Zander). Got from PrI and Ag_2O (Erlenmeyer, *A.* 126, 306).

PROPYL OXYBUTYL KETONE $C_3H_7.CO.CH(OH).C_3H_7$. *Butyroïn.* (180°-190°). Formed from di-*n*-propyl diketone and alcoholic KOH (Klinger a. Schmitz, *B.* 24, 1273). Yields a phenyl-hydrazide [135°].

PROPYL-PHENOL *v.* Cumenol.

PROPYL-PHENOL CARBOXYLIC ACID *v.* Oxy-cuminic acid.

Isopropyl-phenol dicarboxylic acid $C_6H_2Pr(OH)(CO_2H)_2$. [295°]. Formed, together with oxy-cuminic acid, by the action of Na and CO_2 on isopropyl-phenol (Fileti, *G.* 16, 126). Tables or needles, sol. water and alcohol.

***p*-PROPYL-PHENYL-ACETIC ACID** $C_3H_7.C_6H_4.CH_2CO_2H$. [52°]. Formed by saponifying the nitrile, which is got from *ω*-chloro-cymene, alcohol, and KCy at 100° (Rossi, *A. Suppl.* 1, 139). Small needles (from hot water).—AgA′: slender needles.

References.—Amido- and Oxy-propyl-phenyl-acetic acid.

PROPYL-PHENYL-AMINE *v.* Amido-phenyl-propane and Propyl-aniline.

ISOPROPYL-PHENYL- *v.* Cumyl-.

ISOPROPYL-PHENYL-CINNAMIC ACID $Pr.C_6H_4.C(CHPh).CO_2H$. [184°]. Formed from $Pr.C_6H_4.CH_2.CO_2Na$, benzoic aldehyde, and Ac_2O (Magnanini, *G.* 15, 509). Needles (from dilute alcohol).—CaA'_2.—AgA′.

ISOPROPYL-PHENYL-*p*-COUMARIC ACID. *Methyl derivative* $Pr.C_6H_4.C(CO_2H)$:$CH.C_6H_4.OMe$. [199°]. Formed from $Pr.C_6H_4.CH_2.CO_2Na$, anisic aldehyde, and Ac_2O (Magnanini, *G.* 15, 511). Prisms (from alcohol).—AgA′.

DI-*p*-PROPYL-DI-PHENYL-CYANAMIDE $C(N.C_6H_4Pr)_2$. [168°]. Formed by heating

$CS(NH.C_6H_4Pr)_2$ with benzene and PbO (Francksen, *B.* 17, 1228). Needles.

PROPYL-BENZONITRILE *v.* *Nitrile* of Cuminic acid.

ISOPROPYL - DI - PHENYL - ETHYLENE **$C_6H_5.CH:CH.C_6H_4Pr$.** [84°]. Formed by heating phenyl-acetic acid with cuminic aldehyde and NaOAc at 250° (Michael, *Am.* 1, 314). Scales (from alcohol), v. sl. sol. hot water.

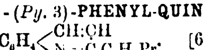
DI - *p* - PROPYL - DIPHENYL - GUANIDINE $NH:C(NH.C_6H_4Pr)_2$. [113°]. Formed by heating di-propyl-di-phenyl-thio-urea with alcoholic NH_3 and PbO (Francksen, *B.* 17, 1225). Needles, v. sol. warm alcohol and ether.—**Platinochloride** $(C_{19}H_{25}N_3)_2H_2PtCl_6$: yellowish-brown pp.

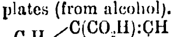
Tri-propyl-tri-phenyl-guanidine $C_6H_4PrN:C(NH.C_6H_4Pr)_2$. Formed by heating $CS(NH.C_6H_4Pr)_2$ with $C_6H_4Pr.NH_2$, alcohol, and PbO. Amorphous resin, v. sol. alcohol.—$B'_2H_2PtCl_6$: brown powder.

pn-**PROPYL-PHENYL METHYL KETONE** $CH_3.CO.C_6H_4Pr$. (259° i.V.). S.G. $^{\underline{15}}$ ·979. Formed from *n*-cumene, AcCl, and $AlCl_3$ (Widmann, *B.* 21, 2224). Colourless liquid. Yields an **oxim** [54°], which melts at 44° after fusion. The **phenyl-hydrazide** [92°] forms six-sided hatchet-shaped tables.

Isomeride $CH_3.CO.C_6H_4Pr$. (253°). Yields an **oxim** [71°] and a **phenyl-hydrazide** [82°].

ISOPROPYL-PHENYL PHOSPHATE $PO(O.C_6H_4Pr)_3$. (375°-380° at 280 mm.). Got from isopropyl-phenol and PBr_5 (Fileti, *G.* 16, 130). Viscid liquid, insol. water, sol. alcohol.

p - **ISOPROPYL - (*Py.* 3) - PHENYL - QUINOLINE** $C_{18}H_{17}N$ *i.e.*  $C_6H_4<\begin{matrix}CH:CH\\N=C.C_6H_4Pr\end{matrix}$ [60°]. Formed by heating its carboxylic acid with soda-lime (Döbner, *A.* 249, 102). Needles, sl. sol. water. — $B'_2H_2PtCl_6$ 2aq. — $B'_2H_2Cr_2O_7$. — **Picrates:** [195°]; plates (from alcohol).

Carboxylic acid  $C_6H_4<\begin{matrix}C(CO_2H):CH\\N\text{———}C.C_6H_4Pr\end{matrix}$. [201°]. Formed from cuminic aldehyde, pyruvic acid, and aniline (Döbner). Yellow plates (from HOAc).—AgA′: white powder.

p-**PROPYL-PHENYL-THIOCARBIMIDE** $C_6H_4Pr.N:CS$. (263°). Formed by heating di-propyl-di-phenyl-thio-urea with syrupy H_3PO_4 (Francksen, *B.* 17, 1223). Oil, volatile with steam, v. sol. alcohol and ether.

p-**PROPYL-PHENYL-THIO-UREA** $C_{10}H_{14}N_2S$ *i.e.* $NH_2.CS.NH.C_6H_4Pr$. [159°]. Formed from amido-phenyl-propane hydrochloride and ammonium sulphocyanide (Francksen, *B.* 17, 1222). Needles, sol. alcohol and ether.

Di-propyl-di-phenyl-thio-urea $CS(NH.C_6H_4Pr)_2$. [138°]. Formed from amido-phenyl-propane, CS_2, and alcohol (F.). Plates.

PROPYL-PHENYL-UREA $C_{10}H_{14}N_2O$ *i.e.* $NH_2.CO.NHC_6H_4Pr$. [143°]. Formed by the action of potassium cyanate on amido-phenyl-propane hydrochloride (Francksen, *B.* 17, 1225). Plates, sol. hot alcohol. insol. water.

Di-*p*-propyl-di-phenyl-urea $CO(NHC_6H_4Pr)_2$. [205°]. Formed by heating amido-phenyl-propane with urea. Formed also by the action of $COCl_2$ on amido-phenyl-propane in benzene, and by heating amido-phenyl-propane sulphate with a saturated solution of potassium cyanate. Needles, v. sol. ether and hot alcohol.

PROPYL PHOSPHATE $PO(OPr)_3$. Formed, together with PrCl and $PO(OH)_2(OPr)$ (which is sol. water) by the action of PCl_5 on *n*-propyl alcohol (Winssinger, *Bl.* [2] 48, 111). Oil. V. sl. sol. water, its insolubility being greatest at 75°. Cannot be distilled, even *in vacuo.*

ISOPROPYL-PHOSPHINE $PrPH_2$. (41°). Formed, together with Pr_2PH (118°) and Pr_3P, by heating PrI with PH_4I and ZnO for 6 hours at 100° (Hofmann, *B.* 6, 292). Liquid, with penetrating odour. Readily absorbs oxygen, taking fire on a hot day.—B′HI: decomposed by water.

Tri-isopropyl-phosphine Pr_3P. Oil. Forms red crystals with CS_2.—Pr_3PHI. Large crystals, v. sol. water.—Pr_4PI. Cubes or octahedra.

Di-chloro-isopropyl-phosphine $PrPCl_2$. (c. 135°). Formed by heating $HgPr_2$ with PCl_3 (Michaelis, *B.* 13, 2175). Liquid.

Reference.—Oxy-tri-propyl-phosphine.

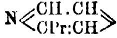
PROPYL PHOSPHITE $P(OPr)_3$. (240°). S.G. $^{\underline{15}}$ 1·004. Formed from PCl_3 and NaOPr (Jaehne, *A.* 256, 282). Liquid.

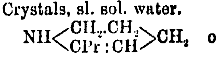
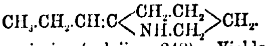
ISOPROPYL-ISOPHTHALIC ACID $C_6H_3Pr(CO_2H)_2$ [1:3:5]. [285°]. Formed by heating pyruvic acid with isobutyric aldehyde and $Ba(OH)_2$ (Doebner, *B.* 23, 2380; 24, 1748). Plates (from dilute alcohol, v. sl. sol. cold water). —BaA″ 2½aq. CaA″ 2½aq.—Ag_2A'' aq.

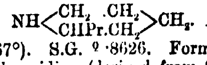
PROPYL-PHYCITE. According to Fauconnier (*C. R.* 107, 629), the substance described under this name by Carius (*A.* 134, 71) is glycerin.

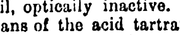
PROPYL-PIPERIDINE *v.* Propyl-pyridine hexahydride.

PROPYL-PROPANE *v.* Hexane.

(*a*)-**PROPYL-PYRIDINE** $C_8H_{11}N$ *i.e.*  $N\ll\begin{matrix}CH.CH\\CPr:CH\end{matrix}\gg CH$. *Conyrine.* (168°). Formed by distilling coniine hydrochloride with zinc-dust (Hofmann, *B.* 17, 825; Ladenburg, *A.* 247, 20). Light oil, with blue fluorescence. Yields picolinic acid [134°] on oxidation. Reduced by conc. HIAq at 290°. to coniine.—$B'_2H_2PtCl_6$. [160°] and [172°]. Orange monoclinic tables. *a:b:c* = 1·0522:1:1·5356; β = 87° 13′.—B′MeI. Oil.—$B'_2Me_2PtCl_6$. Crystals, sl. sol. water.

Tetrahydride  $NH<\begin{matrix}CH_2.CH_2\\CPr:CH\end{matrix}>CH_2$ or  $CH_3.CH_2.CH:C<\begin{matrix}CH_2.CH_2\\NH.CH_2\end{matrix}>CH_2$. This is (γ)-coniceine (vol. ii. p. 248). Yields coniine on reduction with tin and HCl (Lellmann a. Müller, *B.* 23, 680).

Hexahydride  $NH<\begin{matrix}CH_2.CH_2\\CHPr.CH_2\end{matrix}>CH_2$. *Inactive coniine.* (167°). S.G. $^{\underline{0}}$ ·8626. Formed by reducing (*a*)-allyl-pyridine (derived from (*a*)-methyl-pyridine and paraldehyde) in alcoholic solution with sodium (Ladenburg, *B.* 19, 2579; *A.* 247, 80). Oil, optically inactive. Can be separated by means of the acid tartrate into a dextro- modification (coniine) and a lævo- modification.—B′HCl. [203°] (L.); [213°] (L. a. M.). V. sol. water.—$B'_2H_2PtCl_6$.—$B'_2H_2CdI_4$. [118°].

(β)-**Propyl-pyridine**  $N\ll\begin{matrix}CH.CH\\CH:CPr\end{matrix}\gg CH$. ***Collidine.*** (170°). Got by passing nicotine through a red-hot tube (Cahours a. Etard, *J.* 1881, 928). Yields nicotinic acid on oxidation.

(α) - Isopropyl - pyridine $\mathrm{N}<\substack{\mathrm{CH.CH}\\ \mathrm{CPr{:}CH}}>\mathrm{CH}$. (159°). S.G. $\frac{0}{0}$ ·9342. Formed, together with the (γ)-isomeride, by heating pyridine with PrI and PrI at 290° (Ladenburg, *B.* 17, 772, 1121; 18, 1587; *A.* 247, 22). Liquid, with unpleasant odour, sl. sol. water. Gives picolinic acid on oxidation with $KMnO_4$.—$B'_2H_2PtCl_6$. [170°]. Hexagonal rhombohedra, *a*:*c* = 1:·9489. —$B'HAuCl_4$. [91°].—$B'C_6H_3N_3O_7$. [116°]. Needles. Mercuric chloride double salt: [90°].—$B'MeAuCl_4$. [128°].

Tetra-hydride $C_8H_{13}N$. (164°). S.G. $\frac{0}{0}$ ·896. Formed from the hexahydride, Br, and NaOHAq (Ladenburg, *B.* 20, 1646).—$B'_2H_2PtCl_6$. [189°]. Tables.

Hexahydride $C_8H_{17}N$ *i.e.* $\mathrm{NH}<\substack{\mathrm{CH_2\ .CH_2}\\ \mathrm{CHPr\ .CH_2}}>\mathrm{CH_2}$. (159°). S.G. $\frac{0}{0}$ ·8668. Formed by reduction in alcoholic solution by Na (Ladenburg, *A.* 247, 73). Liquid, more sol. cold than hot water. Converted by MeI into $\mathrm{NMe}<\substack{\mathrm{CH_2\ .CH_2}\\ \mathrm{CHPr.CH_2}}>\mathrm{CH_2}$ (167°). CS_2 yields $(C_8H_{17}N)_2CS_2$ [105°].—B'HCl. [210°]. Trimetric prisms; *a*:*b*:*c* = ·814:1:·419. — B'HBr. [233°].—B'HI. [243°].—$B'_2H_2PtCl_6$. [193°]. Monoclinic prisms; *a*:*b*:*c* = ·977:1:1·385; β = 89° 38′.—*$B'_2H_2CdI_4$. [133°].

ν-Propyl-pyridine hexahydride $\mathrm{NPr}<\substack{\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}}>\mathrm{CH_2}$. (149°–150°). Formed from piperidine and PrI (Ladenburg, *B.* 14, 1348). Liquid.—$B'_2H_2SnCl_6$: monoclinic crystals.

ν-Isopropyl-pyridine hexahydride $\mathrm{NPr}<\substack{\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}}>\mathrm{CH_2}$.—$B'_2H_2SnCl_6$: monoclinic crystals (Hjortdahl, *J.* 1882, 1085).—$B'_2H_2PtCl_6$.

(γ) - Isopropyl - pyridine $\mathrm{N}<\substack{\mathrm{CH.CH}\\ \mathrm{CH{:}CH}}>\mathrm{CPr}$. (178°). S.G. $\frac{0}{0}$ ·9439. Formed as above, being separated by means of the platinochloride, which is more soluble than that of the (α)-isomeride. Oil. Yields isonicotinic acid [305°] on oxidation.—$B'_2H_2PtCl_6$. [205°]. Plates.

Hexahydride $\mathrm{NH}<\substack{\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}}>\mathrm{CHPr}$. (171°). Formed by reducing (γ)-isopropyl-pyridine in alcoholic solution by Na. Fuming liquid, v. sol. cold water.—$B'_2H_2PtCl_6$. [172°]. Golden prisms, sl. sol. water.

References.—OXY-PROPYL-PYRIDINE and OXY-PROPYL-PIPERIDINE.

PROPYL PYRIDYL KETONE *v.* PYRIDYL PROPYL KETONE.

PROPYL - PYROGALLOL $C_9H_{12}O_3$ *i.e.* $C_6H_2Pr(OH)_3$. [80°]. Got by heating its di-methyl ether with conc. HClAq at 130° (Hofmann, *B.* 8, 67; 11, 329). Prisms (from benzene), v. e. sol. water and alcohol. $FeSO_4$ colours its aqueous solution blue (Pastrovitch, *M.* 4, 182).

Methyl ether $C_6H_2Pr(OH)_2(OMe)$. (290° cor.). S.G. $\frac{15}{15}$ 1·023. Occurs, together with the di-methyl ether, in beech-wood tar (Pastrovitch). Oil, with smoky smell. Gives an intense bluish-green colour with $FeCl_3$ in alcohol. —$C_6H_2Pr(OK)_2(OMe)$. Pearly crystals (from dilute alcohol).—$C_6H_2Pr(OAc)_2(OMe)$. [83°]. Needles (from alcohol).—$C_6Br_2Pr(OAc)_2(OMe)$. [79°]. Golden needles.

Di-methyl ether $C_6H_2Pr(OH)(OMe)_2$. *Picamar.* (c. 286° cor.). Occurs in beech-wood tar (Reichenbach, *A.* 8, 224; Niederist, *M.* 4, 487). Oil, with bitter, burning taste. Reduces salts of Au and Ag. Yields the di-methyl ether of di-oxy-quinone on oxidation.—$C_{11}H_{15}O_3K$. Pearly leaflets (from spirit).—$C_{11}H_{15}AcO_3$. [87°]. Monoclinic prisms; *a*:*b*:*c* = ·39:1:·547; β = 96° 29′.—$C_{11}H_{13}Br_2AcO_3$ [101°]. Trimetric prisms; *a*:*b*:*c* = ·99:1:1·93.—$C_{11}H_{15}BzO_3$. [91°].

Tri-methyl ether $C_6H_2Pr(OMe)_3$. (164°). Formed from propyl-pyrogallol and MeI (Will, *B.* 21, 2020).

n-PROPYL-PYRROLE $C_7H_{11}N$ *i.e.* $\mathrm{NPr}<\substack{\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}}$. (147°). Formed from potassium pyrrole and PrI (Zanetti, *B.* 22, 2518). Liquid.

Isopropyl-pyrrole C_4H_4PrN. (174°). Formed by boiling pyrrole with acetone and $ZnCl_2$ (Dennstedt a. Zimmermann, *B.* 20, 851; 21, 1480). Liquid. Dry HCl passed into its ethereal solution forms $(C_7H_{11}N)_2HCl$, a crystalline salt yielding a liquid base (c. 287°) and a picrate $(C_7H_{11}N)_2C_6H_3N_3O_7$ [146°]. Ac_2O forms $C_4H_3Pr{:}NAc$ (222°–232°) and $C_4H_2AcPr{:}NH$ [64°] (251°).

ISOPROPYL-PYRRYL STYRYL KETONE $NHC_4H_2Pr.CO.CH{:}CHPh$. [143°]. Formed by boiling $NHC_4H_2Pr.CO.CH_3$ with benzoic aldehyde and dilute KOHAq (Dennstedt a. Zimmermann, *B.* 20, 853). Yellow crystals.

(*B.* 3)-**ISOPROPYL-QUINOLINE** $C_{12}H_{13}N$ *i.e.* $\substack{\mathrm{CH{:}CH.C.CH{:}CH}\\ \mathrm{CPr{:}CH.C.N=CH}}$ *Cumoquinoline.* Formed by heating (*Py.* 3)-chloro-isopropyl-quinoline with a solution of HI in HOAc (Widman, *B.* 19, 267). Oil, easily volatile in steam.—Salts: $B'_2H_2PtCl_6 2aq$. [220°].—Picrate: [206°].—Chromate: [c. 92°]. Large red prisms.

Methylo-iodide B'MeI. [c. 200°].

(*Py.* 2)-**Isopropyl-quinoline** $\mathrm{C_6H_4}<\substack{\mathrm{CH{:}CPr}\\ \mathrm{N=CH}}$. [c. 10°]. (275°–280°) at 715 mm. Formed by distilling its (*Py.* 3)-carboxylic acid (Spady, *B.* 18, 3383). Liquid, v. sol. alcohol and ether.—$B'_2H_2PtCl_6$.—$B'_2H_2Cr_2O_7$.—$B'C_6H_3N_3O_7$: long slender needles.

(*Py.* 3)-**Isopropyl-quinoline** $\mathrm{C_6H_4}<\substack{\mathrm{CH{:}CH}\\ \mathrm{N=CPr}}$. (255°). Formed by heating its (*Py.* 1)-carboxylic acid with soda-lime (Doebner, *B.* 20, 279; *A.* 242, 279). Oil, smelling like quinoline.—$B'_2H_2PtCl_6 2aq$: yellow needles.—$B'C_6H_3N_3O_7$. [150°]. Yellow plates (from alcohol).

Reference.—CHLORO- and OXY- ISOPROPYL-QUINOLINE.

(*Py.* 2)-**ISOPROPYL-QUINOLINE** (*Py.* 3)-**CARBOXYLIC ACID** $\mathrm{C_6H_4}<\substack{\mathrm{CH{:}CPr}\\ \mathrm{N=C.CO_2H}}$. [189°]. Formed by oxidation of (*Py.* 2,3)-isopropyl-isobutyl-quinoline with CrO_3 and dilute H_2SO_4 (Spady, *B.* 18, 3379). Plates (from dilute alcohol).—$AgHA'_2HNO_3$.—$(HA')_2H_2PtCl_6$: prisms.

(*Py.* 3)-**Isopropyl-quinoline** (*Py.* 1)-**carboxylic acid** $\mathrm{C_6H_4}<\substack{\mathrm{C(CO_2H){:}CH}\\ \mathrm{N=\!=\!=CPr}}$. [146°]. Formed, together with $C_{19}H_{20}N_2O$ [222°], by adding aniline to an alcoholic solution of isobutyric aldehyde and pyruvic acid (Doebner, *A.* 242, 276; *B.* 20, 279). Prisms (containing $1\frac{1}{2}$aq).—

HA'HCl. — $(HA')_2H_2PtCl_6aq.$ — $(HA')_2HAuCl_4$: lemon-yellow needles.—AgA'.

PROPYL SILICATE $Si(OPr)_4$. (226°). S.G. $\underline{15}$ ·915 (Cahours, *C. R.* 76, 1383). On heating with $SiCl_4$ at 160° it yields $(PrO)_3SiCl$ (209°) and $(PrO)_2SiCl_2$ (187°).

DI-PROPYL-DI-STYRYL KETONE $(C_3H_7.C_6H_4.CH:CH)_2CO$. [106°]. Formed from cuminic aldehyde, acetone, alcohol, and NaOHAq (Claisen a. Ponder, *A.* 223, 148). Prisms.

ISOPROPYL-STYRYL-PHENOL. *Methyl ether.* $C_6H_4Pr.CH:CH.C_6H_4OMe$. [152°]. Got by heating $C_6H_4Pr.C(CO_2H):CH.C_6H_4OMe$ (Magnanini, *G.* 15, 513). Pearly scales (from alcohol).

PROPYL-SUCCINIC ACID $C_7H_{12}O_4$ *i.e.* $CO_2H.CH_2.CHPr.CO_2H$. *Oxy-hexic acid.* [92°]. Formed by heating pentane tri-carboxylic acid (Waltz, *B.* 15, 608; *A.* 214, 59). Got also by reducing oxy-hexic acid with zinc and H_2SO_4 (Gorboff, *J. R.* 1887, 605; Walden, *B.* 24, 2036).

Iso-propyl-succinic acid *v.* PIMELIC ACID.

Di-isopropyl-succinic acid $C_{10}H_{18}O_4$ *i.e.* $CO_2H.CHPr.CHPr.CO_2H$. [168°]. The ether is formed from α-bromo-isovaleric ether and finely-divided silver (Hell a. Mayer, *B.* 22, 48). Dendritic crystals (from water).—BaA″ 5aq. S. 7·7 at 17°.—CuA″ aq. S. ·099 at 24°.—SrA″ 3aq.—CaA″ 4aq.—MgA″ 7aq.—CoA″ 7aq.—NiA″ 5aq.—CdA″ 4aq.—MnA″ 7aq. S. 4·71 at 21°.—ZnA″.—PbA″.—Ag_2A''. S. ·062 at 20°.

Isomeride $C_{10}H_{18}O_4$. [200°]. Accompanies the preceding acid. Granular crystals. —BaA″ 2aq.—SrA″ 4aq.—CaA″ 2aq.—MgA″ 5aq.—MnA″ 3aq —NiA″ 4aq.—CuA″ 3aq.—CdA″ 3aq.—ZnA″.—PbA″.—Ag_2A''.

Reference.—OXY-PROPYL-SUCCINIC ACID.

TETRA-PROPYL-SUCCINIMIDINE $C_{16}H_{31}N_3$ *i.e.* $\left.\begin{matrix}CH:C(NPr_2)\\CH_2.C(NPr_2)\end{matrix}\right>N$. Got from succin-imido-ethyl ether hydrochloride, $NHPr_2$, and alcohol at 50° (Pinner, *B.* 23, 2930).—$B'2HNO_3$. [53°].—$B'_2H_2PtCl_6$. [174°]. Needles, sl. sol. hot water.

PROPYL SULPHATES.

Propyl sulphuric acid $PrO.SO_2.OH$. Formed from propyl alcohol and H_2SO_4 (Chancel, *C. R.* 87, 410). — KA': needles, v. sol. water. — BaA'_2 3aq (Schmidt, *Z.* 1870, 576).

Di-propyl sulphate Pr_2SO_4. Formed from propyl alcohol and $ClSO_2.OH$ (Mazurowska, *J. pr.* [2] 13, 162). Oil.

DI-*n*-PROPYL SULPHIDE Pr_2S. (142°) (Winssinger, *Bl.* [2] 48, 109). S.G. $\underline{17}$ ·814 (C.). Occurs in raw petroleum (Mabery a. Smith, *B.* 22, 3303). Formed by heating K_2S with PrCl or PrI in alcohol (Cahours, *C. R.* 76, 133). Fetid oil. Bromo-acetic acid forms the acid $Pr_2SBr.CH_2.CO_2H$, which yields $Pb_3A'Br_5$ and $Pb_2A'Br_3$ (Letts, *Tr. E.* 28, 586).

Compounds with platinum salts (Blomstrand, *J. pr.* [2] 38, 354, 498). — $(Pr_2S)_2PtCl_2$. Occurs in three varieties: (α) [46°] S. (alcohol) 15·6 at 15°, (β) [86°], and (γ) [63°]. Alcoholic KOH (1 mol.) acting on the (α)-compound forms crystalline $(Pr_2S)_2PtCl(OH)$.—$(Pr_2S)(Et_2S)PtCl_2$: syrup.—$(Pr_2S)_2Pt_2Cl_4$. [185°].—$(Pr_2S)_2PtCl_4$. [139°].—$(Pr_2S)PtClI$. Prisms.—$(Pr_2S)_2PtBr_2$. [105°].—$(Pr_2S)_2PtBr_4$. [141°].—$(Pr_2S)_2PtBr_2Cl_2$. [129°].—$(Pr_2S)_2PtI_2$. [133°]. Red prisms.—$(Pr_2S)_2Pt_2I_4$. [161°]. Crystals.—$(Pr_2S)(Et_2S)PtI_2$. [115°]. — $(Pr_2S)(Pr_2S)PtI_2$ [131°].—$(Pr_2S)_2Pt(NO_2)_2$. Occurs in two forms [210°] and [195°].—$(Pr_2S)_2Pt(NO_2)_4$. Occurs in two varieties, an oil and a crystalline body [70°] which yields $(Pr_2S)_2Pt(NO_2)(OH)$ [145°].—$(Pr_2S)_2PtCrO_4$. Red prisms (from chloroform). $(Pr_2S)_2PtC_2O_4$: crystalline pp.—$(Pr_2S)_2Pt(SCN)_2$: yellow pp.—$(Pr_2S)_2PtCl_2HgCl_2$. [82°]. Trimetric crystals, $a:b:c$ = ·554:1: ·591.

Propylo-iodide SPr_3I. Yields the compound $(SPr_3Cl)_2PtCl_4$ (Cahours).

Isopropyl sulphide Pr_2S. (121° i.V.). Formed by distilling PrI with alcoholic K_2S (Henry, *B.* 2, 495; Beckmann, *J. pr.* [2] 17, 459). Oxidised by $KMnO_4$ to Pr_2SO_2 [36°]. Yields Pr_2SHgCl_2.

Compounds with salts of platinum (Blomstrand):—$(Pr_2S)_2PtCl_2$. [163°].—$(Pr_2S)_2PtBr_2$. [174°].—$(Pr_2S)_2PtI_2$. [176°].—$(Pr_2S)_2Pt(SCN)_2$. [102°]. — $(Pr_2S)_2Pt(NO_2)_2$. Prisms, decomposing at 210°.—$(Pr_2S)_2PtI_4$. [139°].

Di-propyl disulphide Pr_2S_2. (193°). (Spring a. Legros, *B.* 15, 1940).

Di-isopropyl disulphide Pr_2S_2. (175°). A product of the action of Na and MeI on isopropyl mercaptan in ether (Obermeyer, *B.* 20, 2928).

PROPYL SULPHOCYANIDE PrSCN. (163°). Liquid (Schmidt, *Z.* 1870, 576).

Isopropyl sulphocyanide PrSCN. (150°) (Henry, *B.* 2, 496); (153°) (Gerlich, *A.* 178, 90). S.G. $\underline{20}$ ·963. Formed from PrI and potassium sulphocyanide. Liquid, decomposed by boiling water. H_2S yields $NH_2.CS_2Pr$ [97°].

DI-*n*-PROPYL SULPHONE Pr_2SO_2. [30°]. Formed by oxidising Pr_2SO (Winssinger, *Bl.* [2] 48, 111). Scales, sol. water, alcohol, and ether Volatile with steam.

Di-isopropyl sulphone Pr_2SO_2. [36°]. Got by oxidising Pr_2S with $KMnO_4$ (Beckmann, *J. pr.* [2] 17, 459). V. sol. water and HClAq. Not affected by reducing agents.

DI-PROPYL SULPHONE DICARBOXYLIC ACID $SO_2(CHEt.CO_2H)_2$. *Sulpho-dibutyric acid.* [152°]. Formed from $SO_2(CH_2.CO_2Et)_2$, EtI, and NaOEt (Lovén, *B.* 17, 2817). Dimetric octahedra.

Di-isopropyl sulphone dicarboxylic acid $SO_2(CMe_2.CO_2H)_2$. [188°]. Formed from $SO_2(CH_2.CO_2Et)_2$ (1 mol.), MeI (4 mols.) and NaOEt (4 mols.) (Lovén, *B.* 17, 2824).

DI-PROPYL SULPHOXIDE Pr_2SO. [15°]. Got by oxidising Pr_2S with dilute HNO_3 (S.G. 1·2) (Winssinger, *B.* 16, 329; *Bl.* [2] 48, 110). Needles, sol. water, alcohol, and ether. Decomposed by heat. Readily reduced to Pr_2S. Calcium nitrate forms $(Pr_2SO)_85Ca(NO_3)_2$, a fibrous mass [80°].

β-ISOPROPYLTHIENYL ETHYL KETONE $C_4H_2PrS.CO.C_2H_5$. (251°). Formed from (β)-isopropyl-thiophene, propionyl chloride, and $AlCl_3$ (Thiele, *A.* 267, 136). Oil, volatile with steam. Appears to yield isopropyl-thienyl-glyoxylic acid on oxidation with alkaline $KMnO_4$.

PROPYL-THIENYL GLYOXYLIC ACID $C_4H_2PrS.CO.CO_2H$. Formed by oxidising propyl thienyl methyl ketone with alkaline $KMnO_4$ (Ruffi, *B.* 20, 1745). Solid.—AgA'.

PROPYL-THIENYL METHYL KETONE $C_4H_2PrS.CO.CH_3$. (255°). Formed by the action of AcCl and $AlCl_3$ on a solution of (α)-propyl-thiophene in ligroïn (Ruffi, *B.* 20, 1744). Liquid. Yields an oxim [55°] and a phenyl-hydrazide [60°].

Isopropylthienyl methyl ketone $C_4H_2PrS.CO.CH_3$. (237°). Formed from isopropyl-thiophene, AcCl, and $AlCl_3$ (Thiele, *A.* 267, 187). Oil. Yields a crystalline oxim and phenyl-hydrazide.

PROPYL-DI-THIO-BIURET $C_5H_{11}N_3S_2$ *i.e.* $NH_2.CS.NH.CS.NHPr$. [121°]. Formed from sodium cyanamide and propyl-thiocarbimide (Hecht, *B.* 25, 754). Crystalline mass, v. sl. sol. cold water.

PROPYL-THIOCARBIMIDE PrN:CS. (153°). S.G. $\frac{0}{0}$ ·9909; $\frac{99}{0}$ ·8924. Formed from propylamine and CS_2 followed by $HgCl_2$ (Hecht, *B.* 23, 281, 1662). Pungent liquid, sl. sol. water, miscible with alcohol and ether. Sodium cyanamide and alcoholic MeI form NHPr.CS.NCyMe [115°]. In the same manner may be prepared NHPr.CS.NCyEt [56°], $NHPr.CS.NCyC_3H_5$ [50°], NHPr.CS.NCyPr [56°] crystallising in needles, and $NHPr.CS.NCy.CH_2Ph$ [113°].

Isopropyl-thiocarbimide PrN:CS. (137°). Pungent liquid (Jahn, *M.* 3, 168).

PROPYL DI-THIO-CARBONATE PrO.CS.SH. Unstable oil.—PrO.CS.SK. Formed from CS_2 and KOH dissolved in propyl alcohol (Scala, *G.* 17, 78). Silky needles. Its aqueous solution gives an orange pp. with $CuSO_4$. Iodine forms oily $(PrO.CS)_2S_2$ decomposing at 180°. – PrO.CS.SMe. (202°). Oil.—PrO.CS.SEt. (216°).

(*a*)-**PROPYL-THIOPHENE** C_4H_3PrS. (158° cor.). S.G. ^{19} ·974. Formed from iodo-thiophene, PrBr, and Na (Meyer a. Kreis, *B.* 17, 1561). Oil. Yields (*a*)-thiophenic acid on oxidation.

Isopropyl-thiophene C_4H_3PrS. (154° cor.). S.G. $\frac{16}{16}$ ·9695. Formed from PrBr, thiophene, and $AlCl_3$ (Schleicher, *B.* 19, 672). Oil with powerful odour. With HOAc, phenanthaquinone, and H_2SO_4 it gives a deep violet colour.

β-Isopropyl-thiophene $\left.\begin{matrix}CPr:CH\\CH:CH\end{matrix}\right>S$. (158°). Formed by distilling sodium isopropyl-succinate with P_2S_5 (Thiele, *A.* 267, 133). Oil, smelling like benzene, insol. water, miscible with alcohol, ether, and benzene. Forms $C_3H_7.C_4H_2S.HgCl$ [137°] crystallising from alcohol in white needles, and $C_3H_7.C_4HS(HgCl)_2$ as white grains, insol. alcohol (Volhard, *A.* 267, 183).

References. — BROMO-, IODO-, and NITRO-PROPYL-THIOPHENE.

PROPYL-THIOPHENE CARBOXYLIC ACID $C_4H_2PrS.CO_2H$. [57°]. Formed from iodo-propyl-thiophene, $ClCO_2Et$, and sodium-amalgam; the product being saponified by alcoholic potash (Ruffi, *B.* 20, 1743). Needles (from warm water), or plates (from dilute alcohol).

PROPYL THIOSULPHATE. The salt $PrS.SO_3Na$ 5aq is made from $Na_2S_2O_3$ and PrI (Spring a. Legros, *B.* 15, 1938).

PROPYL-THIO-UREA $NHPr.CS.NH_2$. [110°]. Formed from propyl-thiocarbimide and NH_3Aq in the cold (Hecht, *B.* 23, 283). Four-sided plates, sol. alcohol.

Isopropyl-thio-urea $NHPr.CS.NH_2$. [157°]. Plates (Jahn, *M.* 3, 168).

Di-propyl-thio-urea $CS(NHPr)_2$. [71°]. Formed in the preparation of propyl thiocarbimide. Pearly plates (from water).

Di-isopropyl-thio-urea $CS(NHPr)_2$. [161°]. Needles (from hot water) (Jahn).

PROPYL-TOLUENE *v.* CYMENE.

PROPYL-TOLUIC ACID *v.* CYMENE CARBOXYLIC ACID.

n-**PROPYL-*p*-TOLUIDINE** $C_{10}H_{15}N$ *i.e.* $C_6H_4Me.NHPr$. (232°). S.G. $\frac{23}{4}$ ·9296. μ_D = 1·5367. S.V. 197·53. R_∞ = 82·5. Formed by heating *p*-toluidine (1 mol.) with PrI (1 mol.) for two days at 160°; the yield being 90 p.c. of the theoretical amount (Hori a. Morley, *C. J.* 59, 36). Purified by means of the nitrosamine. Oil. Salts.—B'HCl. [151°]. Needles (from boiling benzene), v. sol. water and alcohol.—$B'H_2C_2O_4$. [173°]. S. (alcohol) 1·4 at 21°. Ppd. on mixing alcoholic solutions of the base (1 mol.) and oxalic acid (1 mol.). Sl. sol. cold water and alcohol.—$B'_2H_2C_2O_4$. [117°]. Occurs in the filtrate from the preceding salt, and formed also when a large excess of base is added to a cold alcoholic solution of the acid oxalate. Crystals, m. sol. cold water and alcohol. Decomposed by boiling water, $B'H_2C_2O_4$ being ppd.—$B'_2H_4FeCy_6$.

Nitrosamine $C_6H_4Me.NPr.NO$. Oil, not solid at –20°. Decomposes below 100°.

Isopropyl-*p*-toluidine $C_6H_4Me.NPr.NO$. (220° uncor.). S.G. $\frac{23}{4}$ ·9129. μ_D = 1·5322. S.V. 199·57. R_∞ 81·4. Formed by heating PrI with *p*-toluidine for two days at 130° (Hori a. Morley, *C. J.* 59, 34). Got also by heating diazo-toluene toluide $C_7H_7.N_2.NHC_7H_7$ with alcoholic NaOEt and PrI for 5 hours on the water-bath, distilling off the alcohol, pouring into water, and decomposing the pp. with HCl. Oil.

Salts.—B'HCl. [171°]. Wax-like crystals (from alcohol) or needles (from benzene), v. sol. water.—$B'_2H_2C_2O_4$. [130°]. S. (alcohol) 5·76 at 22°. Crystals (from dilute alcohol). The acid oxalate is not easily crystallisable.—$B'_2H_4FeCy_6$.

Nitrosamine $C_6H_4Me.NPr.NO$. [59°]. S. (alcohol) 65 at 22°. Yellowish crystals (from alcohol), not volatile with steam.

Reference.—OXY-PROPYL-TOLUIDINE.

PROPYL-UREA. $NH_2.CO.NHPr$. [107°]. Formed from propyl cyanate and NH_3, and from potassium cyanate and propylamine sulphate (Chancel, *Bl.* [3] 9, 101). Long needles, sol. water and alcohol. Its oxalate and nitrate are v. sol. water. Decomposed by HClAq in a sealed tube at 160° into NH_3, NH_2Pr, and CO_2. *Butyryl derivative* $NHPr.CO.NH(CO.C_3H_7)$. [99°]. Formed by the action of cold KOHAq on a mixture of butyramide (2 mols.) and bromine (1 mol.) (Hofmann, *B.* 15, 757). Colourless plates, sl. sol. water.

Isopropyl-urea. *Isobutyryl derivative* NHPr.CO.NH.COPr. [86°]. Formed in like manner from the amide of isobutyric acid. Tables, sol. alcohol and ether.

u-**Di-propyl-urea** $NH_2.CO.NPr_2$. [57°]. Formed from dipropylamine and KCyO. Needles (from alcohol). Its oxalate crystallises in needles, sl. sol. water.

s-**Di-propyl-urea** $CO(NHPr)_2$. [105°]. (255°). Got by boiling the corresponding thio-urea with HgO and water (Hecht, *B.* 23, 285), or from PrCyO and aqueous NH_2Pr. White plates (from water). Sl. sol. cold water, v. sol. alcohol and ether. Its salts are decomposed by water.

Di-propyl-urea $C_7H_{16}N_2O$ *i.e.* $NH_2.CO.NPr_2$. [76°]. Formed from propylamine sulphate and potassium cyanate (Von der Zande, *R. T. C.* 8, 228). Needles. An ethereal solution of aldehyde forms $CH_3.CH(NH.CO.NPr_2)_2$ [118°]. Chloral hydrate gives $CCl_3.CH(OH).NH.CO.NPr_2$ [128°] and in aqueous solution $(C_7H_{16}N_2O)C_2HCl_3O$ aq [51°]. Œnanthol in ethereal solution gives $C_7H_{14}(NH.CO.NPr_2)_2$ [113°].—$B'_2H_2C_2O_4$. [103°]. —$B'C_6H_3N_3O_7$. [135°].—$B'2HNO_3$.

***s*-Di-isopropyl-urea** $CO(NHPr)_2$. Formed as a by-product in the production of isopropyl cyanate from isobutyric bromo-amide and Na_2CO_3 (Hofmann, *B.* 15, 756). Needles, sol. alcohol, insol. ether.

***u*-Di-isopropyl-urea** $NH_2.CO.NPr_2$. [103°]. Formed by evaporating a solution of isopropylamine sulphate with potassium cyanate (Von der Zande, *R. T. C.* 8, 231). Crystals (from ether). An ethereal solution of aldehyde forms $CH_3.CH(NH.CO.NPr_2)_2$ [147°]. Chloral in ethereal solution gives $CCl_3.CH(OH).NH.CO.NPr_2$ [121°]. —$B'_2H_2C_2O_4$. [111°]. Needles. —$B'C_6H_3N_3O_7$. [134°]. Needles. —$B'HNO_3$. [79°].

Reference.—DI-BROMO-PROPYL-UREA.

PROTAGON *v.* LECITHIN.

PROTAMINE $C_9H_{21}N_5O_3$ or $C_{16}H_{31}N_9O_4$. Occurs in the seminal substance of the salmon in November (Miescher, *B.* 7, 376; Piccard, *B.* 7, 1714). Gummy mass, insol. alcohol and ether, sol. water with alkaline reaction. Its salts give with K_4FeCy_6 a milky pp. composed of minute drops. Salts.—$(C_9H_{21}N_5O_3)_2H_2PtCl_8$ (M.); $C_{16}H_{31}N_9O_4H_2PtCl_6$ (P.). Yellow powder.

PROTEIDS. (Πρωτεῖον, 'pre-eminence.') This name is given to a large group of organic compounds which are also known as 'albuminous.' The word 'proteid' itself has been retained simply as a convenient general term, and not as implying any adherence to the theory, first advanced by Mulder, that they all contain a complex molecule to which he gave the name of 'protein.' The word *albumin* is now limited to a certain class of proteids, and the word *albuminoid*, though it is still largely used synonymously with proteid, is restricted by physiological chemists to a class of nitrogenous substances (which includes such substances as gelatin and mucin) which are not proteids, but still in certain reactions resemble those substances closely.

Proteids are never absent from the protoplasm of active living cells, whether animal or vegetable, and they are indissolubly connected with every manifestation of organic activity. A definition of proteids is not possible in the logical sense. Gamgee (*Physiol. Chem.* p. 4) gives in the following sentences a terse description of these substances, which must take the place of a definition: 'Proteids are highly complex, and for the most part non-crystallisable compounds of carbon, hydrogen, nitrogen, oxygen, and sulphur, occurring in a solid viscous condition or in solution in nearly all the solids and liquids of the organism. The different members of the group present differences in physical, and to a certain extent in chemical, properties; they all possess, however, certain common chemical reactions, and are united by a close genetic relationship.'

In vegetables the proteids are constructed out of the simpler chemical compounds which serve as their food. In animals such a synthesis never occurs, but the proteids are derived directly or indirectly from vegetables. By the action of certain digestive juices all proteids are capable of being converted into closely allied substances called peptones, which after absorption undergo reconversion into proteids.

Although much work has been done in attempting to unravel the constitution of the proteids, there is at present but little positive to be said on this point. All we can do is to give the result of the experiments that have been performed which show the classes of products yielded by the proteids, and to enumerate the various theories held by different observers concerning their constitution.

The various proteids differ somewhat in elementary composition within the limits of the following numbers (Hoppe-Seyler, *Handbuch d. Phys. und Path.-Chem. Analyse*, 4to Aufl. p. 223):

	C	H	N	S	O
From	51·5	6·9	15·2	0·3	20·9
To	54·5	7·3	17·0	2·0	23·5

The various decompositions that proteids undergo may be conveniently stated under the following heads:—

a. Decomposition in the body. In the alimentary canal the proteids are converted into proteoses (albumoses) and peptones; this change is probably due to hydration. Under the influence of the pancreatic ferment, a certain class of peptones called hemi-peptones are further acted upon, resulting in the formation of leucine, tyrosine, aspartic acid, ammonia, and protein-chromogen (a substance coloured purple by bromine). Putrefactive processes due to bacteria in the small intestine also occur; these result in the formation of indole, skatole, phenol, and oxy-acids. Ethereal hydrogen sulphates can be detected in the urine as a result of these putrefactive changes (Baumann, *H.* 10, 123); when putrefaction is hindered by the administration of large doses of iodoform in dogs, these products do not appear in the urine (V. Morax, *H.* 10, 318). One of the sources of hippuric acid in the urine of flesh-feeders is the phenyl-propionic acid that results from the putrefaction of proteids in the alimentary tract (Salkowski, *B.* 12, 648; Tappenier, *Z. B.* 22, 236).

After the proteids have been absorbed from the alimentary canal, they become assimilated by the tissues, and there undergo combustion or metabolism, the chief ultimate products being water, carbonic acid, and urea. It is probable that glycocine, leucine, creatine, and ammonium carbonate are intermediate products in this change. Urea had not been obtained from proteids by experiments performed outside the body until quite recently, when Drechsel (*B.* 23, 3096) has succeeded in obtaining a crystalline base lysatin by acting on casein with zinc and hydrochloric acid. Lysatin yields urea when boiled with baryta water. It has also been demonstrated, by experiments on animals, that proteid food gives rise to glycogen in the liver, and to fat in the subcutaneous and other tissues. That proteids can be converted into fats is also shown by the occurrence of *adipocere* in the muscular tissues after death.

b. Action of heat. By dry distillation the proteids yield an oily liquid called *Dippel's oil*, which contains ammoniacal salts of the fatty acids, amines, and aromatic compounds.

c. Action of putrefaction. The chief products are ammonia, ammonium sulphide, carbonic acid, volatile fatty acids, lactic acid, amines, leucine, tyrosine, and other complex aromatic compounds.

d. Action of acids and alkalis. Prolonged boiling with strong sulphuric or hydrochloric acid, or fusion with caustic alkalis, gives rise to a large number of products, of which the following are the most important: leucine, tyrosine, aspartic acid, and glutamic acid. Prolonged heating with dilute acids gives rise to hydrolytic decomposition (Hermann) and the formation of albumoses and peptones (Neumeister, *Z. B.* 23, 381).

The effect of heating proteids with caustic baryta was investigated by Nasse, and subsequently by Schützenberger (*Bl.* Feb. 15, March 5 and 15, 1875). Ammonia was evolved, and carbonic acid remained in combination with barium; these two products occurred in the same ratio as would result from urea similarly treated. In addition oxalic acid, acetic acid, tyrosine, amido-acids of the fatty acid series (especially leucine, butylamine, and amido-butyric acid), acids allied to glutamic and aspartic acids, and lastly a dextrin-like substance, were found in the residue. Schützenberger (*A. Ch.* [5] 16, 289) explains the mechanism of the reaction as follows: the proteid molecule, losing ammonia and carbon as carbonic oxalic, and acetic acids, and assimilating water, is converted into a mixture of glucoproteins $C_nH_{2m}N_2O_4$, containing as its principal term $C_8H_{18}N_2O_4$; by the prolonged action of baryta at a high temperature these split up partly into leucines or amido- acids of the acetic series $C_nH_{2n+1}NO_2$ and leuceïnes or amido-acids of the acrylic series $C_nH_{2n-1}.NO_2$, and partly into double compounds formed by the union of glucoproteins and leuceïnes with the leucines. For Schützenberger's recent attempts to synthesise proteids see *C. R.* 112, 198.

e. Action of hydrochloric acid and stannous chloride. Ammonia, aspartic acid, glutamic acid, leucine, and tyrosine are the chief products (Hlasiwetz a. Habermann, *Anz. Wien. Acad.* 1872, 1873; *A.* 159, 304; 169, 150; *J. pr.* 7, 397).

f. Action of oxidising agents. By means of manganese dioxide and sulphuric acid, or potassium chromate and sulphuric acid, many fatty and aromatic compounds are formed. Nitric acid produces first a yellow insoluble substance, xantho-proteic acid, which dissolves on further action, and yields ultimately para-oxybenzoic and oxybenzoic acids.

Mulder (*J. pr.* 16, 129; 17, 312; *A.* 31, 129) obtained by the action of potash on proteids a substance which is now called alkali-albuminate, but which was regarded by Mulder to be the base of all proteids; he gave it the name 'protein.' Various definite compounds of protein were described, such as oxyprotein, trioxyprotein, sulphoproteic acid, &c. Liebig (*A.* 57, 132) was the first to disprove these assertions, and the only remnant of this theory now is the term 'proteid.' For recent work on this subject and the related one of sulphur in proteids see Danilewski (*H.* 7, 440), and Krüger (*Pf.* 43, 244).

Gerhardt was of opinion that all the proteids are identical in constitution and molecular arrangement, but differ from one another in the nature of the mineral substance with which they are associated. He designated the common organic element by the name 'albumin,' and it may be mentioned that in the elaboration of his theory he regarded egg albumin as the neutral albumate of sodium, and fibrin as a compound of albumin with earthy phosphates. Proteids, however, have been separated from all but traces of mineral matter, and still exhibit their peculiar characteristics; careful elementary analysis also has shown that there is a difference of the percentage amounts of carbon, nitrogen, sulphur, &c., in various proteids. Nevertheless, it is still a fact that some of the distinguishing features of certain proteids are due to the adhering salt; for instance, the coagulation of caseinogen by rennet occurs only in the presence of calcium salts (Hammarsten).

Gautier (*Chimie appliquée à la Physiologie,* i. 251) states that the proteids behave as amides of the higher homologues of lactic and tartaric acids, and residues of aromatic acids; hence when proteids are oxidised there is a simultaneous production of fatty acids, of aromatic compounds, and doubtless of bodies analogous to urea; the products furnished by different proteids are not in the same proportions. It must, therefore, follow that the different radicles they contain differ not only in arrangement but in relative proportion, and sometimes even in their nature. It was Nasse who first observed (*Pf.* 6, 589) that the nitrogen in proteids appears to exist in two conditions, a certain fraction of it being more unstable and apparently more feebly combined than the rest. This view was fully confirmed by Schützenberger in the experiments already alluded to. The latter observer regards the proteids as complex *ureides, i.e.* combinations in various proportions of urea with amido-acids, some of which belong to the leucine series, others to the aspartic series. Representing albumin by the empirical formula $C_{72}H_{112}N_{18}O_{22}S$ (Lieberkühn), it yields, when decomposed by caustic baryta, urea, acetic acid, a sulphur-containing body, and a substance with the formula $C_{68}H_{132}N_{14}O_{24}$, which may on further hydration be split up into the substances already mentioned (glucoproteins, leucines, leuceïnes, &c.).

Pflüger's view relative to the constitution of the proteids (*Pf.* 10, 251) may be thus summarised. One of the most striking features of the proteids is the difference that exists between non-living proteid matter, such as white of egg, and that which forms part of living protoplasm. The former may remain for years without undergoing decomposition, and is indifferent to neutral oxygen; while the latter is continually decomposing, undergoing intramolecular changes, and lives by breathing oxygen. The assimilation of proteid food is looked upon by Pflüger as an ether-like combination of a molecule of living proteid with one of the non-living proteid, water being eliminated. This union of isomeric molecules, which forms a heavy mass but still remains a simple molecule, may be conceived to go on indefinitely. In this process it seems probable that the nitrogen of the food proteid, which exists there in combination as amides, passes into combination with carbon, so that in living proteid it is combined in the form of cyanogen. This view is strengthened by the fact that substances like uric acid, creatine, and guanine, are products of proteid metabolism, while such compounds are never obtained from non-living proteid material. O. Loew (*Die chemische Kraftquelle im Lebenden Protoplasme*, Munich, 1882, *B. A.* 1885, p. 1075) has also found that a striking difference between living and non-living proteids is the fact that the former reduce silver nitrate, probably owing to some radicle of the nature of aldehyde, whereas the latter do not behave in this way. He suggests that albumin is a condensation product of aspartic aldehyde. The simplest formula for Schützenberger's leuceïne $C_4H_7NO_2$ is also that of aspartic aldehyde.

Latham (*Brit. Med. Journ.* [1] 1886, 629) regards albumin as a compound of cyan-alcohols united to a benzene nucleus. The cyan-alcohols resemble proteids in readily undergoing condensation and intramolecular changes; and, moreover, the various products of the disintegration of proteids can also be obtained as the decomposition products of these cyan-alcohols. See also Drechsel's art. in Ladenburg's *Handw. d. Chem.* 3, 541; Beilstein's *Handb.* 3, 1258.

GENERAL PROPERTIES OF PROTEIDS.

1. *Indiffusibility.* Solutions of proteids are non-diffusible. They belong to Graham's class of colloid substances. Peptones, and to a less extent albumoses, are, however, diffusible. This property of indiffusibility enables us to separate proteids from saline admixtures, and also to separate various proteids from one another: *e.g.* if a mixture of albumin and globulin in a saline solution be dialysed, the salts pass out, the albumin remains within the dialyser in solution, while the globulin, which is insoluble in water, is precipitated.

2. *Action on polarised light.* Proteids all rotate the plane of polarised light to the left. The following table gives the specific rotatory power for the yellow line D of some of the chief proteids:

Proteid	Observer	Value of $[\alpha]_D$
Serum albumin	Hoppe-Seyler (*Zeit. f. Chem. und Pharm.* 1864, 737)	−56°
	Starke (*Maly's Jahrs.* 11, 17)	−60°
Egg albumin	Hoppe-Seyler	−33·5°
	Haas (*P.* 12, 378)	−38·08°
Fibrinogen	Haas (*C. C.* 1876, 295, 811, 824)	−59·75°
	Hermann (*H.* 11, 508)	−43°
Sodium albumate	Haas	−55°
Syntonin (from egg albumin)	Haas	−63·12°
Syntonin (from myosin)	Hoppe-Seyler	−72°
Casein (in weak $MgSO_4$ solution)	Hoppe-Seyler	−80°
Serum-globulin	Haas	−59·75°
Various albumoses	Kühne a. Chittenden (*Z. B.* 20, 51)	−70° to 80°

According to Haas, these numbers are unaltered by the salts adherent to the proteids.

3. *Heat coagulation.* Most of the native proteids are coagulated by heating their solutions, but more especially the globulins and albumins. By this means the character of the original proteid is lost, and all are converted into an exceedingly insoluble substance, called 'coagulated proteid.' When several proteids are mixed in a solution, if their temperature of coagulation differs, it is possible to separate them by a process of 'fractional heat coagulation.' The heat coagulation temperature of various proteids is usually characteristic, but it can be varied somewhat by additions of small quantities of acid or alkali; the former lowers, the latter heightens, the coagulation temperature. Alkali albumin in the latter case is not coagulable by heat, and forms so readily that it is advisable to have the solution either perfectly neutral or faintly acid before performing the experiment. Rendering the liquid faintly acid with weak (2 p.c.) acetic acid also renders the flocculi of precipitate larger and easier to filter off. The alkalinity of a liquid is always increased, or its acidity diminished, after the separation of a heat coagulum. Various neutral salts in excess also cause the coagulation temperature to vary; sodium chloride lowers the temperature, while magnesium sulphate has little or no effect. A solution of proteid enters into an opalescent condition a few degrees below that at which the separation of *flocculi* begins. In the dry state proteids are rendered insoluble, like coagulated proteid, at a temperature of 110°C. On the influence of salts on coagulation temperatures, see Limbourg (*H.* 13, 450). Haycraft criticises the method of fractional heat coagulation (*Pr. Roy. Soc. Edin.* 1888-9, 361). It is defended by numerous observers (for references see Halliburton, *J. Physiol.* 13, 806; Hewlett, *ibid.* 798).

The following table gives the heat coagulation temperatures of some of the most important proteids:

Proteid	Temperature of heat coagulation
Egg albumin	72·8°C.
Serum albumin *a*	72·3°
Vitellin	75°
Serum globulin	75°
Fibrinogen	56°
Myosin	56°
Crystallin	93°
Hæmocyanin	65°

4. *General tests for proteids.* Solutions of the proteids are precipitated by strong mineral acids, acetic acid and potassium ferrocyanide, by acetic or oxalic acid together with a large addition of concentrated solutions of neutral salts, by basic lead acetate, by mercuric chloride, by copper sulphate, by tannic acid, by saturation with powdered potassium carbonate, ammonium sulphate or sodio-magnesium sulphate, and by alcohol.

Strong acids and salts of the heavy metals produce a precipitate of coagulated proteid, or of metallic albuminate; in the latter case the metal can be removed by treatment with sulphuretted hydrogen, and the proteid again obtained unaltered. Neutral salts like ammonium sulphate, or sodio-magnesium sulphate, completely precipitate all proteids but peptones, and in an uncoagulated condition—*i.e.* they can be re-dissolved in water or weak saline solutions, and exhibit their characteristic properties. Alcohol precipitates proteids, and after long contact with the precipitate converts them into 'coagulated proteid.' The following reactions are those most frequently employed in the detection of proteids in solution:

(*a*) *The xanthoproteic reaction.* Nitric acid is added; this usually produces a precipitate, but in the case of peptones, or if the quantity of proteid is very small, it does not. The mixture is then boiled, when the liquid and the precipitate turn yellow (xanthoproteic acid); if it is boiled sufficiently long with excess of acid the precipitate dissolves. Addition of ammonia causes the yellow colour to become orange. A similar reaction is given by gelatin and keratin. Analyses of xanthoproteic acid and its compounds made by Mulder and others are not of any value, as it has since been shown that this yellow substance is not constant in composition. The reaction is due to the aromatic radicle undoubtedly present in all proteids. On colour reactions of proteids see Salkowski (*H.* 12, 215), Gnezda (*Pr.* 47, 202), Pickering (*J. Physiol.* 14).

(*b*) The liquid is rendered strongly acid with acetic acid, and solution of potassium ferrocyanide added, which throws down the proteid as a white flocculent precipitate.

(*c*) *Millon's reaction.* Millon's reagent[1] causes a white precipitate of the proteid. On boiling this precipitate and the surrounding liquid, both turn a brick-red colour. If only a trace of proteid is present there may be no initial precipitation. This test is given also by tyrosine, and it is in all probability owing to the aromatic radicle in proteids that those substances give it.

(*d*) Addition of a trace of copper sulphate and excess of potassium hydroxide causes a violet solution. In the case of albumoses and peptones the colour produced is a pink one (biuret reaction). See also Gnezda a. Pickering (*loc. cit.*) for similar reactions with nickel and cobalt.

(*e*) Proteids when dissolved in glacial acetic acid and treated with strong sulphuric acid exhibit a violet colour and faint fluorescence, and if sufficiently concentrated show an absorption spectrum very like that of urobilin (Adamkiewicz, *B.* 8, 161).

The reactions which are applicable to proteids which will not dissolve in water or neutral saline liquids, are the xanthoproteic, Millon's, and the Adamkiewicz colour reactions.

Quantitative Estimation of Proteids.

A large number of different methods of estimating quantitatively the amount of proteid in a solution have been proposed and used; the polarimetric method has been much employed (Hoppe-Seyler, *Virchow's Archiv*, 11, 547). Among gravimetric methods various precipitants of proteids have been suggested, *e.g.* tannin and sodium chloride (Girgensohn, *N. R. P.* 22, 557); hydrochloric acid and potassio-mercuric iodide (Brücke, *Sitz. W.* 1871), &c.; but the following methods are those most frequently employed:

(*a*) *Clinical method.* The rough method generally used for the comparison of albuminous urines consists in acidulating the urine, if it is alkaline, with acetic acid and then boiling it in a graduated tube. The flocculi which form are allowed to settle, and the proportion of the precipitate to the total volume of the liquid read off and expressed in fractions, such as a half, a tenth, and so on. Esbach's tubes are graduated to correspond to percentages of proteid; the precipitant being picric acid.

(*b*) *Precipitation by heat.* 50 to 100 c.c. of water are boiled and an accurately-weighed amount of albuminous fluid, about 15 or 20 g., poured in. The fluid is boiled for some minutes, a few drops of two per cent. acetic acid added, until the precipitate separates in flakes from a clear liquid. The precipitate is collected on a weighed filter, washed with water, alcohol, and ether, and finally dried, weighed, incinerated, and the ash deducted. This method is obviously applicable only to such proteids as are coagulable by heat.

(*c*) *Precipitation by alcohol.* An accurately measured or weighed quantity of the liquid is mixed with three or four times its volume of spirits of wine, and set aside for some hours; the precipitate is then collected, washed with spirit, hot absolute alcohol, ether, warm water, and finally dried and weighed as before (Hoppe-Seyler, *Handbuch*, *3te Aufl.* 312). Or the liquid may be neutralised with acetic acid and mixed with ten times its volume of strong alcohol, and then boiled, the precipitate being treated as before (A. Schmidt, *Pf.* 11, 10; A. Hoffmann, *Virchow's Archiv*, 1879, 255).

(*d*) *Precipitation with ammonium sulphate.* Since Kühne (*Z. B.* 22, 423) has fully shown that saturation with this salt causes complete precipitation of all proteids but peptones, this method may be employed as follows for the quantitative estimation of these proteids:—The liquid is shaken or stirred with excess of the powdered salt, filtered, and the precipitate washed with saturated solution of ammonium sulphate. The filter with adherent proteid and salt is dried at 110°, by which means the proteid is rendered insoluble, and the salt can then be washed away with distilled water. The precipitate is then washed with alcohol and ether, dried, and weighed as before.

Classification of Proteids.

I. *Albumins.* These are proteids which are soluble in water, and not precipitable from their solutions by saturation with sodium chloride or magnesium sulphate. They are coagulated by heat. The important members of the group are egg albumin, serum albumin, and lactalbumin.

II. *Globulins.* These are proteids which are insoluble in water; they are soluble in dilute solutions of neutral salts; and are precipitated in an uncoagulated condition by saturation with sodium chloride and magnesium sulphate. They are coagulated by heat. The most important members of the group are: serum globulin, fibrinogen, myosin, crystallin, and globin.

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[1] *Millon's reagent.* Equal quantities of mercury and strong nitric acid are mixed and gently warmed till the mercury is dissolved. The solution is diluted with twice its bulk of water, and the copious precipitate which forms allowed to settle. The supernatant liquid is the reagent.

III. *Albuminates.* This name is applied to the metallic compounds of proteids, and also to acid albumin or syntonin, and alkali-albumin. Restricting the term to the two latter substances, they may be defined as proteids insoluble in water or in solutions of neutral salts, but readily soluble in dilute acids or alkalis. Their solutions are not coagulated by heat.

IV. *Proteoses.* These are proteids which are not coagulable by heat, and most of them are precipitable by saturation with certain neutral salts. They are precipitated by nitric acid, the precipitate dissolving on the application of heat and reappearing when the solution is cooled. They resemble peptones in being slightly diffusible, and in giving the biuret reaction. They are formed from other proteids as the result of the action of proteolytic ferments on them, being an intermediate stage in the formation of peptones. They are also found in certain animal and vegetable tissues. The best-known members of the group are the albumoses.

V. *Peptones.* These are proteids which are very soluble in water; they are not precipitated by heat, by saturation with any neutral salt, nor by nitric acid. They are completely precipitated by tannin, by excess of absolute alcohol, and by potassio-mercuric iodide; incompletely by phosphotungstic acid, phosphomolybdic acid, and picric acid. They give the biuret reaction. Peptones are subdivided into hemipeptones, those which yield leucine and tyrosine as the further result of pancreatic digestion, and antipeptones, those which do not.

VI. *Insoluble proteids.* This class includes a number of proteids varying in their reactions which cannot be included in any of the foregoing classes, but which all resemble one another in their extreme insolubility in various reagents. This class includes fibrin, coagulated proteid, lardacein, antialbumid, and gluten.

DESCRIPTION OF THE PROPERTIES OF INDIVIDUAL PROTEIDS.

It will now be convenient to take the most important members of the various foregoing groups, and describe the characteristic properties of each. The animal proteids will be taken first.

CLASS I., ALBUMINS.—**Egg albumin.** This is the albumin occurring in white of egg; it may be separated from the globulin, which also occurs in that situation, by precipitating the latter with dilute acetic acid, or by saturation with magnesium sulphate. It is coagulated at a temperature of 70°-73°C. By fractional heat coagulation further pps. are obtained at 76° and 82° (Corlin a. Berard, *Arch. de Biol.* 9, 1). Its specific rotation is −35·5°. It is precipitated by agitation with ether. Crystalline egg albumin may be obtained by addition of an equal vol. of sat. sol. of ammonium sulphate and filtration to remove oviglobulin. On slow evaporation of the filtrate, crystals of egg albumin form (Hofmeister, *H.* 14, 165; Gabriel, 15, 456).

Lieberkühn ascribed to albumin the formula $C_{72}H_{112}N_{18}SO_{22}$, Schützenberger $C_{240}H_{392}N_{65}O_{75}S_3$, Harnack (*H.* 5, 207) $C_{204}H_{322}N_{52}O_{66}S_2$. Since Lieberkühn attempted to establish the molecular weight of albumin by preparing and analysing the copper compound, various investigations have been published bearing on the nature and composition of the compounds of albumin with the heavy metals, and especially with copper (F. Rose, Mitscherlich, Harnack, Bielitzki, Ritthausen, Lassaigne, &c. Further particulars will be found, with references to literature, in a paper by R. H. Chittenden and H. H. Whitehouse in *Studies from the Laboratory of Physiol. Chem., Yale University*, 2, 95). The results obtained are most contradictory, and illustrate that numerous compounds may be obtained by slightly modifying the conditions of precipitation; they are also very liable to dissociation. The only other proteid the metallic compounds of which have been studied is myosin; the percentage amount of the various metals in the compounds obtained differ from those formed from egg albumin (Chittenden a. Whitehouse, *l.c.*).

Uses of albumin. It is much used for clarifying vinous and syrupy liquids, as when boiled with it the heat coagulum carries down colouring matter and other impurities. In cookery white of egg is employed for this purpose, but in large operations, such as sugar refining, blood serum is used. Albumin is also largely used in photography, and in calico-printing for fixing colours. Its property of forming a hard compound with lime renders it useful as a cement in repairing earthenware. Spoilt albumin in print works may be recovered for practical purposes by the action of pepsin (Wagner a. Witz, *D. P. J.* 119, 166).

Serum albumin. This is the albumin occurring in serum. Its specific rotation is −56°. Fractional heat coagulation, and elementary analysis show that it is probably not a single proteid but consists in warm-blooded animals of three, α, β, and γ, coagulating respectively at 73°, 77°, 84° (*v.* BLOOD). Aronstein a. A. Schmidt (*Pf.* 2, 1) stated that serum albumin completely freed from salts by prolonged dialysis does not coagulate by heat. This statement has not been confirmed by subsequent observers, who have found it impossible to free serum albumin from ash by this method, and have attributed the non-coagulation to a slight alkaline residue (Heynsius, *Pf.* 9, 514; Winogradoff, 2, 605; Hinzinga, 2, 392; Haas, 2, 378). On ash-free albumin see also Harnack, *B.* 22, 3046; 23, 3745. Serum albumin is not coagulated by ether. It is the proteid which most frequently occurs in morbid urine.

Serum albumin is not precipitated by saturating the serum with magnesium sulphate; if, however, the globulin precipitated by this method be filtered off, and the filtrate saturated with sodium sulphate, the albumin is precipitated; this is due to the formation of sodio-magnesium sulphate ($MgSO_4.Na_2SO_4.6H_2O$) in the liquid (Halliburton, *Journ. of Physiol.* [5] 152). Albumin having nearly the same characters as serum albumin is found also in milk, muscle, lymphatic glands, and other tissues in small quantities.

CLASS II., GLOBULINS. — **Serum globulin.** (Synonyms, *paraglobulin, fibrinoplastin, serum-casein.*) This is the globulin occurring in serum. It is soluble in weak solutions of sodium chloride; it is partially precipitated when the percentage of sodium chloride reaches 0·03 to 0·07, re-dissolved on the addition of more salt, and again precipitated, though never completely, when the amount of salt present is 20 p.c. It is completely precipitated by saturation with magnesium sulphate. It does not coagulate on the addition of fibrin ferment, and probably takes no part in the formation of fibrin (*v.* art. BLOOD; *v.* also Hammarsten, *Pf.* 17, 447; 18, 89). Its heat coagulation temperature is 75°C.

The following methods have been suggested for the separation of the globulin from the albumin of serum:

(*a*) Dialysis. When the salts are dialysed out, the globulin is precipitated, the albumin remains in solution.

(*b*) Dilute the serum to 10 or 15 times its volume with water, and pass a stream of carbonic acid through it, the globulin is precipitated (A. Schmidt, *Arch. f. Anat. u. Physiol.* 1862, 429); it is also partially precipitated by the addition of very weak acetic acid when the serum is similarly diluted (Panum, *Arch. f. Pathol. Anat.* 4); it was on account of this that a special alkali albumin or serum casein was formerly believed to exist in the blood.

(*c*) Saturation with sodium chloride precipitates the globulin, leaving the albumin in solution (A. Schmidt).

(*d*) Saturation with magnesium sulphate (Hammarsten). This is the only method commonly employed which effects a complete separation. Kauder has stated that half-saturation with ammonium sulphate will act similarly, and Halliburton (*loc. cit.*) that sodium acetate and sodium nitrate may also be used.

Serum globulin may be estimated quantitatively in serous liquids in the following way: a weighed or measured quantity of the liquid is saturated with magnesium sulphate, the precipitate collected on a weighed filter and washed with a saturated solution of magnesium sulphate, and then dried at 110°C. for some hours; the proteid is thus rendered insoluble, and is freed from the salt by washing with water and alcohol. The precipitate is again dried on the filter to constant weight, weighed, and subsequently ignited and the ash deducted. In such a liquid as serum, viz. one containing a mixture of globulin and albumin, the latter may be estimated by deducting the amount of globulin from the amount of total proteids present.

Cell globulin found in lymph cells and other cellular structures coagulates at 47°–50°. A globulin (myoglobulin) which coagulates at 63°C. but otherwise resembles serum globulin exists in muscle plasma.

Fibrinogen. This proteid, which occurs in blood plasma, very closely resembles the preceding; it differs from serum globulin in being completely precipitable by half-saturation with sodium chloride, and may thus be separated from that proteid (Hammarsten, *Pf.* 19, 563). It is precipitable by a stream of carbonic acid, but it is necessary to dilute the plasma with at least 20 times its volume of water before precipitation occurs, whereas serum globulin is precipitated when the dilution is less. It is coagulated by heat at 56°C. The heat coagulum is a very sticky one; the low temperature at which fibrinogen coagulates forms the basis of a method for estimating it quantitatively: the coagulated proteid formed from the fibrinogen at 56°C. is collected on a weighed filter, washed with distilled water and alcohol, dried at 110°C., and finally weighed, ignited, and the amount of ash deducted (Fredericq). Under the influence of the fibrin ferment, fibrinogen is converted into fibrin; it is due to this change that blood coagulates when drawn, the fibrin entangling the blood corpuscles to form the clot. The term fibrinogen has been recently extended by Wooldridge to other ill-defined proteid substances which he considers to be precursors of fibrin. These are probably nucleo-albumins mixed with lecithin. For latest views on blood coagulation with references see Halliburton (*J. Physiol.* 13, 829; Goulstonian Lecture No. 3, *Brit. Med. Jl.* March 1893).

Plasmine. The term 'plasmine' was given by Denis (*Mémoire sur le Sang*, Paris, 1859) to the precipitate produced by saturating blood plasma with common salt; this has since been shown to consist of the two proteids, fibrinogen and serum globulin; serine was the name given to the proteid left in solution, or, as it is now called, serum albumin.

Myosin. This is the proteid which is formed after the death of muscle; the muscle plasma separates into a clot composed of myosin, and muscle serum, as blood plasma separates into fibrin and blood serum. This produces a stiffening of the muscles called *rigor mortis.* The name given to the proteid precursor of myosin in the living muscle is myosinogen. The clot of myosin formed by diluting with water a saline extract of flesh is not so coherent as that of fibrin; it is readily soluble in 10 p.c. sodium chloride solution, from which it is precipitable by saturation with that salt or with magnesium sulphate; it forms a heat coagulum in such a solution at 56°C. Myosin is converted with great readiness into acid albumin or syntonin by weak hydrochloric acid; A. Danilewsky regards the compound so formed as being not ordinary syntonin but a combination of HCl with myosin, from which by suitable treatment myosin is recoverable. After long-continued dialysis, myosin can be freed from salts, and is thus rendered exceedingly insoluble, both in saline solutions and in dilute hydrochloric acid (A. Danilewsky, *H.* 5, 158; Halliburton, *Journ. of Physiology*, 8, 136). (See also MUSCLE.)

Vitellin. A proteid present in yolk of egg, which, although it resembles globulins in certain particulars, differs from them in not being precipitable by saturation with sodium chloride. Solutions coagulate at 70°–75°C. It is prepared by treating the yolk of hen's egg with ether, by which reagent most of the fatty and colouring matters are dissolved; vitellin remains undissolved as a white granular substance, which is insoluble in water, but readily soluble in dilute saline solutions. Nuclein appears to be united closely to, and may be obtained from, vitellin.

Crystallin. This was once called globulin, but that term has been extended to the whole group. It is obtained from the crystalline lens of the eye, composing, according to Berzelius, 35·9 p.c. of that structure. Its saline solutions become opalescent at 73°, but a coagulum is not deposited till 93°C. is reached. According to

Lehmann (*Physiol. Chem.* 1, 366) the formation of a heat coagulum is accompanied by the development of an acid instead of an alkaline reaction, as is the case with other proteids; he accounts for this by supposing that crystallin is united to ammonio-sodic phosphate, which, on the application of heat, is resolved into ammonia and acid phosphate of soda. Valenciennes and Fremy (*C. R.* 44, 1122) state that other proteids are found in the lens, and have given the name phaconin to one in that of fishes (*v.* also Béchamp, *C. R.* 90, 1255).

Hæmoglobin. When a solution of hæmoglobin, the red pigment of the blood, is heated, the liquid becomes turbid, and a coagulum of a reddish-brown colour separates out between 70° and 80°C. Heat decomposes the hæmoglobin into two substances insoluble in water, one coagulated proteid, the other a colouring matter, hæmatin, which contains all the iron of the hæmoglobin. A similar decomposition occurs when hæmoglobin is acted on by strong acids or alkalis, or by excess of alcohol. Preyer described the proteid substance under the term *globin*, which is insoluble in water, and which swells in solutions of sodium chloride and sodium hydrate without dissolving. Kühne concludes from the action of reagents that a mixture of proteids rather than a single proteid results from the decomposition of hæmoglobin; these would, however, seem to belong to the globulin class from the fact that hæmoglobin is precipitable from its solutions by saturation with such neutral salts as precipitate other globulins, and also by a stream of carbonic acid (*v.* art. HÆMOGLOBIN).

Hæmocyanin. This is a proteid associated with a colouring matter which takes the place of hæmoglobin as an oxygen-carrier in the blood of certain crustacea, arachnida, gastropoda, and cephalopoda. It was first described by Fredricq in the blood of the octopus; the blood which comes to the gills being colourless, and that leaving them being blue: the blue pigment is due to a loose combination of the proteid with oxygen, which, like oxy-hæmoglobin, parts with its oxygen to the tissues. Copper takes the place of the iron of hæmoglobin in this compound. It has not been separated into a pigment and a proteid, as hæmoglobin has. It coagulates by heat at 65°, and is precipitated by saturation with neutral salts, and by dialysis like other globulins (for references see Halliburton, *Journ. of Physiol.* 6, 300; Griesbach, *Pf.* 50, 473).

CLASS III., ALBUMINATES.

Acid albumin. If a small quantity of dilute acid (hydrochloric or acetic) be added to serum or egg-albumin, no precipitation occurs, but after a short time it will be found that the albumin no longer coagulates on heating, and that its dextrorotatory power is increased. The albumin has been converted into acid albumin. On carefully neutralising such a solution with weak alkali, the whole of the proteid matter is thrown down as a white precipitate, which is soluble in excess of the alkali, and may be re-precipitated by neutralisation with weak acid, and again dissolved by excess of the acid, and so on. Acid-albumin is soluble in solutions of alkaline carbonates; it is precipitated, like globulin, by saturation with sodium chloride or magnesium sulphate.

Acid-albumin may also be formed in a similar way from any globulin; myosin, for instance, is converted into acid albumin or syntonin, as it was first termed by Liebig, when prepared from muscle. The parapeptone of Meissner, which is formed in the first stages of peptic digestion, is also identical with acid albumin.

Alkali albumin. If, instead of dilute acid, dilute alkali be added to an albumin or globulin, coagulation by heat is similarly prevented, and the whole of the proteid is thrown down by neutralisation, and is soluble in excess of either acid or alkali. The name alkali-albumin is given to the proteid thus altered by alkali. Like acid albumin it is soluble in solutions of alkaline carbonates, and precipitated by saturation with sodium chloride or magnesium sulphate. In the presence of alkaline phosphates it is necessary to add more acid to obtain a precipitate than if the alkaline phosphate were absent; the acid is just used to convert the alkaline into neutral phosphate. When heated with strong solution of potassium hydrate, potassium sulphide is not formed.

Lieberkühn's jelly. When either tribasic phosphoric acid, acetic or tartaric acids, which do not precipitate moderately concentrated solutions of albumin, is added in excess to concentrated serum or white of egg, a jelly is produced which liquefies like gelatin on heating, and again solidifies on cooling. A similar jelly is formed by adding a strong solution of potash to serum or white of egg. This substance, called Lieberkühn's jelly, is regarded as a variety of acid or alkali albumin respectively; it is soluble with difficulty in water; the aqueous solution remains, however, clear when boiled, and is precipitated by neutralisation.

Compounds of albumin with acids. On account of the present uncertain state of our knowledge concerning the constitution of the proteids, the statements concerning compounds which have been described of albumin with various acids must be received with caution, as is also the case with metallic albuminates (see *Egg albumin*).

Trinitro-albumin $C_{72}H_{105}(NO_2)_3N_{18}SO_{22}$ is prepared by triturating or shaking dried and powdered albumin with 14 or 15 times its weight of nitric acid (HNO_3); a gelatinous mass is the result, and on pouring this into water the insoluble light-yellow tinted compound separates out. If the gelatinous mass be left to itself at a temperature below 10°, a small quantity of nitrogen tetroxide is given off, and a solution formed which, when diluted with water, deposits a dark-yellow tasteless *hydroxytrinitro-albumin*, $C_{72}H_{100}(NO_2)_3N_{18}(OH)_2(SO_2.OH)O_{27}$. Both these compounds dissolve without alteration in dilute alkalis, from which solution they are precipitated in yellow flocculi on addition of acid (O. Loew, *J. pr.* [2] 5, 433). If, instead of using nitric acid, a mixture of concentrated nitric and sulphuric acids be employed, a bitter yellow powder, insoluble in water, alcohol, or dilute acids, but soluble in dilute alkalis, is obtained which is called *hexnitro-albumin sulphonic acid*, $C_{72}H_{101}(NO_2)_6(SO_2.OH)N_{18}SO_{22}$; on treating this with ammonium sulphide, *hexamido-albumin* *sulphonic acid* $C_{72}H_{101}(NH_2)_6(SO_2.OH)N_{18}SO_{22}$ is formed; this is decomposed by strong alkalis with evolution of ammonia, and by nitric acid with evolution of red fumes. It is insoluble in dilute acids, but readily dissolves in concentrated ones (O. Loew, *J. pr.* [2] 3, 180).

Gelatinous compounds of albumin with acids are prepared by leaving it twenty-four hours in a parchment paper dialyser and a dilute acid in the outer vessel. For a quantity of albumin represented by Lieberkühn's formula, $C_{72}H_{112}N_{18}SO_{22}$, the compounds contain 2 mols. nitric, 2 mols. hydrochloric, 1 mol. sulphuric, and 1½ mols. phosphoric acid (G. S. Johnson, *C. J.* 27, 734).

Casein and Caseinogen. Caseinogen is the chief proteid in milk. By the action of rennet it is converted into a curd called casein. Caseinogen is thrown down by the addition of acetic or mineral acids, especially if the milk be first diluted; this precipitate when freed from fats is insoluble in water, soluble in dilute acids or alkalis (and alkaline carbonates), and re-precipitable by acidulation. It may also be prepared from milk by saturating it with magnesium sulphate, followed by washing the precipitate with saturated solution of that salt till the washings contain no albumin, and then re-dissolving the precipitated caseinogen by adding water. The salt still adherent to the precipitate enables it to dissolve; the fat remains undissolved on the filter. Such a neutral solution of caseinogen becomes cloudy on heating, and the cloudiness disappears on cooling if the heating has not lasted too long. Lubavin states that caseinogen differs from alkali albumin in the following particulars: (1) when caseinogen is treated with caustic potash potassium sulphide is produced; (2) on digestion with artificial gastric juice, caseinogen yields a substance containing phosphorus, whereas an albuminate can be prepared from white of egg which contains no phosphorus (Lubavin, *Hoppe-Seyler's Med. Chem. Untersuch.* 1871, 463). C. Wurster (*B.* 20, 263) states that when hydrogen peroxide is passed through a solution of egg albumin in the presence of sodium chloride and an acid (lactic, acetic, phosphoric, or sulphuric) a proteid insoluble in water is thrown down, which he states to be a mixture of gelatinous acid albumin with a large quantity of proteid similar to caseinogen; he further supposes that hydrogen peroxide plays an important *rôle* in the living tissues of the body, and that the caseinogen of milk may be produced from the proteids of the blood by a similar means. The precipitate produced by adding ether to yolk of egg is also stated to have properties similar to caseinogen (Bopp, *A.* 79, 16).

Most of the older writers use the word casein to include both it and caseinogen. Different varieties of casein have been described by different observers; Berzelius, Braconnot, and others described *soluble casein*, soluble in water, and *insoluble casein*, insoluble in water (*v.* also Bopp, *l.c.*). The soluble casein probably consisted of the other proteids present in milk in addition to casein. More recently the view has, however, been again advanced that the only proteid in milk is casein; and that the apparent presence of albumin and other proteids is due to the action of reagents or ferments (Duclaux, *C. R.* 98, 373, 438, 526; E. Pfeiffer, *Maly's Jahrber.* 14, 177). H. Struve (*J. pr.* 29, 70, 110) distinguishes between casein which forms the envelopes of the fat globules, and that which exists in solution in the milk; both, however, have the same properties. A. Danilewsky (*H.* 7, 433) states that casein can be separated into *caseo-protalbin*, soluble in hot 50 p.c. alcohol, and *caseo-albumin*, insoluble in that reagent. Hammarsten (*H.* 7, 227) has, however, shown that this behaviour of casein depends in part upon its content of calcium phosphate, the presence of which impurity depends upon the use of hydrochloric acid in the precipitation of the casein, which acid does not favour the removal of the salt as well as acetic acid. Hammarsten, moreover, showed by elementary analysis that casein is a single body; this has been confirmed by Chittenden and Painter (*Studies from the Lab. of Physiol. Chem.*, Yale Univ. 2, 156). The two last-named observers obtain the following as the percentage composition of casein: C, 53·30; H, 7·07; N, 15·91; S, 0·82; P, 0·87; O, 22·03. Hammarsten (*H.* 7, 269) and Ritthausen (*Maly's Jahrsber.* 1873, 28) have also published elementary analyses of casein.

It is owing to the presence of caseinogen that when rennet is added to milk a curd is produced, which is composed of the clotted casein and entangled fat globules; the whey or liquid residue contains the sugar, albumin, and salts of the milk. The spontaneous coagulation that sometimes occurs in milk is due either to the precipitation of caseinogen by lactic acid formed from lactose by fermentation, or to aërobic organisms which act like rennet. The coagulation that occurs when milk is boiled is due, not to the casein, but to the albumin in the milk. The ferment coagulation is a process which is entirely different from the precipitation by acid. A solution of pure caseinogen in dilute alkali will not coagulate on the addition of rennet; if, however, a small quantity of calcium phosphate or chloride be added, coagulation readily occurs. If caseinogen, precipitated by acetic acid, be well washed with water till the reaction is nearly neutral, and then neutralised with solid calcium carbonate, a pasty mass is formed which, on the addition of rennet thereto, sets into a solid clot; but here again if the caseinogen has been washed free from calcium phosphate rennet has no such action. This dependence of the rennet coagulation on the presence of earthy phosphate has been worked out by Hammarsten. The ferment causes the change from caseinogen to casein. The lime salt combines with the latter and precipitates it. Hammarsten showed that on the coagulation of caseinogen by rennet a whey albumin easily soluble in water is formed in addition to the clot of casein. Soxhlet (*J. pr.* [2] 6, 1) states that alkaline solution of artificially prepared alkali albumin also coagulates on the addition of rennet, but this statement has not been confirmed. Metacasein is a name given to an early stage of the action of rennet and pancreatic juice on caseinogen. It coagulates by heat (Roberts, *Proc. Roy. Soc.* 1881; Edkins, *Journ. Physiol.* 12, 193).

Casein in the milk of different animals is stated by Simon to vary slightly; thus human casein is yellowish-white, and very friable; it is incompletely precipitated from its aqueous solu-

tion by alum or by acetic acid. Casein from cow's milk is less soluble in water, and becomes viscid and horny on drying. Canine milk gives a casein which does not become viscid and horny when dried, and is less soluble in water. Human casein is much more easily digested than that of cow's milk, which is more viscid, and sets into a more solid clot under the influence of the rennet ferment of the gastric juice. For recent papers on casein see Ringer, *Journ. Physiol.* 11, 464; 12, 164; Halliburton, 11, 459; Sebelien, 12, 95; Hewlett, 13, 798.

Class IV., Proteoses.—Under the name proteose it is convenient to include the large number of products which are intermediate in the formation of peptones from other proteids. Similar substances are formed by the action of both the peptic and tryptic ferment; those formed from fibrin or egg albumin have received the name of albumose; from globulin, globulose; from casein, caseose; from vitellin, vitellose, &c. These various substances resemble each other in their general reactions, and differ from one another in origin, slightly in percentage composition, and in a few minor reactions. The albumoses are those which have been most studied. It will be sufficient here to describe the properties of the varieties of albumose. The globuloses, vitelloses, &c., are divided into similar varieties, with corresponding prefixes.

The properties of these substances have been chiefly worked out by Kühne and Chittenden. The names first given to them were propeptone (Kühne) and *a* peptone (Meissner). Kühne then adopted the name albumose, and subdivided the albumoses into hemi-albumoses, those which are converted into hemi-peptones, and anti-albumoses, those which are converted into anti-peptones. Ampho-albumose is a term which includes both hemi- and anti- varieties.

The following are the chief albumoses:

(i.) Proto-albumose, soluble in distilled water and weak saline solutions, partly precipitated by saturating its acidified solutions with sodium chloride. It is also precipitated by mercuric chloride and by copper sulphate.

(ii.) Hetero-albumose, insoluble in distilled water, soluble in weak saline solutions, and completely precipitated therefrom either by dialysing out the salt or by saturation with sodium chloride. It is precipitable by mercuric chloride only in acid solutions; it is precipitated by copper sulphate. By heating its saline solutions a cloudiness is produced, which is not caused by the formation of coagulated proteid, since it readily disappears on the addition of weak acid or alkali. By the action of alcohol hetero-albumose is partially converted into an insoluble product (dys-albumose).

(iii.) Deutero-albumose. This is the albumose most nearly allied to peptone. It is soluble in distilled water, and in saline solutions; it is not precipitated by saturation with sodium chloride. It is precipitable by nitric acid only in the presence of excess of salt, and then does not dissolve so readily on heating as in the case of the other albumoses. It is precipitable by mercuric chloride, but not by copper sulphate. It can be separated from peptones by saturation with ammonium sulphate, which precipitates deutero-albumose but not peptones. For latest work on this see Kühne, *Z. B.* 29, 1.

The above reactions are those in which the albumoses differ from one another; they resemble one another in their characteristic behaviour with nitric acid (already described), and in giving the biuret reaction. Neumeister says that in the formation of peptones from albumin, in the first stage of digestion, proto-albumose (chiefly a hemi-product), hetero-albumose, and anti-albumid (an insoluble product only partially further changed, and that into antipeptone) are formed. Deutero-albumose is in all cases an intermediate product between these and the final peptones.

The following are the chief papers published in reference to this subject. On albumoses: Kühne and Chittenden, *Z. B.* 20, 11; R. Neumeister, *ibid.* 23, 381; Chittenden and Bolton, *Studies from the Physiol. Lab., Yale Univ.* 2, 126. On globuloses: Kühne and Chittenden, *Z. B.* 22, 409. On vitelloses: Neumeister, *ibid.* 23, 402. On caseoses: Chittenden and Painter, *Studies from the Physiol. Lab., Yale Univ.* 2, 156. On the digestion of casein: H. Thierfelder, *H.* 10, 577. On benzoylated ethers of the albumoses: Schrötter, *B.* 22, 1950.

Class V., Peptones.—The general reactions of these substances and of their chief varieties, hemi- and anti- peptone, have been already described. It is only since the introduction of the method of separating them from other proteids by saturating a solution containing such a mixture with ammonium sulphate that they have been obtained free from proteoses. Most of the peptones of commerce consist almost entirely of proteoses. Peptones have also been described as occurring in milk, and in certain animal and vegetable tissues, whereas these proteids are in reality proteoses artificially formed during manipulation. Certain properties previously ascribed to peptones, *e.g.* a power of preventing blood from coagulating after intravenous injection, are now known to be due to proteoses.

When peptones are formed artificially a bitter taste is developed; what this is due to is unknown. Pure peptone has a meaty or cheesy taste; the albumoses are also free from bitterness. It is exceedingly difficult to dry pure peptone, and when dry it hisses and froths, with evolution of heat on the addition of water.

Anti-peptone—and the same appears to be true of other anti- products of digestion (*e.g.* anti-albumid)—do not only not yield leucine and tyrosine on further pancreatic digestion, but appear not to contain the tyrosine radicle; they do not give Millon's reaction, and do not yield tyrosine on boiling with sulphuric acid.

(For the most recent paper on peptones, methods of purification, and ultimate analysis, see Kühne and Chittenden, *Z. B.* 22, 423.)

Class VI., Insoluble proteids.

Fibrin. This is the proteid formed from fibrinogen, probably under the influence of a ferment derived from the white corpuscles of the blood. It is owing to its formation that blood clots after withdrawal from the body (see Blood). It may be prepared pure by washing the clot free from corpuscles by a stream of water, or better, by allowing the plasma freed from corpuscles to coagulate, and then it is washed free from other proteids by water. It is a white elastic solid, usually exhibiting fibrillation under a high magnifying-power. It is insoluble in water, partially soluble in dilute saline solutions, the proteid which goes into solution having the properties of serum globulin. Fibrin possesses the power of liberating oxygen from solutions of hydrogen peroxide. Fibrin swells up in cold weak hydrochloric acid (0·1 p.c.); it dissolves, forming acid albumin, on heating it with weak hydrochloric acid. It is readily digested by pepsin or trypsin, yielding albumoses and peptones. Hasebroek (*H.* 11, 348) and A. Herrmann (*ibid.* 11, 508) state that a first product in the digestion of fibrin is a substance with many of the properties of fibrinogen. (For elementary analyses and varieties of fibrin see Hammarsten, *Pf.* 22, 484; 30, 437. See also *Fibrinogen.*)

Coagulated proteid. This is proteid converted by heat or alcohol into a coagulum. It is insoluble in water or dilute acids or alkalis; it is, however, like fibrin, readily digestible by proteolytic ferments.

Lardacein (so-called amyloid or albuminoid substance). This is formed in the disease known as waxy degeneration, the cells of the liver, spleen, and other organs being replaced by this substance. It is coloured brownish-red by iodine, hence the name amyloid (Virchow). Kekulé and Schmidt showed that it was a proteid. It is insoluble, like coagulated proteid, and it has been usually stated that it is not dissolved by gastric juice. Kostiurina (*C. C.* 1887, 120) finds, however, that it is soluble in pepsin solution acidified with hydrochloric acid.

The *vegetable proteids* have the same general reactions, and may be divided into the same classes as the animal proteids. Their percentage composition is also approximately the same, but varies with individual members of the group, as is the case with the animal proteids. Leucine, tyrosine, asparagine, and other amides are found in plants, which may perhaps be stages in the formation of proteids from the union of inorganic nitrogen with certain non-nitrogenous compounds in the plant tissues (C. O. Müller, *L. V.* 1886, 326). Various observers have found in vegetable tissues a crystallisable proteid, often spoken of as an albumin, but which has since been shown to consist of a globulin (vitellin). These crystals were first observed by Hartig (*Botan. Zeitung*, 1885, 881). Maschke obtained crystals from Para nuts by extracting them with water at 50°; the crystals formed on evaporating this extract at the same temperature (*J. pr.* 74, 436). Similar crystals have been obtained by Schmiedeberg (*H.* 1, 205), by Drechsel (*J. pr.* [2] 19, 331), Ritthausen (*J. pr.* 131, 481). G. Grübler obtained octahedral crystals from pumpkin seeds and castor-oil seeds by cooling to 7° a sodium chloride extract of the seeds made at 70° (*J. pr.* 131, 105). The aleurone grains of plants have been investigated by S. H. Vines (*Pr.* 30, 387; 31, 62); in the peony, castor-oil plant, blue lupin, and many other plants. Vines found that the grains are either wholly or partially composed of proteids, and classifies them according to whether (1) they are soluble in water, in which case they consist of vegetable peptone or hemi-albumose, (2) soluble in 10 p.c. sodium chloride solution, and (3) partially soluble in 10 p.c. sodium chloride solution. In the two latter cases globulins and albumins are also present. For recent work on crystallised vegetable proteids see Osborne, *Am.* 14, No. 8.

Class I., Vegetable albumins.—In addition to the crystalline body just described, the position of which in our classification is properly in the next group, there are in vegetable juices true albumins. These have been prepared and analysed from rye by Jones (*A.* 40, 66), from wheat flour by Dumas and Cahours (*A. Ch.* [3] vi), by Boussingault (*ibid.* [2] 63, 225), from potatoes by Rüling (*A.* 58, 306), in the latex of several caoutchouc-yielding plants by J. R. Green (*Pr.* 40, 28), and in papaw juice by Martin (*J. Physiol.* 6, 336). Such albumins are coagulated by heat at about 70°, and are not precipitated by saturation with sodium chloride, magnesium sulphate, nor by acetic acid. The myrosin of mustard seeds also resembles vegetable albumin, and myco-protein from yeast and bacteria is also stated to be an albumin (Schaffler, *J. pr.* 131, 302).

Class II., Vegetable globulins.—These were first described by Vines (*l.c.*), and have since been classified by Martin (*Proc. Physiol. Soc.* 1887, 8), who has found them in the flour of wheat, rye, and barley, in papaw juice, and in the seeds of *Abrus precatorius* (jequirity). He divides them into two classes: vegetable myosins and vegetable paraglobulins. The myosins coagulate at 55°–60°, are precipitated by dialysing the salt away from their solutions; but this precipitate is no longer a globulin, being insoluble in saline solutions. It has the properties of an albuminate, *i.e.* soluble in weak acid or alkali and precipitated by neutralisation. A similar transformation occurs when a solution of the myosin, especially a dilute solution, is placed in an incubator at 35°–40° for twelve to eighteen hours. The vegetable paraglobulins coagulate at 70°–75°C., and are not transformed into albuminates, either by dialysis or by a long exposure to a temperature of 35°–40°. This classification does not include *plant vitellin* (phytovitellin), the crystalline form of which has been already alluded to. The crystals are membraneless, doubly refracting, and the proteid of which they consist has all the reactions of vitellin prepared from yolk of egg. This vitellin was found to be free from nuclein and lecithin, and may be regarded as the purest globulin yet known. Elementary analysis gave C 52·43, H 7·12, N 18·1, S 0·55 p.c. (For further analyses of vegetable proteids see Barbière, *J. pr.* 126, 114.)

Class III., Vegetable albuminates.—**Legumin and conglutin.** Legumin, or vegetable casein, was discovered by Einhof in 1805, and called by him végéto-animale (*N. allgem. J. D. Ch.* v.; A. Gehlen, vi. 126, 548), in peas, beans, and lentils. Proust, H. Vogel, Boullay, Braconnot, and Liebig considered it to be identical with the casein of milk. Dumas and Cahours found that it contained less carbon and more nitrogen than casein (Gerhardt, *Traité*, 4, 491). The composition and properties of this proteid have been more recently studied by Ritthausen. He prepared it by extracting pulverised peas, beans, lentils, and vetches with dilute alkali, precipitating the strained liquid with acetic acid, washing the precipitate with alcohol on a filter, and finally drying over sulphuric acid. It dissolves both in cold and boiling water; on analysis the following percentages were obtained: From peas, lentils, vetches, and field beans—C 51·48; H 7·02; N 16·77; O 24·32; S 0·40. From garden beans—C 51·48; H 6·92; N 41·71; O 26·35; S 0·45. Treated with sulphuric acid it yields leucine, tyrosine, glutamic, and aspartic acids. The legumin of almonds and lupines, called by Ritthausen conglutin, is richer in nitrogen, more glutinous, and more soluble in acetic acid (Ritthausen, *J. pr.* 103; 65, 78, 193, 273; [2] 26, several papers; *Z.* [2] iv. 528, 541; vi. 126; *Gm.* xviii. 427, 437). Legumin differing slightly in properties and composition has been prepared from many other sources.

In spite, however, of the vast amount of work which has been done on this subject, and which is only briefly alluded to in the foregoing paragraph, the existence of this substance is now pretty generally denied. Fresh seeds or vegetable tissues and juices contain no proteids of the casein or albuminate group, and all the substances hitherto designated plant casein are artificial products produced by the alkali used to extract them from the various globulins and albumins which exist there normally (Hoppe-Seyler, *Physiol. Chemie*, Theil i. 75). Although Ritthausen defends his views (*C. C.* 1877, 567, 586) on the ground chiefly of the concordance of numerous elementary analyses, the recent work of Vines, Green, and Martin confirms Hoppe-Seyler's statement. For proteids of oats see Osborne, *Am.* 13, 327, 385; 14, 212; of maize, Osborne a. Chittenden, *ibid.* 13, 453, 529; 14, 20; of flax, Osborne, *ibid.* 14, No. 8.

Class IV.—Vegetable proteoses.—These were first described by Vines (*l.c.*) in aleurone grains, and spoken of as hemi-albumose by him. They were previously regarded as peptones. Martin (*J. Physiol.* 6, 336) has given the name phytalbumose to these substances. In papaw juice he found two phytalbumoses: *α-phytalbumose*, with which the ferment papaïn is associated; this resembles the proto-albumose of Kühne a. Chittenden, but differs from it in the fact that copper sulphate and saturation with sodium chloride do not precipitate it; *β-phytalbumose*, which resembles hetero-albumose, except that it is not precipitated by dialysing out the salts from its solutions, nor by copper sulphate, nor by mercuric chloride. Green (*Pr.* 40, 28) has described an albumose in latex; and Martin has found another albumose—*insoluble phytalbumose*—in wheaten flour (*Brit. Med. Jour.* 1886, 2, 104; see also under Gluten).

Class V.—Vegetable peptones.—True peptone does not apparently exist as such in vegetable tissue; as the result of peptic or pancreatic digestion, however, peptones are formed with intermediate products (proteoses), as in the case of animal proteids. Some, moreover, are further acted on yielding leucine and tyrosine. It is interesting to notice that in the digestion of the proteids of papaw juice by papaïn, a proteolytic ferment present in that juice, no true peptones, but only phytalbumoses, are formed. Papaïn, however, which acts like trypsin best in an alkaline medium, forms true peptones with animal proteids (Martin, *J. Physiol.* 5, 213; 6, 336). For ferments in pineapple juice see Chittenden, *Trans. Connecticut Acad.* 8, 1. It appears probable that such ferments are widespread in the vegetable kingdom to convert the proteid of the cotyledons into peptone-like substances, and so render it available for food in the growing plant.

Class VI.—Insoluble vegetable proteids.—Gluten. This is the most important of the vegetable proteids which falls under this head. When wheat flour is made into a paste its stickiness is due to the presence of gluten, which can be obtained free from starch by washing the paste with water; this is most conveniently done by kneading the paste in a muslin bag under running water. Gluten is tenacious, almost tasteless, of a light brownish-grey colour; on being burnt it emits the smell of burnt horn, and on destructive distillation yields the same products as animal proteids. It dissolves in strong acids and alkalis; it also dissolves, but very slowly, in 0·2 p.c. hydrochloric acid (Bouchardat, *C. R.* 14, 962). Gluten has been stated to possess amylolytic powers, converting starch first into dextrin and then into dextrose. Taddei (*Giornale fisica di Brugnatelli*, 12, 360) first showed that gluten consists of two substances—one soluble, the other insoluble in alcohol. Ritthausen called the part insoluble in alcohol vegetable fibrin, and the part soluble in alcohol, and to which the stickiness of the gluten is due, he subdivided into two substances, *mucedin* or vegetable mucin, and *glutin*, *gliadin* or vegetable gelatin. These are extracted with boiling alcohol of 70-80 p.c. This extract becomes turbid on cooling, and after half the alcohol has been distilled off mucedin is deposited in flocculi. It may be purified by re-dissolving it in hot alcohol, and re-precipitating by cooling. The gliadin remains in solution in cold alcohol. Mucedin is soluble in cold dilute acetic acid, but when precipitated from this solution by ammonia, or left in contact with or boiled with water or dilute alcohol, it is converted into an insoluble substance like fibrin. Gliadin forms a solution in alcohol which resembles varnish; on evaporating the alcohol it is obtained in a form resembling animal gelatin. It is more soluble in hot than cold water, and is precipitated by tannic acid, basic lead acetate, and mercuric chloride. The analyses of crude gluten, and of glutin, give approximately the same percentage composition as other proteids (Ritthausen, *J. pr.* 74, 193, 384).

Gunsberg (*J. pr.* 85, 213) regards mucedin as consisting simply of fragments of suspended fibrin; he states that gliadin is also not a distinct proximate principle, for cold water extracts from it a brown substance containing nitrogen and sulphur, and the residue has nearly the same composition as animal gelatin. Martin (*Brit. Med. Jour.* 1886, 2, 104) has shown that gluten does not exist in flour as such, but is formed by the action of water (perhaps also by a ferment action) on the proteids pre-existent in the flour. The doctrine of a ferment action is supported by the fact that washing flour with water at a low temperature (2°C.) does not lead to the formation of gluten. Johannsen (*Ann. Agronom.* 14,

420) has advanced evidence against the ferment theory. Gluten is insoluble in cold water, and in 10 to 15 p.c. sodium chloride solution. It dissolves partially in alcohol and in boiling water. Both these extracts contain the same substance, which is an albumose (insoluble phytalbumose), and it corresponds to Ritthausen's mucedin and gliadin. The insoluble residue, which is not sticky, may still be called gluten fibrin, and it is soluble in 0·2 per cent. hydrochloric acid. The flour itself contains two proteids: (1) A myosin coagulating between 55° and 60°, precipitated by sodium chloride and magnesium sulphate; and (2) a soluble phytalbumose. Both can be extracted from flour by 10–15 p.c. sodium chloride solution. They are considered to be the precursors of gluten, according to the following scheme:

$$\text{Gluten} = \begin{cases} \text{Gluten-fibrin—precursor: myosin} \\ \text{Insoluble albumose – precursor: soluble albumose} \end{cases}$$

The more wheaten flour has been extracted with a 10 or 15 p.c. sodium chloride solution the less is the yield of gluten when it is subsequently treated with water.

The proportion of gluten in wheat flour varies considerably according to climate, soil, temperature, &c.; the best flour containing 10–11 p.c., inferior kinds 8–9 p.c. In the moist state gluten weighs about three times as much as when dry. The flours of barley, rye, and oats contain only a trace of gliadin, or albumose, as it may now be regarded; hence these flours, containing mostly gluten-fibrin or its precursor, cannot be made into such a sticky paste as can be made with wheat flour. Gliadin also does not exist in leguminous seeds; it is said to be present in the juice of the grape and other fruits, and is held in solution there by tartaric or other vegetable acids.

Appendix A.—*Proteids in urine.* Normal urine contains no proteid. The chief facts concerning proteids in morbid urine are treated fully in medical works (MacMunn's *Clin. Chem. of Urine*, Halliburton's *Chem. Physiol.*), but may be here briefly summarised as follows:

When urine contains blood (which may be detected by the microscope or spectroscope) or pus (which may be also detected microscopically), it of necessity contains a certain amount of proteid derived from these contaminations. In paroxysmal hæmoglobinuria, the urine may contain hæmoglobin or methæmoglobin independently of the presence of blood corpuscles. In the various forms of Bright's disease, the unhealthy kidney allows the proteids of the blood to diffuse into the urine, the most common and abundant being serum albumin. Serum globulin is usually also present, and is recognised by the fact that saturation with magnesium sulphate in the neutralised urine precipitates it (A. Ott, *C. C.* 1886, 540). A crystalline globulin was found in urine by Paton, *Lab. Rep. R. Coll. Phys. Edin.* 4, 47.

Clinical observers do not as a rule attempt to distinguish, however, between the various forms of proteid that occur in urine, but speak of them all under the name of albumin. The most commonly applied tests for its detection are:—(1) To boil the upper part of a test tube full of urine; any cloudiness produced is then seen in contrast to the clear urine below. If any precipitate occurs it is insoluble in acetic acid, so distinguishing it from phosphates. If the urine is neutral or alkaline it is necessary always to acidify with acetic acid either before or after boiling, in order to obtain a precipitate. The clinical method of estimating the proteid quantitatively has been already described. (2) Nitric acid causes a precipitate in the cold. If urine contains but little proteid, it may be detected by pouring the urine on to the surface of some nitric acid in a narrow test tube, the ring of precipitate at the junction of the two liquids is then clearly seen (Heller). The difficulty of carrying nitric acid about has led to the adoption more recently of methods in which test papers saturated with various reagents, picric acid, potassio-mercuric iodide, &c., are added to the urine. A committee of the Clinical Society have recently presented a report in which the relative advantages of various methods of detecting albumin in urine are discussed (*Clin. Soc. Trans.* 19, 339). They have investigated Dr. Oliver's test papers just mentioned; Dr. Pavy's pellets of citric acid and potassium ferrocyanide; Dr. Johnson's picric acid solution; Sir W. Roberts's acid brine test; acetic acid and boiling nitric acid; and a solution of potassio-mercuric iodide with citric acid. The last named is the most delicate reagent in the list; the test papers and pellets are not so delicate but are more convenient; the picric acid test has the advantage of being also applicable for recognising (after the addition of potash) sugar as well as albumin.

Besides albumin and globulin in urine, other proteids may sometimes occur; viz. (1) egg albumin—this occurs after a very large ingestion of eggs as food; (2) Bence-Jones albumin, so called after its first observer, has been shown to be a form of hemi-albumose—it occurs in cases of osteomalacia; (3) peptones or deutero-albumose occurs in many suppurative diseases, and doubtless originates from the disintegration of pus cells; (4) casein has been stated to occur in chylous urine, but there are considerable doubts as to the accuracy of this statement; (5) mucin occurs not only in suspension in the mucus from the urinary tract, but it appears to be occasionally present dissolved in the urine—it is precipitable therefrom by acetic acid. It is probably not true mucin, but a nucleo-albumin.

Appendix B.—*Proteids as poisons.* For effects on blood pressure, &c., of albumoses and peptones, *v.* Pollitzer, *J. Physiol.* 7, 283. The poison of venomous snakes has also been shown to depend on the proteids contained therein (Weir Mitchell), and not to any alkaloid, ptomaine, or cobric acid (W. Blyth, *An.* 1, 204). Wolfenden has separated a globulin, albumin, syntonin, and albumose from the venom of the cobra and daboia; for the action of these *v. J. Physiol.* 7, 327; see also Kanthack, *ibid.* 13, 272. The poisonous principle abrin of Abrus or Jequirity is also proteid (Martin, *Pr.* 42, 331). The subject of proteid poisons has recently risen into prominence, as it is found that the micro-organisms of many diseases produce these toxalbumoses. Koch's tuberculin owes its activity to similar substances. The poisons produced in anthrax, diphtheria, &c., are also proteid in nature. For references see Halliburton's *Chem. Physiol.* German translation; Martin, *Brit. Med. Journal*, March and April 1892. On the other hand, certain proteids (globulins or nucleo-albumins) are protective and destroy micro-organisms. They are termed alexines by Daremberg, Buchner, and Hankin. For Hankin's most recent paper, see *Centr. Bacteriol.* 12, Nos. 22 and 23.

APPENDIX C.—*Albuminoids.* The term 'albuminoid' is still used by some synonymously with proteid; it will be here restricted to a number of substances which resemble proteids in many points, but which differ from them in others.

Collagen. This is the substance of which the white fibres of connective tissue are composed, and which by the action of boiling water is converted into gelatin. Collagen is prepared from tendons by Rollett's process as follows: the finely-divided tissue is soaked in water to remove proteids, and then for some days in lime water to dissolve the mucin-holding cementing substance between the fibres. The insoluble matter is washed first with water, then with weak acetic acid, and then again with water. The residue consists of collagen, mixed, however, with small quantities of elastin and nuclein. With very dilute acids or alkalis collagen swells and becomes transparent.

The organic material which composes one-third of the substance of bone consists mainly of a substance identical with collagen, and which has been termed *ossein* by some writers. The organic basis of dentine (but not of the enamel of tooth) is also collagenous.

Gelatin. When the white fibres are subjected to the action of boiling water, or of water heated under pressure, as in a Papin's digester, or to the long-continued action of dilute acids at the ordinary temperature, they dissolve, and the solution contains a substance called gelatin. Gelatin may be similarly prepared from bones. Isinglass is gelatin prepared from the swimming bladder of the sturgeon; an inferior kind is made from fish bones. Glue is the crude product obtained by boiling down hides, bones, &c. (*v.* Ure, *Dictionary of Arts, &c.*, [2] 324, 376). Pure gelatin is prepared from commercial gelatin by soaking the latter in distilled water for some days to remove salts; it is then dissolved in hot distilled water, and filtered while hot into 90 p.c. alcohol. The gelatin separates in the form of white thready masses, which can be subsequently dried. Thus prepared it contains only 0·6 p.c. of ash.

Gelatin is insoluble in cold, but soluble in hot water; on cooling the hot watery solution it sets into a jelly (gelatinises); this property is possessed by solutions as weak as 1 p.c., it is lost by prolonged boiling, or instantly by heating to 140° in sealed tubes. Gelatin is insoluble in alcohol, ether, and chloroform. Aqueous solutions are powerfully lævorotatory, the rotatory power being influenced by the temperature and reaction of solution; at 30° $[\alpha]_D = -130$ (Hoppe-Seyler). Gelatin is not precipitated by acetic acid nor by a solution of lead acetate; it may be thus distinguished from chondrin. It is not precipitated by acetic acid and potassium ferrocyanide, nor by the majority of metallic salts which precipitate proteids. Tannic acid even in very dilute solutions precipitates it; it is on the formation of the last-named precipitate that the conversion of hides into leather is brought about.

Schützenberger and Bourgeois ascribe to gelatin the formula $C_{76}H_{124}N_{24}O_{29}$. Hofmeister (*H.* 2, 315) finds that by heating gelatin it loses water, and is converted into collagen, which he therefore considers an anhydride of gelatin; his formula for gelatin is $C_{102}H_{151}N_{31}O_{39}$.

By the action of boiling water, gelatin loses after 25 hours its power of gelatinising, and it is split up into two peptone-like bodies, *semiglutin* (sparingly soluble in 70–80 p.c. alcohol and precipitated by platinum tetrachloride) and *hemicollin* (soluble in 70–80 p.c. alcohol, not precipitated by platinum tetrachloride). Similar substances are formed by the action of the peptic or pancreatic ferment, but ultimately true gelatin peptones (not precipitable by saturation with ammonium sulphate), leucine, glycocine, and volatile fatty acids are formed. (The foregoing account of gelatin is very largely taken from Gamgee's *Physiol. Chem.*, p. 252.) Many bacteria liquefy gelatine. On digestion of gelatin see Chittenden, *J. Physiol.* 12, 23, 34. The most recent work on the decomposition products of gelatin has been done by Schützenberger. On heating gelatin at 200° with barium hydroxide, one-fifth of the total nitrogen is converted into ammonia; carbonic and oxalic acids are also formed, these products being in the ratio of the products of decomposition of urea and oxamide. The other products are amido-acids of the acetic series, the most important being glycocine, alanine, amido-butyric acid and leucine, and acids of an homologous series $C_nH_{2n}N_2O_4$, the value of *n* varying from 8 to 10. These latter acids are difficult to isolate; at 100°–120° they are converted into anhydrides; they do not yield derivatives with acetic anhydride, but with ethyl iodide in the presence of an alkali they yield di-ethyl derivatives. The general results lead to the conclusion that gelatin is formed by the combination with elimination of water of 1 mol. urea or oxamide with 2 groups $C_nH_{2n}N_2O_4$ and 4 groups $C_nH_{2n+1}NO_2$, *n* being 2, 3, 4, or 6, with a mean value of 3·5 (*v.* Schützenberger a. Bourgeois, *C. R.* 82, 262; Schützenberger, *C. R.* 102, 1296) Both gelatin and albumin yield on treatment with alcoholic hydrochloric acid a diazo-compound $C_5H_6N_2O_2$ (Buchner a. Curtius, *B.* 19, 850).

The question of the part played by gelatin, which is an easily-digestible substance in nutrition, is very important practically, jellies especially being given to invalids. The question was first investigated by J. Etzinger (*N. R. P.* 23, 535), and subsequently by Voit (*Z. B.* 8, 297). Voit's chief result showed that gelatin will not entirely replace proteids, but that animals rapidly waste which are fed on it alone, but, in conjunction with a certain small amount of proteid, it is capable of maintaining nitrogenous equilibrium as well as if the only nitrogenous food taken was proteid in nature. These results have been since very generally confirmed (*v.* S. Pollitzer, *Pf.* 37, 301). Voit distinguishes between circulating and organic albumin; gelatin can never yield the latter, but it may replace the former in so far as it prevents the conversion of organic into circulating albumin. Gelatin also diminishes the waste of fat in the body.

Mucin. This body forms the chief constituent of the ground substance of connective tissue, the other organic constituent being a globulin very like serum globulin. Mucin is especially abundant in the 'jelly like' tissue of the umbilical cord, and in the vitreous humour. The cement-substance of epithelia behaves similarly to microscopic reagents (especially silver nitrate, by which it is stained brown owing to a deposit of metallic silver), and is probably of the same chemical nature as the ground substance of connective tissue; both are soluble in alkalis. Mucin forms the chief constituent of mucus, and gives the sliminess to the secretion of mucous membranes. In mucus it is suspended in an alkaline exudation from the blood and mixed with the *débris* of epithelium cells, and a few white blood corpuscles. The mucin itself is here formed by the protoplasm of certain cells of the epithelium becoming altered, so that it becomes swollen and brightly refracting; the globule of mucin so formed is discharged, leaving a so-called goblet cell. In mucous glands, such as the submaxillary salivary gland, a very similar replacement of protoplasm by mucin (or mucigen, as it is called when inside the secreting cells) takes place. Mucin is also largely contained in the surface secretion of several invertebrate animals, *e.g.* the snail. Mucin is contained in submaxillary saliva; the metalbumin and paralbumin (*q. v.*) of ovarian cysts is a very similar substance. The substance which confers sliminess to the bile and the synovial fluid, formerly considered to be mucin, has been shown to consist of a nucleo-albumin (*q. v.*).

The methods of preparation of mucin from its various sources differ; from tendon (*v.* Rollett, *Sitz. W.* 30, 308; Löbisch, *H.* 10, 40); from submaxillary gland (Obolensky, *Pf.* 4, 336; Hammarsten, *H.* 12, 163); from bile (Gautier, *Chimie Appliquée à la Médecine*, 2, 126; Paijkull, *H.* 12, 196). Eichwald, Hammarsten, and others have prepared it from snails (*Pf.* 36, 373), and Giacosa (*H.* 7, 40) from the membranes of frog's eggs. These methods depend upon the fact that mucin is soluble in weak alkalis, *e.g.* lime water or dilute baryta water, and can be precipitated from this solution by acetic acid, in excess of which it is not soluble. Hammarsten finds, however, that submaxillary mucin is easily decomposed by lime water and similar weak alkaline fluids; he, therefore, uses water to extract the mucin. Hammarsten has shown that considerable differences exist in mucin according to its origin; this was previously suspected from the divergencies in elementary composition. Tendon mucin (C, 48·3; H, 6·44; N, 11·75; S, 0·81 p.c., Loebisch) and submaxillary mucin (C, 48·84; H, 6·8; N, 12·32; S, 0·8, Hammarsten) are very much alike in elementary composition, but differ in their reactions; *e.g.* tendon mucin is not easily decomposed by weak alkalis, nor is it so easily soluble in weak hydrochloric acid as submaxillary mucin. These forms of mucin differ still more from those obtained from *Helix pomatia*; Hammarsten, indeed, has shown that two distinct varieties of mucin, from the foot and mantle respectively, can be obtained from this snail.

Mucin gives the xanthoproteic, Millon's, and the Adamkiecwicz reactions; it is precipitated, but not rendered insoluble, by saturation with sodium chloride or magnesium sulphate, and by alcohol. It is precipitated by acetate of lead, but by no other metallic salt (except the submaxillary mucin, which is precipitated by several), it is not precipitated by tannic acid nor by boiling; acetic acid gives a characteristic stringy precipitate. Mucin yields, when boiled with strong sulphuric acid, leucine and tyrosine, and when boiled with caustic soda pyrocatechin (Obolensky). When boiled with dilute sulphuric acid for a few hours, mucin yields a reducing sugar, but one which is not capable of the alcoholic fermentation, and albumin is also formed. Landwehr regards mucin as a compound of a proteid and a non-reducing carbohydrate ($C_6H_{10}O_5$) which has most of the properties of plant gum; he calls it animal gum (*Pf.* 39, 193). At one time this carbohydrate was regarded as a variety of glycogen which gave no colour with iodine (achrooglycogen).

Met-albumin and paralbumin. These two proteid-like substances are fairly constantly found in the fluids removed from ovarian cysts (Scherer), and occur occasionally in other cysts and in ascitic fluid also. Metalbumin is a form of mucin (pseudomucin); paralbumin differs from metalbumin by giving a precipitate when it is boiled; it is probably a mixture of pseudomucin with albumin, and can indeed be prepared by mixing these two substances. Both yield reducing sugars when boiled, and both contain animal gum (D. Hammarsten, *Maly's Jahresb.* 11, 11; Landwehr, *H.* 8, 114; *Pf.* 39, 193; Oerum, *Maly's Jahrsb.* 14, 459).

Nuclein. This is the name given to the substance which composes the nuclei of cells. It was prepared by Lauder Brunton from the red blood corpuscles of birds and snakes; the nuclei were freed from adhering stroma and hæmoglobin by repeated agitation with ether and water (*Journ. of Anat. and Physiol.* 2nd series, 3 91). Nuclein resembles mucin in its solubilities. Plosz found, however, that it contained phosphorus (Hoppe-Seyler, *Med. Chem. Untersuchungen*, Heft 4, 460), and considered it was identical with the nuclein which Miescher separated from the nuclei of white corpuscles (*ibid.*). Miescher separated the nuclein from the other constituents of the cells by subjecting them to artificial gastric digestion, nuclein, like mucin, being indigestible by pepsin. Miescher ascribes to it the formula $C_{29}H_{49}N_9P_3O_{22}$. Nuclein has also been separated from the brain (Jaksch, *Pf.* 13, 469) to the amount of 0·14 p.c. (Geoghegan, *H.* 1, 330), and from the liver; it is probably present in all parts where nucleated cells occur. Miescher has also described nuclein as occurring in the yolk of hens' eggs; it has also been described in milk. A. Kossel (*H.* 10, 248) has shown that the nuclein of yolk and milk differ from that of cell nuclei in containing iron, and by not yielding guanine and hypoxanthine when decomposed at a high temperature by weak acids. *Adenine* $C_5H_5N_5$ is described by Kossel as being an intermediate product between cell nuclein and hypoxanthine. Nuclein is present in vegetable cells also, and adenine can also be obtained from this. It is present in yeast (Hoppe-Seyler) and mildew; in tea leaves (Kossel), in poppy, earth nut, rape and cotton cake; also in palm nut, but the proportion P:N is different in the nuclein prepared from this source (Klingenberg a. A. Stutzer, *B. C.* 1883, 204). Miescher's formula for nuclein must, indeed, be received with caution; there are either several varieties of nuclein—for elementary analyses show great discrepancies—or else, as Worm Müller (*Pf.* 8, 190) supposes, it is no definite chemical individual, but the different nucleins are mixtures of an organic phosphorus compound with varying quantities of proteids. Recent work on nuclein has shown that this phosphorus compound is nucleic acid (Altmann, *Arch. f. Anat. u. Phys.* 1888. 524). For artificial nuclein made by adding phosphoric acid to albumin see Liebermann, *B.* 21, 598; Pohl, *H.* 13, 292; Malfatti, *B. d. Naturwiss. Med. Ver.* Innsbruck, 1891-2; Kossel, *Verh. physiol. Ges.* Berlin, Oct. 21, 1892. See also numerous papers by Kossel, Krüger, and others on adenine and nuclein bases in last few volumes of *H.* For iron compounds of nuclein see Bunge's *Physiol. Chem.* This hæmatogen is probably the normal iron-containing food. The chromatin and plastin of histologists are respectively phosphorus-rich and phosphorus-poor nucleins. For iron in the nucleus see Macallum, *P.* 49, 488.

Nucleo-proteids. Nucleo-albumin. E. Merck (*D. P. J.* 261, 316) calls nucleo-proteids substances which, when boiled with water under pressure or treated with acids, alkalis, or ferments, are resolved into nuclein and albumin; for instance, vitellin and casein (*v.* also Lubavin, Hoppe-Seyler, *Med. Chem. Unters.* p. 447), Hammarsten gives the name nucleo-albumin to a class of proteid-like bodies which are very like globulins, being precipitated from their solutions by saturation with sodium chloride or magnesium sulphate; they are also precipitated by acetic acid, but, unlike mucin, are soluble in excess. On gastric digestion of a clear solution, an insoluble phosphorus-containing substance, like nuclein, is formed. Many nucleo-albumins have the physical characters of mucin, and the sliminess of bile and synovia is due to such bodies (Hammarsten, *H.* 12, 173, on synovia; *Maly's Jahrsber.* 12, 1882, on bile-mucin; Paijkull, *H.* 12, 196). The chief proteid constituent of all protoplasm is nucleo-albumin (Halliburton's Goulstonian Lectures, *Brit. Med. Journ.*, March 1893). Wooldridge's tissue fibrinogens are also nucleo-albumins (for ref. see above lectures).

Chondrin. This is the substance obtained from cartilage by boiling; the mother substance of chondrin in the matrix of the cartilage is termed chondrigen. Hot aqueous solutions of chondrin gelatinise on cooling like those of gelatin. Aqueous solutions are precipitated by the same reagents that precipitate solutions of gelatin and of mucin. It is strongly lævorotatory; its rotatory power in solutions of different strengths has been studied by de Bary (*Med. Chem. Unters.* i. 71). Very great discrepancies exist between the results of various analyses (see table comparing analyses by Mulder, Fischer a. Bödecker, Schützenberger a. Bourgeois, and *v.* Mehring in Gamgee's *Physiol. Chem.* p. 270), hence considerable doubts have been entertained of its being a chemical individual. It gives the reactions both of mucin and gelatin; on being boiled with dilute acids it yields a lævogyrate reducing sugar, called by de Bary chondriglucose (*v.* also Fischer a. Bödecker, *A.* 117, 111), but is now regarded as identical with that obtained from mucin, Landwehr considering that animal gum is contained in chondrin as in mucin (*Pf.* 39, 204, 40). Morochowitz was the first to arrive at the conclusion that chondrin is a mixture of gelatin and mucin (*Verhandl. d. naturhist. med. Vereins zu Heidelberg*, 1, Heft 5); mucin can be extracted from it with lime or baryta water, and pure gelatin is left behind. On this assumption chondrigen = collagen + mucin. It must, however, be mentioned, in opposition to this view, that Hoppe-Seyler (*J. pr.* 56, 129) and Otto (*Z.* [2] 4, 628) state that on treating chondrin with dilute sulphuric acid it yields leucine, but no tyrosine or glycosine. The most recent work on chondrin shows that it is chondroitic acid rather than mucin which is present (C. T. Mörner, *H.* 12, 396; Skand, *Arch. Physiol.* 1, 210; Krukenberg, *Z.B.* 20, 307; Schmiedeberg, *Arch. exp. Path. u. Pharm.* 1891, 355).

Elastin. This substance is the very insoluble material of which the elastic fibres of connective tissue are composed. It may be prepared from the *ligamentum nuchæ* by boiling it with ether and alcohol to remove fatty matters, then for 36 hours with water to remove the collagen. The residue is boiled with strong acetic acid, and afterwards with concentrated caustic soda till the fibres begin to swell; it is then treated with weak acetic acid, water, and lastly for 24 hours with hydrochloric acid. The acid is removed by washing with water, and the residue has still all the characters of fresh elastic tissue, and has the following percentage composition: C, 55·45; H, 7·41; N, 16·19; O, 20·89 (Müller, *Zeit. f. Nat. Med.* 3, 10, Heft 2). For recent analyses see Chittenden, *Z. B.* 25, 368.

Elastin is not soluble in any liquid which does not decompose it. It is soluble in boiling concentrated caustic potash, in concentrated nitric and sulphuric acids. It is digestible by both pepsin and trypsin; the former ferment being the more active (A. Ewald a. W. Kühne, *Die Verdauung als histol. Methode*). Peptones are ultimately formed; there are also intermediate bodies of the nature of albumoses (Horbaczewski, *C. C.* 1885, 843). Elastin when treated with sulphuric acid yields leucine but no tyrosine.

Keratin. This substance replaces the protoplasm in the cells of certain epidermal structures, viz. the superficial layer of the epidermis itself, nails, horns, hoofs, feathers, and the cuticle and fibrous substance of hairs. It is prepared by successively boiling the tissue with ether, alcohol, water, and dilute acids; the insoluble residue is keratin.

Subjected to the prolonged action of water under pressure at 150°-200° it yields a turbid solution. It is also dissolved by boiling with alkalis, and on the addition of acids to this solution sulphuretted hydrogen is given off, the sulphur in keratin, which varies considerably in amount, being very loosely combined. Horn swells in dilute acetic acid, dissolves in boiling glacial acetic acid, and in nitric acid; it yields aspartic acid, volatile fatty acids, leucine and tyrosine when boiled with dilute sulphuric acid;

when burnt it gives off a characteristic smell. The following are the chief analyses that have been made (Hoppe-Seyler, *Physiol. Chem.*, Th. 1, p. 90):—

—	Hair (v. Laer)	Nails (Mulder)	Horn (Tilanus)	Hoof (Mulder)
C	50·60	51·00	51·03	51·41
H	6·36	6·94	6·80	6·96
N	17·14	17·51	16·24	17·46
O	20·85	21·75	22·51	19·49
S	5·00	2·80	3·42	4·23

Neurokeratin. This is a substance which forms an irregular framework in the medullary sheath of nerve fibres, which resembles keratin in its general behaviour, but differs from it in being less easily soluble in boiling solutions of caustic potash (Ewald a. Kühne, *Verhandl. d. naturhist. med. Vereins zu Heidelberg*, vol. i. Heft 5; Kühne a. Chittenden, *Z. B.* 26, 291). This substance is interesting, as both the epidermis and the nervous system are derived from the epiblast of the embryo.

Chitin. This substance forms the chief constituent of the skeletal octodermal tissues of invertebrate animals, especially arthropoda. A list of situations in which it has been described is given in Gamgee's *Physiol. Chem.* p. 299; to these must be added the pen of cuttlefishes (Krukenberg), the cartilages and other mesodermal tissues of sepia and the king-crab (Halliburton, *Pr.* 38, 75). In crustacea it is often impregnated with calcareous matter, and in the odontophore of molluscs with silica. It is prepared from the wing-cases or shells by boiling them with caustic soda. The chitin remains insoluble. It may be dissolved in cold concentrated hydrochloric acid, and the solution precipitated by the addition of water. It is colourless, amorphous, insoluble in water, alcohol, ether, acetic acid, dilute mineral acids, and solutions of the alkalis. It is dissolved by concentrated mineral acids. (On the solubilities of chitin *v.* Krukenberg, *Z. B.* 22, 480.)

The formula for chitin is $C_{15}H_{26}N_2O_{10}$ (Ledderhose, *H.* 2, 213; 4, 139). Berthelot (*C. R.* 47, 227) stated that it yields a fermentable sugar on boiling it with sulphuric acid; and Sandwick considered it to be an amine derivative of a carbohydrate with the formula $N(C_{12}H_{20}O_{10})$. Ledderhose showed, however, that the reducing substance is a nitrogenous body, glucosamine; and when chitin is heated with acids it takes up the elements of water, and yields glucosamine and acetic acid,

$$2C_{15}H_{28}N_2O_{10} + 6H_2O = 4C_6H_{13}NO_5 + 2C_2H_4O_2.$$

Glucosamine is an amido- derivative of grape sugar ($C_6H_{12}O_6 - OH + NH_2 = C_6H_{13}NO_5$); it forms salts, of which the hydrochloride is formed by boiling chitin with hydrochloric acid; this is a crystalline substance soluble in water, and in solution dextrorotatory ($\alpha_D = +70·6°$). The pure base prepared by the action of barium hydrate on the sulphate of glucosamine crystallises from alcohol in the form of needles. It is not fermentable. (The foregoing account of elastin, keratin, and chitin is largely taken from Gamgee's *Physiol. Chem.*, which see for fuller details.)

Skeletins. This term is applied by Krukenberg (*Z. B.* 22, 241) to a number of nitrogenous but sulphur-free substances, including conchiolin, spongin, &c., found in the skeletal tissues of invertebrates; they are probably all like chitin amido- derivatives of carbohydrates. The substances are all very insoluble.

Conchiolin ($C_{30}H_{48}N_9O_{11}$) forms the organic basis of the shells of mussels and snails. On decomposition it yields leucine, perhaps glycocine, but no tyrosine nor reducing substance. It does not give the xanthoproteic, Millon's, nor the Adamkiewicz reactions. The cementing substance between the eggs of various molluscs, whose shells and egg capsules contain conchiolin, is coloured red by heating with Millon's reagent, and contains a body allied to keratin. **Corneïn** (from corals) ($C_{30}H_{44}N_9O_{13}$) differs from conchiolin by giving a red colour with Millon's test.

Spongin, the organic basis of the common sponge, yields as decomposition products leucine and glycocine (Städeler), but no tyrosine. It does not give any of the colour reactions mentioned above; it also resembles conchiolin by yielding on digestion peptone-like substances which differ from true peptones and albumoses by not giving the three colour reactions just mentioned; they thus differ from keratin, which is not digestible.

Fibroin, the chief constituent of insects' cocoons and spiders' threads, behaves to all three tests like an ordinary proteid, and on decomposition yields leucine, glycocine, and tyrosine. Fibroin is soluble when heated in sealed tubes in glacial, acetic, and other organic acids (A. Ledow, *Maly's Jahrsbericht*, 13, 32). For silk see Weyl, *B.* 21, 1407, 1529.

Hyalins and Hyalogens. The term 'hyalin' is applied to the chief constituent of the walls of hydatid cysts. Krukenberg states (*Z. B.* 22, 261) that the substance is present in the cyst wall as hyalogen, an insoluble substance which by the action of alkalis is changed into hyalin, which is easily soluble in water. Hyalogen is also converted into hyalin by heating with water (under pressure) at 150°C. (For elementary composition *v.* Lücke, *Virchow's Archiv*, 19, 189). By heating with sulphuric acid hyalin yields a sugar, probably glucose, which is dextrorotatory and capable of the alcoholic fermentation, and in this hyalin resembles mucin.

Krukenberg has extended the terms hyalogen and hyalin to other similarly related bodies obtained from various sources. The edible bird's nest has properties very like those of mucin (*v.* J. R. Green, *J. Physiol.* 6, 40), and is the result of the activity of certain glands described by Bernstein (*Journ. Ornithologie*, 1859. 111) as being remarkably developed in the nest-building season. Krukenberg finds that it is chiefly composed of a hyalogen (*neossine*), which yields as its hyalin, *neossidine*. *Chondrosine* is a hyalogen, obtained from the sponge *Chondrosia reniformis*. The vitreous humour from the eyes of oxen and pigs was found to contain a hyalogen, whereas the cornea did not yield one, but was found to consist chiefly of collagen, and a proteid allied to myosin. *Spirographin*, which largely composes the skeletal tissues of the worm *Spirographis* is also a hyalogen, but differs from others by yielding when acted on by alkalis not only a hyalin, *spirographidin*, but also pyrocatechin. The hyalogens are not acted on by gastric juice; some are, some are not attacked by trypsin. W. D. H.

PROTEÏN *v.* PROTEÏDS.

PROTEOSES *v.* PROTEÏDS.

PROTO-ALBUMOSE *v.* PROTEÏDS.

PROTOCATECHUIC ACID $C_7H_6O_4$ *i.e.* $C_6H_3(OH)_2.CO_2H$[4:3:1]. Mol. w. 154. [199°] (Hlasiwetz); [194°] (Barth a. Schmidt, *B.* 12, 1265). S. 1·9 at 14°; 10 at 60° (Tiemann a. Nagai, *B.* 10, 211). Occurs in the fruit of *Illicium religiosum* (Eykman, *R. T. C.* 4, 47).

Formation.—1. By potash-fusion from piperic acid (Strecker, *A.* 118, 280), catechin (Kraut, *A.* 128, 285), maclurin (Hlasiwetz a. Pfaundler, *A.* 127, 351), guaiac resin (Hlasiwetz a. Barth, *A.* 130, 346), kino (Stenhouse, *C. J.* 28, 6), caffeïc acid (Hlasiwetz, *A.* 142, 219), cinchona-red (Rembold, *A.* 143, 273), asafœtida (Hlasiwetz a. Barth, *A.* 138, 61), angelica-resin (Brünner, *N. R. P.* 24, 641), many other resins, the methyl- derivative of sulpho-*p*-oxy-benzoic acid (Malin, *A.* 152, 109), sulpho-*m*- and sulpho-*p*-oxy-benzoic acids (Barth, *C. J.* 24, 829), and iodo-*p*-oxy-benzoic aldehyde (Tiemann a. Herzfeld, *B.* 10, 213).—2. By heating piperonylic acid with HClAq at 150° (Fittig a. Remsen, *A.* 159, 129).—3. By the action of Br and water on quinic acid (Hesse, *A.* 112, 52; 122, 221; Fittig, *A.* 168, 111).—4. By heating pyrocatechin with water and ammonium carbonate at 140° (Miller, *C. J.* 41, 400).

Properties.—Tufts of monoclinic needles (containing aq), sol. water, alcohol, and ether, nearly insol. boiling benzene. $FeCl_3$ colours its aqueous solution bluish-green, the colour changing to red on addition of alkalis. $FeSO_4$ colours solutions of its salts violet. $Pb(OAc)_2$ gives a pp., sol. acetic acid. Crystallises with *p*-oxy-benzoic acid as $(C_7H_6O_4)C_7H_6O_3$ 2aq, which yields $PbC_{14}H_{10}O_7$ 2aq (Hlasiwetz, *A.* 134, 276). Reduces aqueous $AgNO_3$ on heating or on adding NH_3Aq. Does not reduce Fehling's solution.

Reactions.—1. Split up by *dry distillation* into CO_2 and pyrocatechin.—2. *Soda-fusion* gives 55 p.c. of the theoretical amount of pyrocatechin.—3. *Bromine* in the cold forms bromo-protocatechuic acid. Br at 100° yields tetra-bromo-pyrocatechin.—4. N_2O_3 passed into the ethereal solution forms oxalic acid (16·5 p.c.), carboxy-tartronic acid (10 p.c.), di-nitro-di-oxy-quinone (·5 p.c.), trinitrophenol (4 p.c.), (*a*)-di-nitro-phenol [114°] (3·5 p.c.), and nitro-*p*-oxy-benzoic acid (1 p.c.) (Gruber, *B.* 12, 514).—5. H_2SO_4 (25 pts.) at 140° forms a very small quantity of tetra-oxy-anthraquinone (rufiopin) (Nölting, *Bl.* [2] 37, 395).—6. Heating with As_2O_5 at 160° or exposing a solution in Na_2CO_3Aq to the air forms catellagic acid $C_{14}H_{10}O_7$? which resembles ellagic acid and forms an orange solution in nitric acid.

Salts.—BaA'_2 5aq.—$Ba_3(C_7H_3O_4)_2$ (dried at 130°) (Barth, *A.* 142, 246).—CaA'_2 4aq.—CaA'_2 3aq.—$Pb_3A'_2O_2$.—PbA'_2 2aq.

Acetyl derivative $C_6H_3(OAc)_2.CO_2H$. [153°]. Crystals (Herzig, *M.* 6, 872).

Methyl ether MeA'. [134·5°]. Needles.

Ethyl ether EtA'. [134° cor.]. Prisms (Matsmoto, *B.* 11, 129).

m-Methyl derivative $C_6H_3(OH)(OMe).CO_2H$ [4:3:1]. *Vanillic acid.* [207°]. S. ·12 at 14°; 2·5 at 100°. *Formation* (Tiemann, *B.* 8, 509, 1123; 9, 52, 419; 10, 59, 202; 11, 122).—1. By exposing moist powdered vanillin to the air.—2. By oxidising coniferin with dilute $KMnO_4$.—3. From its acetyl derivative, which is got by the action of $KMnO_4$ on acetyl-eugenol, acetyl-ferulic acid, and acetyl-creosol.—4. Together with isovanillic acid by heating $C_6H_3(OMe)_2CO_2H$ with HClAq at 140°. *Properties.*—Needles (from water), v. e. sol. alcohol, m. sol. ether. Has no smell. May be sublimed. Gives no colour with $FeCl_3$. *Reactions.*—1. Split up by HClAq (S.G. 1·1) at 150° into protocatechuic acid and MeI.—2. *Potash-fusion* yields protocatechuic acid.—3. By heating with MeI (2 mols.) and KOH (2 mols.) it is converted into $C_6H_3(OMe)_2.CO_2Me$.—4. Yields guaiacol on distillation with lime.—5. The Ca salt yields vanillin on distilling with calcium formate.

Methyl ether of the ***m-Methyl derivative*** MeA'. [63°]. (286°).

Ethyl ether of the ***m-Methyl derivative*** EtA'. [44°]. (292°).

Acetyl derivative of the ***m-Methyl derivative*** $C_6H_3(OAc)(OMe).CO_2H$. [142°]. Needles (from dilute alcohol).

Benzoyl derivative of the ***m-Methyl derivative.*** [178°] (Tiemann, *B.* 15, 2068).

p-Methyl derivative $C_6H_3(OMe)(OH).CO_2H$ [4:3:1]. *Isovanillic acid.* [250°]. S. ·06 at 15°; ·7 at 100°. Formed with other products by heating protocatechuic acid with MeI and KOH at 150°. Got also by heating hemipic acid with HClAq (Matthiessen a. Foster, *A. Suppl.* 2, 378), and, together with vanillic acid, by digesting $C_6H_3(OMe)_2CO_2H$ with dilute HClAq at 140° (Tiemann). The acetyl derivative is got by oxidation of the acetyl derivative of isoferulic acid (hesperetic acid) by $KMnO_4$ (Tiemann a. Will, *B.* 14, 963), and likewise by oxidation of the acetyl derivative of betelphenol $C_6H_3(OMe)(OH).C_3H_5$ [4:3:1] (Bertram a. Gildemeister, *J. pr.* [2] 39, 349). Prisms, v. sol. alcohol and ether. May be sublimed. Its aqueous solution is not coloured by $FeCl_3$. Yields a nitro- derivative [173°] and an ***acetyl derivative*** $C_6H_3(OMe)(OAc).CO_2H$ [207°].

Di-methyl derivative $C_6H_3(OMe)_2.CO_2H$. *Veratric acid.* [174°] (T.); [181°] (G.). S. ·05 at 14°; ·6 at 100°. Occurs in small quantity in sabadilla seeds (Merck, *A.* 29, 188). Formed by heating at 140° protocatechuic acid (1 pt.) with MeI (4 pts.) and KOH (1 pt.) dissolved in MeOH (Kölle, *A.* 159, 241). Produced also by oxidation of $C_6H_3Me(OMe)_2$ (Tiemann, *B.* 8, 1138), of methyl-eugenol (Graebe, *A.* 158, 282), of papaverine (Goldschmidt, *M.* 6, 378), and of di-methyl-caffeïc acid (Tiemann a. Will, *B.* 14, 962). Formed also by saponifying its amide, which is made by the action of $Cl.CONH_2$ on $C_6H_4(OMe)_2$ in CS_2 in the presence of $AlCl_3$ (Gattermann, *A.* 244, 71). Veratric acid is a product of the action of alcoholic soda on pseudaconitine, on veratrine (Wright a. Luff, *C. J.* 33, 160, 353), and on hexa-methyl-quercetin (Herzig, *M.* 5, 83), and of fused potash on papaveraldine (Goldschmidt, *M.* 7, 493). Veratric acid is also got by the action of KOH on pseudo-opianic acid (W. H. Perkin, jun., *C. J.* 57, 1068).

Properties.—Slender needles (containing aq). From hot solutions (above 50°) it separates in anhydrous crystals. V. e. sol. alcohol and ether. $FeCl_3$ gives no colour. Distillation with lime forms $C_6H_4(OMe)_2$. Potash-fusion yields protocatechuic acid. HIAq at 160° forms MeI and protocatechuic acid. HClAq forms vanillic and also iso-vanillic acids.—Salts.—NaA′ 2aq.—BaA′$_2$ 6aq. — AgA′. — Ethers. — MeA′ [60°] (c. 300°).—EtA′. [44°]. (296°).

Di-ethyl derivative $C_6H_3(OEt)_2.CO_2H$. [166°]. Formed by saponifying its ether, which is made from protocatechuic acid, alcoholic potash, and EtI (Kölle, *A.* 159, 240). Got also by heating hexa-ethyl-quercetin with alcoholic potash at 150° (Herzig, *M.* 5, 78). Needles (from alcohol).—KA′ ½aq.—BaA′$_2$ 3aq.—AgA′.—Ethyl ether EtA′. [57°]. Crystals.

Methyl-ethyl derivative $C_6H_3(OMe)(OEt).CO_2H$ [3:4:1]. [194°]. Formed by oxidation of ethyl-vanillin (Tiemann, *B.* 8, 1130), of ethyl-eugenol (Wassermann, *A.* 179, 379; Balbiano, *G.* 11, 416), and of di-ethyl-curcumin (Jackson a. Mencke, *Am.* 4, 90). Needles, almost insol. cold water.—BaA′$_2$ 4aq: needles.

Methyl-propyl derivative $C_6H_3(OMe)(OPr).CO_2H$ [3:4:1]. Formed by oxidation of the propyl derivative of eugenol (Cahours, *Bl.* [2] 28, 314). Needles.

Methyl-carboxymethyl derivative $C_6H_3(OMe)(O.CH_2CO_2H).CO_2H$ [3:4:1]. [256°]. Formed from $C_6H_3(OMe)(O.CH_2.CO_2H).CHO$ by oxidation (Elkan, *B.* 19, 3056). Yields CuA″ as a green insoluble pp.

Methylene derivative $CH_2{:}O_2{:}C_6H_3.CO_2H$. *Piperonylic acid.* [228°]. Occurs in para-coto bark (Hesse a. Jobst, *A.* 199, 63). Prepared by oxidation of piperonal (Fittig a. Mielck, *A.* 152, 40). Got by heating protocatechuic acid with potash and CH_2I_2 (Fittig a. Remsen, *A.* 168, 94). Piperonylic acid is also formed by the action of $KMnO_4$ on cubebin, on methystic acid (Pomeranz, *M.* 8, 468; 10, 790), on safrole (Eykman, *R. T. C.* 4, 39; Poleck, *B.* 19, 1096), and on the (*a*)-dihydride of piperic acid (Regel, *B.* 20, 415). Needles (from alcohol). May be sublimed. Nearly insol. cold water, m. sol. boiling alcohol. $FeCl_3$ gives a brown pp. in neutral solutions. Dilute HClAq at 170° forms protocatechuic acid. HNO_3 forms nitro-piperonylic acid [172°]. Salts.—NaA′ aq.—KA′ aq.—BaA′$_2$ aq.—CaA′$_2$ 3aq. S. ·625 at 15°.—PbA′$_2$ aq.—CuA′$_2$ aq.—AgA′. Quinine salt $C_{20}H_{24}N_2O_2HA'$aq: needles, sol. hot water. Cinchonidine salt $C_{19}H_{22}N_2OHA'$: needles (Hesse, *A.* 243, 147). — Ethyl ether EtA′. Oil.—Nitrile $CH_2O_2{:}C_6H_3.CN$. [95°]. Formed from the oxim of piperonal and Ac_2O (Marcus, *B.* 24, 3656). Needles, v. sol. alcohol. Alcoholic hydroxylamine at 60° forms the amidoxim $CH_2O_2{:}C_6H_3.C(NH_2){:}NOH$ [151°] which yields B′HCl [193°], and is converted by Ac_2O into

$CH_2O_2{:}C_6H_3.C\lessdot\genfrac{}{}{0pt}{}{NO}{N}\gtrdot CMe$ [110°].

Ethylene derivative $C_2H_4O_2{:}C_6H_3.CO_2H$. [134°]. Formed by heating protocatechuic acid with ethylene bromide and KOH (Fittig, *Z.* [2] 7, 289; *A.* 168, 99). Needles (from hot water). May be sublimed. PCl_5 yields a product whence water reproduces ethylene-protocatechuic acid. PCl_5 at 130° followed by water yields the acid $C_2H_2Cl_2O_2{:}C_6H_3.CO_2H$ [121°].—BaA′$_2$ 2aq.—CaA′$_2$ 2aq: monoclinic crystals.—Ethyl ether EtA′. Oil.

Di-methyl-ethylene ether $C_2H_4(O.C_6H_3(OMe).CO_2H)_2$. Formed by oxidising the ethylene ether of eugenol with $KMnO_4$ (Cahours, *Bl.* [2] 29, 270). Amorphous.

Reference.—NITRO-PROTOCATECHUIC ACID.

Homo-protocatechuic acid *v.* DI-OXY-PHENYL-ACETIC ACID.

Diprotocatechuic acid $C_{12}H_4(OH)_4(CO_2H)_2$. Formed by potash-fusion from divanillin (Tiemann, *B.* 18, 3494). Amorphous, sl. sol. water and alcohol. Coloured bluish-green by $FeCl_3$.

PROTOCATECHUIC ALDEHYDE $C_7H_6O_3$ *i.e.* $C_6H_3(OH)_2.CHO$ [4:3:1]. Mol. w. 138. [150°].

Formation. 1. From piperonal by successive treatment with PCl_5 and water at 100° (Fittig a. Remsen, *Z.* [2] 7, 100; *A.* 159, 148; 168, 97).—2. By heating piperonal with dilute HClAq at 200° (F. a. R.).—3. By heating a solution of pyrocatechin in dilute NaOH with chloroform (Tiemann, *B.* 9, 1269; 14, 2020).—4. By heating vanillin with dilute HCl at 200° (Tiemann, *B.* 7, 620).—5. By heating opianic acid with dilute HCl at 170° (Wegscheider, *M.* 3, 792).

Properties.—Flat needles (from water), v. sol. alcohol, ether, and hot water. $FeCl_3$ colours the aqueous solution green, changing to red on addition of Na_2CO_3. Oxidised by $KMnO_4$ and by potash-fusion to protocatechuic acid. Gives a mirror with ammoniacal $AgNO_3$. Combines with $NaHSO_3$.

m-Methyl derivative. $C_8H_8O_3$ *i.e.* $C_6H_3(OMe)(OH).CHO$. *Vanillin.* Mol. w. 152. [81°]. (285°). S. 1 at 14°; 5 at 80° (Tiemann a. Nagai, *B.* 10, 211). The fragrant constituent of the pods of *Vanilla aromatica* (Gobley, *J.* 1858, 534; Stokkebye, *J.* 1864, 612). Occurs also in the seeds of *Lupinus albus* (Campani a. Grimaldi, *G.* 17, 545), in raw beet-root sugar (Weger, *D. P. J.* 237, 146; Scheibler, *B.* 13, 335; Lippmann, *B.* 13, 662), in gum benzoïn from Siam (Jannasch a. Rump, *B.* 11, 1635), and in small quantity in wood (Singer, *M.* 3, 409). *Formation.*—1. Together with isovanillin, by heating guaiacol with chloroform and NaOHAq (Reimer, *B.* 9, 424; Tiemann, *B.* 14, 2023).—2. By oxidation of coniferin or coniferyl alcohol with chromic acid mixture (Tiemann, *B.* 7, 613).—3. By oxidation of eugenol by $KMnO_4$ (Erlenmeyer, *B.* 9, 273).—4. By heating calcium vanillate with calcium formate (Tiemann, *B.* 8, 1124).—5. By the action of chloroform and potash on vanillic acid (Tiemann, *B.* 9, 1280).—6. By the action of emulsin or of boiling dilute acids on glucovanillin (Haarmann a. Reimer, *C. J.* 46, 1343).—7. From $C_6H_3(OMe)(NO_2).CHO$ by reduction followed by the diazo- reaction (Ulrich, *B.* 18, 2573). *Properties.*—Monoclinic needles, v. sol. alcohol, ether, $CHCl_3$, and CS_2; v. sl. sol. cold, v. sol. hot, ligroïn. Smells and tastes like vanilla. May be sublimed. Acid in reaction, and decomposes carbonates. $FeCl_3$ gives a blue colour. Boiling aqueous $HgCl_2$ containing KNO_2 gives a violet colour (Nickel, *Fr.* 28, 247). Reduces silver solution. Oxidised by moist air to vanillic acid $C_8H_8O_4$. *Reactions.*—1. *Bromine* forms $C_8H_7BrO_3$ [161°].—2. Dilute HCl at 190°

yields MeCl and protocatechuic aldehyde.—3. *Potash-fusion* gives protocatechuic acid.—4. *Sodium-amalgam* reduces it in alcoholic solution to vanillyl alcohol $C_8H_{10}O_3$ as a yellowish oil, and also hydrovanilloïn $C_{16}H_{18}O_6$ [c. 225°] (Tiemann, *B.* 8, 1123).—5. By heating with *di-methyl-aniline* and $ZnCl_2$ it is converted into $C_{21}H_{28}N_2O_2$ [136°] (Fischer a. Schmidt, *B.* 17, 1895)—6. Vanillin (1 mol.) mixed with pyrogallol (2 mols.) is converted by conc. HClAq into 'pyrogallo-vanillein' $C_{20}H_{18}O_8$, which forms colourless crystals, insol. water, v. sol. alcohol, giving isomeric bluish-violet crystals by the further action of HCl (Etti, *M.* 3, 637).—7. Vanillin (1 pt.) boiled with *diacetonamine acid oxalate* (1 pt.) forms the oxalate of vanillodiacetonamine $C_{14}H_{19}NO_3$ (*v.* vol. i. p. 28).—8. Heating with Ac_2O forms the acetyl derivative of vanillin, and also $C_6H_3(OMe)(OAc).CH(OAc)_2$ [89°] crystallising in six-sided tables (Tiemann a. Nagai, *B.* 8, 1143).—9. Boiling aqueous $FeCl_3$ forms divanillin $C_{16}H_{14}O_6$ [304°], whence NaOEt and MeI form $C_6H_2(OMe)_2(CHO).C_6H_2(OMe)_2(CHO)$ [138°] (Tiemann, *B.* 18, 3493).—10. *Chloro-acetic acid* and KOHAq form $C_6H_3(OMe)(OCH_2CO_2H).CHO$ [188°] (Elkan, *B.* 19, 3055). Salts.—$C_8H_7NaO_3$. Needles (from alcohol), sl. sol. NaOHAq.—$Hg(C_8H_7O_3)_2$: crystals, sl. sol. cold water, insol. alcohol.—$Zn(C_8H_7O_3)_2$: crystalline pp. *Estimation.*—Vanilla pods are extracted with ether, the extract shaken with a nearly saturated solution of $NaHSO_3$, the aqueous layer decomposed by H_2SO_4, the vanillin thence extracted by ether, and the extract evaporated (Tiemann a. Haarmann, *B.* 8, 1115).

Acetyl derivative of vanillin $C_6H_3(OMe)(OAc).CHO$. [77°]. Formed slowly by the action of an ethereal solution of Ac_2O on sodium-vanillin in the cold (Tiemann a Nagai, *B.* 11, 646). Flat needles. Combines with bisulphites.

Oxim of vanillin $C_6H_3(OMe)(OH).CH:NOH$. [122°] (Tiemann a. Kees, *B.* 18, 1664; *cf.* Lach, *B.* 16, 1786).

Phenyl-hydrazide of vanillin $C_6H_3(OMe)(OH).CH:N_2HPh$. [105°]. Plates.

Glucoside of vanillin $C_6H_3(OMe)(OC_6H_{11}O_5).CHO$. *Glucovanillin.* [192°]. $[\alpha]_D = -88{\cdot}63$ at 20°. Prepared by slowly adding CrO_3 (8 pts.) in water (100 pts.) to coniferin (10 pts.) dissolved in water (200 pts.), and leaving the mixture to stand for 5 days (Tiemann, *B.* 18, 1596, 1661). Colourless needles (containing 2aq), v. sol. water, m. sol. alcohol, insol. ether. Readily split up by dilute H_2SO_4 or by emulsin into vanillin and glucose. Does not reduce Fehling's solution in the cold. Yields $C_6H_3(OMe)(OC_6H_{11}O_5).CH:N_2HPh$ [c. 195°] and a lævorotatory oxim [152°], crystallising in slender yellow needles (containing aq).

p-Methyl-derivative $C_6H_3(OMe)(OH).CHO$ [4:3:1]. *Isovanillin.* [116°]. Formed by oxidising acetyl-isoferulic acid with $KMnO_4$ and saponifying the resulting acetyl derivative (Tiemann a. Will, *B.* 14, 968). Formed also by heating opianic acid (4 pts.) with water (30 pts.) and HClAq (8 pts. of S.G. 1·17) (Wegscheider, *M.* 3, 789). Monoclinic pyramids, sl. sol. cold water, v. sol. alcohol and ether. May be sublimed. When warm it smells somewhat like vanillin. Its alkaline solutions are yellow. $FeCl_3$ does not colour the aqueous solution. Reduces boiling ammoniacal $AgNO_3$. Forms a very soluble compound with $NaHSO_3$.

Di-methyl derivative $C_6H_3(OMe)_2CHO$. *Methyl-vanillin.* [43°]. (c. 283°). Formed from potassium vanillin and MeI (Tiemann, *B.* 8, 1135), and also by distilling opianic acid with soda-lime (Beckett a. Wright, *C. J.* 29, 164). Needles, v. sl. sol. hot water, v. sol. alcohol and ether. Smells like vanilla.

Methyl-ethyl derivative $C_6H_3(OMe)(OEt).CHO$. [65°]. Formed by boiling potassium-vanillin with EtI and alcohol (Tiemann, *B.* 8, 1129). Prisms, v. sl. sol. hot water. Smells like vanilla.

Methylene derivative $C_8H_6O_3$ *i.e.* $CH_2O_2:C_6H_3.CHO$. *Piperonal.* Mol. w. 150. [37°]. (263°). S. ·2 in the cold. Formed by oxidation of piperic acid in neutral solution by $KMnO_4$ (Fittig a. Mielck, *A.* 152, 35). Formed also by oxidation of the (α)-dihydride of piperic acid by alkaline $KMnO_4$ (Regel, *B.* 20, 415). Transparent prisms (from water), m. sol. hot water, v. sol. alcohol and ether. Smells much like coumarin. Forms a crystalline compound with $NaHSO_3$. Not affected by aqueous alkalis. *Reactions.*—1. By *oxidation*, or by boiling with *alcoholic potash*, it is converted into piperonylic acid $CH_2O_2:C_6H_3.CO_2H$.—2. Reduced by water and *sodium-amalgam* to piperonyl alcohol $C_8H_8O_3$, hydropiperoïn $C_{16}H_{14}O_6$ [202°], and iso-hydropiperoïn [138°]. AcCl converts the hydropiperoïns into $C_{16}H_{12}Cl_2O_4$ [198°] (Remsen a. Fittig, *Z.* [2] 6, 97; *A.* 159, 129).—3. An alcoholic solution of KCy forms piperonyloïn $CH_2O_2:C_6H_3.CH(OH).CO.C_6H_3:O_2CH_2$ [120°], separating from alcohol in yellow crystals (F. M. Perkin, *C. J.* 59, 164).—4. Very dilute HClAq at 200° forms protocatechuic aldehyde.—5. PCl_5 forms liquid $CH_2O_2:C_6H_3.CHCl_2$ (c. 235°) and $C_8H_4Cl_4O_2$, whence cold water forms dichloropiperonal $C_8H_4Cl_2O_3$ [90°].—6. Gaseous HCl, passed into a mixture of *phenyl mercaptan* and piperonal, forms $CH_2O_2:C_6H_3.CH(SPh)_2$ [48°] (Baumann, *B.* 18, 886).—7. Alcoholic *ammonia*, in presence of some HCy, forms $C_{24}H_{18}N_2O_6$, crystallising in prisms [213°], insol. alcohol and ether. Piperonal, heated with alcoholic NH_3 at 70°, forms an isomeric body [172°], crystallising in yellow needles, sol. hot alcohol, insol. water and ether (Lorenco, *B.* 14, 791).—8. Aqueous HCy at 65° forms a compound whence an alcoholic solution of NH_3 yields $CH_2O_2:C_6H_3.CH(NH_2).CN$, converted by boiling HClAq into $C_9H_8O_5$.—9. *Aniline* forms, on heating, $C_{14}H_{11}NO_2$, crystallising in colourless needles [65°] (L.).—10. *p-Phenylene-di-methyl-diamine* gives $C_6H_3(O_2CH_2).CH:N.C_6H_4NMe_2$ [110°] (Nuth, *B.* 18, 575).

Oxim of piperonal $CH_2O_2:C_6H_3.CH:NOH$. [110°]. Needles, v. sol. alcohol (Marcus, *B.* 24, 3656).

Phenyl-hydrazide of piperonal $CH_2O_2:C_6H_3.CH:N_2HPh$. [100°] (M.); [103°] (Rudolph, *A.* 248, 103). Yellow needles.

PROTOPINE $C_{20}H_{19}NO_5$. [202°]. An alkaloid occurring in very small quantity in opium, and obtained from the mother-liquors after the separation of morphine by Gregory's process (Hesse, *Z.* [2] 7, 653; *A. Suppl.* 8, 318). Separated from cryptopine by ppn. of the solution of the mixed hydrochlorides with conc. HClAq, the protopine salt adhering to the sides of the vessel. Crystalline powder (from alcohol), insol. water, sl. sol. hot alcohol, m. sol. chloroform. The alcoholic solution is alkaline in reaction. Sl. sol. ether, separating in spherical groups of prisms. Sl. sol. KOHAq and NH_3Aq. $FeCl_3$ gives no colour. HNO_3 forms a colourless solution, which turns yellow on warming. H_2SO_4 containing ferric sulphate gives a dark-violet solution, turned dirty brownish-green at 150°. The salts have a bitter taste, and do not gelatinise.—$B'_2H_2PtCl_6$ 2aq: yellow crystalline pp.

PRUSSIAN BLUE *v.* Ferric ferrocyanide, vol. ii. p. 334; and Potassium-ferrous ferricyanide, vol. ii. p. 339.

PRUSSIC ACID *v.* Cyanhydric acid, vol. ii. p. 300.

PSATYRIN *v.* Harmin.

PSOROMIC ANHYDRIDE $C_{20}H_{11}O_9$? [264°]. Occurs in *Psoroma crassa*, a lichen growing in Sicily (Spica, *G.* 12, 431). Needles, sol. alcohol and ether, insol. benzene. Yields $C_{20}H_{15}AgO_{10}$ as a flocculent pp.

PSYCHOSINE. A substance got, according to Thudichum (*J. pr.* [2] 25, 19), from brain.

PTEROCARPIN $C_{20}H_{16}O_6$. [152°]. $[\alpha]_j = -211°$ in 4·6 p.c. chloroform solution. Obtained by mixing powdered sandal wood (*Pterocarpus santalinus*) with slaked lime, and extracting with ether. The residue is crystallised from alcohol, and the homopterocarpine dissolved in CS_2, which leaves the pterocarpine (Cazeneuve a. Hugounenq, *A. Ch.* [6] 17, 115). Square tables (from $CHCl_3$), insol. water, m. sol. hot alcohol and hot CS_2. Insol. acids and conc. KOHAq, even on boiling. Bromine forms $C_{20}H_{15}BrO_6$, crystallising in yellowish needles.

Homopterocarpin $C_{24}H_{24}O_6$. [82°–86°]. $[\alpha]_j = -199°$. Obtained as above (C. a. H.). Long needles (from boiling alcohol), insol. water, sol. ether, v. sl. sol. cold alcohol.

Reactions.—1. Bromine gives $C_{24}H_{23}BrO_6$ and $C_{24}H_{18}Br_6O_6$ [270°].—2. On distillation it is largely split up into phenols resembling creosote, and a small quantity of pyrocatechin.—3. Distillation over zinc-dust gives benzene, toluene, ethylene, and CO.—4. HCl gives MeCl and a resin.—5. HI gives MeI.—6. *Potash-fusion* gives phloroglucin.—7. Fuming HNO_3 gives oxalic acid and tri-nitro-orcin [162°]. Not acted upon by sodium-amalgam, phenyl-hydrazine, and Ac_2O.

PTOMAINES. The name 'ptomaïnes' was first applied to poisonous organic bases obtained from dead bodies (πτῶμα, a corpse), but is now usually given to poisonous organic bases formed in the putrefaction of any kind of animal matter. In extracting ptomaines no reagents that would decompose proteids may be used. The bases may be extracted by alcohol, and purified by ppn. with phosphomolybdic acid. In presence of a little HCl the ptomaines are fairly stable, and the solution can then be evaporated and the hydrochlorides extracted from the syrupy residue by absolute alcohol. By this method neuridine hydrochloride can readily be obtained. By the putrefaction of proteids Brieger (Two monographs: *Ueber Ptomaine*, Berlin, 1885; *cf.* Gautier, *Bl.* [2] 48, 10) obtained tri-methyl-vinyl-ammonium hydroxide (neurine) $C_5H_{13}NO$ or $C_2H_3.NMe_3.OH$, muscarine $C_5H_{15}NO_3$ or $CH(OH)_2.CH_2.NMe_3OH$ (vol. iii. p. 444), a base isomeric with ethylene-diamine, neuridine $C_5H_{14}N_2$, gadinine $C_7H_{17}NO_2$, triethylamine, dimethylamine, and trimethylamine. Garcia (*H.* 17, 543) got hexamethylene-diamine $C_6H_{16}N_2$. Herring-pickle contains choline, NMe_3, and NH_2Me. By the putrefaction of the herring NMe_3, NH_2Me, cadaverine $C_5H_{16}N_2$, putrescine $C_4H_{12}N_2$, and gadinine $C_7H_{17}NO_2$ are formed (Bocklisch, *B.* 18, 1922). Gautier and Etard (*C. R.* 94, 1600) from putrid mackerel and putrid horse-flesh obtained a collidine dihydride $C_8H_{13}N$, parvoline $C_9H_{13}N$, and a base $C_{17}H_{38}N_4$. In the putrefaction of proteids poisonous bases are formed in the first five or six days, and are destroyed by further progress of putrefaction. The highly poisonous methyl-guanidine is formed by the action of putrefactive bacteria on beef-broth at 38° (Bocklisch, *B.* 20, 1441). From human corpses Brieger obtained tri-methyl-oxyethyl-ammonium hydroxide $C_5H_{15}NO_2$ or $CH_2(OH).CH_2.NMe_3.OH$ (choline or neurine, vol. iii. p. 498), neuridine $C_5H_{14}N_2$, cadaverine $C_5H_{16}N_2$, putrescine $C_4H_{12}N_2$, saprine $C_5H_{16}N_2$, trimethylamine, methyl-guanidine, tetanine $C_{13}H_{20}N_2O_4$, mydine $C_8H_{11}NO$, mydatoxin $C_6H_{13}NO_2$, and mydaleïne (Brieger, *loc. cit.*; *cf.* Selmi, *Rend. Accad. Sci. Bologna*, 1872; Schwanert, *B.* 7, 1332; Guareschi a. Mosso, *J. pr.* [2] 27, 428; 28, 504; *G.* 13, 493; Beckurts, *Ar. Ph.* [3] 14, 1041). Ptomaines are often produced in animal bodies which, after brief exposure, have been excluded from the air; *e.g.* corpses, sausages, and tinned meat. A crystalline ptomaine can be obtained from the body after arsenical poisoning (Husemann, *Ar. Ph.* [3] 16, 169; 19, 415). The alcoholic solution of hydrochlorides of ptomaines may be ppd. by an alcoholic solution of $HgCl_2$; after twenty-four hours' standing, the pp. is boiled with a large quantity of hot water, which leaves the compounds of peptones and albuminates undissolved. The hot filtrate deposits the mercury double salt of choline (neurine) while the mother-liquor contains the remaining bases. Picric acid added to an aqueous solution of the hydrochlorides ppts. neuridine picrate, while the mother-liquor deposits, on evaporation, broad needles of choline picrate $C_5H_{13}NOC_6H_2(NO_2)_3OH$. Cadaverine and putrescine can be separated by means of their aurochlorides. Saprine is isolated by means of its platinochloride. To distinguish a ptomaine from a vegetable alkaloid, Brouardel a. Boutmy (*C. R.* 92, 1056; *cf.* Tanret, *C. R.* 92, 1163) add a few drops of the solution of the sulphate of the alkaloid to potassium ferricyanide mixed with $FeCl_3$: a dark-blue pp. is formed if a ptomaine be present, while the vegetable alkaloids (except morphine, veratrine, eserine, aconitine; and ergotinine) have no action. The test is, of course, given by many other reducing agents. This ptomaine reaction is given (slowly) by a poisonous liquid alkaloid extracted by Stas's method from the intestines of persons who died of cholera (Villiers, *C. R.* 100, 91). Pouchet (*C. R.* 97, 1560; *cf.* Gautier, *B. C.* 1882, 710; Béchamp, *C. R.* 94, 973) obtained from urine and fæces some alkaloids closely resembling the ptomaines got by putrefaction of proteids out of contact of air. He separated them by decomposing their tannates with $Pb(OH)_2$ in presence of alcohol, the lead being finally removed by H_2S, and the liquid dialysed. $C_3H_5NO_2$ is liquid and dialyses with difficulty; it exhibits the alkaloidal reactions, is resinified by HCl, and reduces platinic chloride. The base $C_7H_{12}N_4O_2$ or $C_7H_{14}N_4O_2$ is crystalline, and passes through the membrane; it is insol. ether, nearly insol. alcohol, is feebly alkaline and yields crystalline salts. From the dialysate the platinochlorides of two crystalline unstable bases $C_5H_{12}N_2O_4$ and $C_7H_{18}N_2O_6$ can be got. Urine which had a tendency to deposit cystin and the fæces of the same patient contained cadaverine and putrescine (Baumann, *H.* 13, 562; *cf.* Dupré a. Bence-Jones, *Pr.* 15, 73; Stadthagen a. Brieger, *Ar. pathol. Anat.* 115, pt. 3). These diamines appear to be absent from normal urine, but present in cholera.

Cadaverine is PENTAMETHYLENE-DIAMINE, vol. iii. p. 305.

Putrescine is TETRAMETHYLENE-DIAMINE.

Mydaleïne is extremely poisonous, while **gadinine** is not poisonous.

Mydine $C_8H_{11}NO$. Occurs in putrid corpses (Brieger, *Ptomaïne*, iii. 25). Has an ammoniacal odour and reduces gold chloride. Not poisonous. —$B'C_6H_3N_3O_7$. [195°]. Broad prisms.

Base $C_7H_{17}NO_2$. Occurs in decaying horse-flesh, four months old (Brieger). Acid in reaction. Poisonous. Does not form a picrate.—$B'HAuCl_4$. [176°]. Needles or plates.

Typhotoxin $C_7H_{17}NO_2$. Formed by the action of the typhus bacillus on muscle (Brieger, *Ptomaïne*, iii. 86). Poisonous base.—$B'HAuCl_4$. [176°]. Prisms.

Mydatoxin $C_6H_{13}NO_2$. Occurs in decaying horse-flesh and corpses (B.). Poisonous. Strongly alkaline.—$B'_2H_2PtCl_6$. [193°]. V. e. sol. water.

Tetanine $C_{13}H_{20}N_2O_4$. Occurs in decaying corpses (Brieger, *B.* 19, 3120), and is formed by the action of the tetanus bacillus on beef. Very poisonous base.—$B'H_2PtCl_6$. Plates.

Base $C_5H_{11}N$. (c. 100°). Accompanies tetanine, and also produces convulsions (B.). Volatile liquid. Its hydrochloride is crystalline [205°].—$B'HAuCl_4$. [130°].—$B'_2H_2PtCl_6$. Plates, decomposed at 240°.

Base $C_{32}H_{31}N$. Oily ptomaine, smelling like hawthorn (Delezinier, *Bl.* [3] 1, 178). In presence of air it acts chemically and physiologically like veratrine. Insol. water, sol. alcohol and ether. Its salts are deliquescent.

Base $C_5H_{11}NO_2$. [156°]. Occurs in putrid flesh and putrid fibrin (E. a. H. Salkowski, *B.* 16, 1192). Crystalline powder, v. e. sol. water. Not poisonous.—$B'HCl$: crystals, v. e. sol. water. —$B'HAuCl_4aq$: yellow crystals.

Base $C_{11}H_{13}NO_3$. *Erysipeline.* Occurs in urine in erysipelas (Griffiths, *C. R.* 115, 667). Prisms, sol. water. Very poisonous.

Base $C_{22}H_{19}NO_2$. Occurs in urine in puerperal fever (G.). Crystalline and poisonous.

Base $C_{10}H_{17}N$. A product of the decomposition of albumen by *Bacterium allii*, which is found in decaying onions (A. B. Griffiths, *C. R.* 110, 416). Minute deliquescent needles (from water), smelling like hawthorn.—$B'_2H_2PtCl_6$: crystalline, sol. hot water.

Base $C_{15}H_{10}N_2O_6$. Occurs in urine of victims to glanders (A. B. Griffiths, *C. R.* 114, 1382). White crystals. Poisonous. Forms crystalline salts.

Base $C_{20}H_{26}N_2O_3$. Occurs in urine in cases of pneumonia (G.). Minute needles, forming an alkaline aqueous solution $[\alpha]_D = 23{\cdot}5°$.

Base $C_8H_{11}N$. (202°). S.G. ^{2} ·9865. Extracted, together with a base $C_{10}H_{15}N$ from putrid cuttle-fish (De Coninck, *C. R.* 106, 858, 1604; 108, 58, 809; 110, 1339; 112, 584). Mobile, strongly-smelling liquid, v. sol. water, alcohol, and ether. Turns brown in air. Appears to be a propyl-pyridine, as it yields nicotinic acid on oxidation by dilute $KMnO_4$ at 90°.—$B'HCl$: deliquescent radiating mass.—$B'_2H_2PtCl_6$. Converted by hot water into B'_2PtCl_4, a nearly insoluble brown powder.—$B'HAuCl_4$.—$B'HBr$.—$B'_2H_2HgCl_4$.—$B'_2H_2Hg_3Cl_8$.—$B'MeI$. Needles, v. e. sol. alcohol.

Base $C_{10}H_{15}N$. (230°). Formed as above. Liquid, smelling like furze. Resinified by air.—$B'HBr$. White deliquescent needles.—$B'HCl$.—$B'_2H_2PtCl_4$.—B'_2PtCl_4. [206°].—$B'HAuCl_4$: yellow pp., decomposed by hot water.

Base $C_{10}H_{13}N$. (200°). Extracted by Stas's method from fibrin that has putrefied for two months (Guareschi a. Mosso. *J. pr.* [2] 27, 428; *J. Th.* 1887, 487). Yields the alkaloidal reactions. Smells like pyridine. Acts physiologically like curare.—$B'_2H_2PtCl_6$: rose-red crystals.

Base $C_{14}H_{20}N_2O_4$. [250°]. Formed in the putrefaction of fibrin, from which it can be extracted, together with the liquid alkaloid $C_{10}H_{13}N$, by chloroform and ether (Guareschi, *G.* 17, 509). Tables (from alcohol), sol. water and alcohol, v. sl. sol. chloroform. Its aqueous solution is neutral. Griffiths (*Bl.* [2] 7, 250; *C. R.* 113, 656) got, from urine of patients suffering from erysipelas, a crystalline ptomaine 'erysipeline' $C_{11}H_{13}NO_3$, sol. water, and very poisonous. It gives the alkaloidal reactions.

The term leucomaines (λεύκωμα, white of egg) is applied by Gautier (*Sur les Alcaloïdes des Tissus Animaux*, Paris, 1886) to alkaloids occurring in the tissues of living animals. From fresh beef and Liebig's extract of beef he obtained xanthocreatinine $C_5H_{10}N_4O$, crysocreatinine $C_5H_8N_4O$, amphicreatinine $C_9H_{19}N_7O_4$, pseudoxanthine $C_4H_5N_5O$, and two feeble bases $C_{11}H_{24}N_{10}O_5$ and $C_{12}H_{25}N_{11}O_5$, both crystallising in tables.

Xanthocreatinine $C_5H_{10}N_4O$. Thin sulphur-yellow tables, v. e. sol. water, sol. boiling alcohol. Gives an odour of roast meat when heated. Resembles creatinine.

Chrysocreatinine $C_5H_8N_4O$. Orange crystals, with feebly alkaline reaction. Sl. sol. water. Resembles creatinine.

Amphicreatinine $C_9H_{19}N_7O_4$. Yellow prisms, sl. sol. water. A weak base, resembling creatinine.

Pseudoxanthine $C_4H_5N_5O$. Yellow crystalline powder, sl. sol. cold water, sol. HClAq and NaOHAq. Reacts with HNO_3 and KOH like xanthine.

Carnine *v.* vol. i. p. 710.

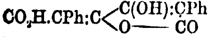
PTYALIN *v.* vol. ii. p. 545.

PTYCHOTIS OIL. The essential oil got from the seeds of *Ptychotis ajowan*, an umbelliferous plant growing in Central India, contains thymol and a terpene $C_{10}H_{16}$ (172°) S.G. ^{12} ·854 (Stenhouse, *C. J.* 9, 234; *cf.* Haines, *C. J.* 8, 289).

PULEGIUM OIL. The essential oil of *Pulegium micranthum*, growing on the Steppes of Southern Russia, contains oily $C_{10}H_{16}O$ (227°)

S.G. 11 ·932 (Butlerow, *J.* 1854, 594). It yields acetic and valeric acid when fused with potash. The oil of *Mentha pulegium* is described under Pennyroyal.

PULVIC ACID $C_{18}H_{12}O_5$ *i.e.*



$CO_2H.CPh:C\left<\begin{matrix}C(OH):CPh\\ O\text{———}CO\end{matrix}\right.$. [215°]. Prepared by the action of cold NaOHAq on a solution of the anhydride in acetone, and also by boiling vulpic acid with milk of lime (Spiegel, *B.* 13, 1630, 2219; 14, 1686; 15, 1550; *A.* 219, 1). Orange crystals or yellow plates (containing EtOH), sol. alcohol and ether, sl. sol. water. Decomposed by baryta-water into phenyl-acetic and oxalic acids. Alkaline $KMnO_4$ oxidises it to phenyl-glyoxylic and oxalic acids. On reduction by zinc-dust and NH_3Aq it gives a mixture of carboxy-cornicularic acid ($C_{18}H_{14}O_5$), cornicularic acid ($C_{17}H_{16}O_3$), and the two dihydrides of cornicularic acid ($C_{17}H_{18}O_3$).

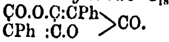
Salts.—BaA″*x*aq: golden plates.—AgHA″: small prisms.—Ag_2A″ aq: long needles.

Methyl ether v. Vulpic acid.

Ethyl ether EtA′. [128°]. Prepared by dissolving the anhydride in alcoholic potash.

Methyl derivative of the methyl ether $C_{18}H_{10}Me_2O_5$. [139°]. Colourless needles.

Anhydride $C_{18}H_{14}O_4$ *i.e.*



$\left.\begin{matrix}CO.O.C:CPh\\ CPh\ :C.O\end{matrix}\right>CO$. [221°]. Formed, together with MeOH, by heating vulpic acid at 200°. Colourless needles, sl. sol. alcohol, insol. water. Converted by ammonia into $C_{18}H_{11}(NH_2)O_4$ [220°] crystallising in yellow prisms.

PUNICIN. *The purple of the ancients.* Extracted from *Purpura capillus* and other shellfish which yield a colourless secretion which becomes purple on exposure to sunlight (Schunck, *C. J.* 35, 589; 37, 613). Obtained in Central America from *Purpura patula.* Yarn dyed by the Indians is warmed with HCl and then with ether. The colouring matter is then extracted with aniline, which on cooling deposits punicin as a crystalline powder, insol. boiling alcohol and ether, sl. sol. benzene and HOAc. Its solution in aniline shows an absorption band between C and D, with a sharp edge towards C. The band resembles that of indigo, but it disappears sooner on standing. In phenol it forms a sky-blue solution. Its solution in conc. H_2SO_4 shows an absorption band between D and E; this disappears on standing, the liquid becoming bright green. Water precipitates the purple from this solution, so that a sulphonic acid is not formed. Punicin begins to sublime at 190°. It is hardly attacked by HNO_3 (S.G. 1·2) or by aqueous CrO_3. With bromine it reacts, forming a body which crystallises from alcohol in yellow needles. Punicin dissolves in aqueous $SnCl_2$, but is deposited again on exposing the solution to air.

PURPLE OF CASSIUS. A purple-coloured solid, obtained by adding $SnCl_2$Aq to $AuCl_3$Aq in presence of a reducing agent; *v.* Tin, oxides of, in this volume.

PURPURIC ACID $C_8H_5N_5O_6$. Not known in the free state.

Salts. — (NH_4)HA″ aq. Murexide. Formed by heating ammonium dialurate; by oxidising uranil with HgO; and by adding ammonia or ammonium carbonate to a mixture of alloxan and alloxantin (Prout, *A. Ch.* 11, 48; Kodweiss, *P.* 19, 12; Liebig a. Wohler, *A.* 26, 319; Fritzsche, *J. pr.* 16, 380; 17, 47; Beilstein, *A.* 107, 176; Laurent, *C. R.* 35, 629; Gregory, *A.* 33, 334). Garnet-red four-sided prisms with golden-green lustre; when dried *in vacuo* it forms a brown powder. M. sol. hot water, forming a purple solution, insol. alcohol and ether. Decomposed by acids with formation of uranil and alloxan. The absorption spectrum has been studied by Hartley (*C. J.* 51, 199).—KHA″. Crystals resembling murexide, forming in cold KOHAq a blue solution decolourised by heat.—NaHA″.—BaA″ 3aq; dark-green powder.—AgHA″ 1½aq: brownish-red powder.—Ag_2A″.

Isopurpuric acid *v.* Tri-nitro-phenol, *Reaction* 5.

Metapurpuric acid *v.* (*a*)-Di-nitro-phenol, *Reaction* 2.

PURPUREO-CHROMIUM SALTS *v.* Chrom-ammonium salts, vol. ii. 159–60.

PURPUREO-COBALT SALTS *v.* Cobalt-amines, vol. ii. pp. 227–8.

PURPUREO-RHODIUM SALTS *v.* Rhodium-ammonium compounds.

PURPURIN *v.* Tri-oxy-anthraquinone.

PURPUROGALLIN $C_{20}H_{16}O_9$. *Pyrogalloquinone.* [256°]. Formed by the slow oxidation of pyrogallol (Struve, *A.* 163, 162; Girard, *Z.* 1870, 86; Wichelhaus, *B.* 5, 848; De Clermont a. Chautard, *C. R.* 94, 1362; 102, 1072; Nietzki a. Steinmann, *B.* 20, 1277; Loew, *J. pr.* [2] 15, 322). Formed also by the action of aqueous KNO_2 on gallic acid (Hooker, *B.* 20, 3259). Obtained also from pyrogallol and quinone (Wichelhaus, *B.* 5, 847; Nietzki, *B.* 18, 1278). Prepared by adding a solution of K_3FeCy_6 (87 g.) in water (330 c.c.) to pyrogallol (20 g.) dissolved in cold water (330 c.c.), and filtering after half an hour; the yield is small (3 g.). Dark-brown needles (from alcohol). May be sublimed. V. sl. sol. water, sl. sol. alcohol, m. sol. ether. Reduces $AgNO_3$ and Fehling's solutions. H_2SO_4 forms a crimson solution changed to violet by HNO_2. Ammonia forms a blue solution, changing through green to dark yellow. Yields naphthalene on distillation with zinc-dust. According to De Clermont and Chautard purpurogallin yields Na_4A^{iv} crystallising in deliquescent needles, Ba_2A^{iv} as crystalline plates, $C_{20}H_{12}Br_4O_9$ as red needles [204°] and $C_{20}H_{12}Ac_4O_9$ [186°]. By heating with H_2SO_4 these chemists obtained SO_2 and $C_{20}H_{12}O_{10}$, which crystallised in brown needles forming a blue solution in KOHAq.

PURPUROXANTHIN *v.* *m*-Di-oxy-anthraquinone.

PURREÏC ACID *v.* Euxanthic acid.

PUTREFACTION *v.* Fermentation.

PUTREFACTIVE ALKALOIDS *v.* Ptomaïnes.

PUTRESCINE *v.* Tetra-methylene-diamine.

PYKNOMETER. This name is sometimes given to various forms of the specific gravity bottle, for determining the relative densities of liquids (*cf.* Densities, relative, vol. ii. p. 373).

PYRANIL-PYROÏC ACID $C_{10}H_{10}NO(CO_2H)$. [165°]. Formed by heating phenyl-amido-pyrotartaric acid $CO_2H.CH_2.CMe(NHPh).CO_2H$ a little above its melting-point for some time (Reissert a. Tiemann, *B.* 19, 622; 21, 1942, 3257; 22, 2281; 24, 314). Crystalline powder, sl. sol.

water, alcohol, and ether. Converted by heating strongly into the phenyl-imides of citraconic acid and of phenyl-amido-pyrotartaric acid. According to Anschütz (*B.* 21, 3252; 22, 731; 23, 895, 2979; *A.* 246, 115; 248, 269), pyranil-pyroïc acid is the mono-anilide of mesaconic acid.

PYRAZINE. This name is used to denote the ring $\mathrm{N}{<}\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}{>}\mathrm{N}$.

Pyrazine hexahydride $C_4H_{10}N_2$ *i.e.* $\mathrm{NH}{<}\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}{>}\mathrm{NH}$. *Piperazine. Di-ethylene-diamine.* [104°–107°]. (137° uncor.). Formed from ammonia and ethylene bromide (Cloez, *Instit.* 1843, 213) or ethylene chloride (Natanson, *A.* 92, 48; 98, 291; Hofmann, *Pr.* 10, 224; 11, 278; *B.* 23, 3297). Formed also by boiling $\mathrm{NO.C_6H_4.N}{<}\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}{>}\mathrm{N.C_6H_4.NO}$ with alcoholic potash (Bischler, *B.* 24, 717). According to Majert a. Schmidt (*B.* 24, 241), it is not identical with spermine. Glittering tables (from water). May be sublimed. Strongly alkaline and absorbs CO_2 from the air.

Reactions.—1. Aqueous NaOCl, saturated with Cl, forms $\mathrm{ClN}{<}\begin{matrix}\mathrm{CH_2.CH_2}\\ \mathrm{CH_2.CH_2}\end{matrix}{>}\mathrm{NCl}$ [71°], crystallising in prisms, v. sl. sol. water, v. sol. alcohol (Schmidt a. Wichmann, *B.* 24, 3243). This body explodes at 80°–85°. Bromine water forms the corresponding di-bromo-piperazine, which is very unstable.—2. *Diazobenzene chloride* and NaOHAq form $Ph.N_2.N{:}C_4H_8{:}N.N_2Ph$ [129°] (S. a. W.).—3. *Benzoic aldehyde* yields the compound $(N{:}C_4H_8{:}N){:}CHPh$ [247°] (Schmidt a. Wichmann, *B.* 24, 3242).—4. *Quinone* forms an amorphous violet-brown body, almost insol. alcohol.—5. *Hydroquinone* in alcoholic solution forms $C_4H_{10}N_2C_6H_6O_2$, crystallising in needles [195°].—6. *Phenol* forms $C_4H_{10}N_22PhOH$ [101°], crystallising from spirit in prisms, v. sol. water.—7. *Oxalic ether* at 110° reacts forming the ether $CO_2Et.CO.N{:}C_4H_8{:}N.CO.CO_2Et$ [124°] crystallising in broad needles (S. a. W.).—8. *p-Chloro-nitro-benzene* at 150° gives the compound $NO_2.C_6H_4.N{:}C_4H_8{:}N.C_6H_4.NO_2$ [248°] (Schmidt a. Wichmann, *B.* 24, 3240).

Salts.—$B''H_2Cl_2$ aq: needles, v. sol. water.—$B''H_2PtCl_6$.—$B''2HAuCl_4$.—$B''H_2HgCl_4$: stellate groups of needles (Sieber, *B.* 23, 326).—$B''C_6H_2(NO_2)_3OH$: yellow needles.—Carbonate: [162°–165°].—Urate: $B''C_5H_4N_4O_3$. The phosphate and the bismutho-iodide are crystalline.

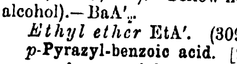
Di-acetyl derivative $C_4H_8N_2Ac_2$. [138·5°]. (above 310°). Formed from piperazine and Ac_2O. Needles, v. e. sol. water and alcohol.

Nitrosamine $NO.N{:}C_4H_8{:}N.NO$. [158°] (Ladenburg, *B.* 24, 2640; Schmidt, *B.* 24, 3245; *G. P.* 12, 59222). Reduced by zinc-dust and HOAc to $NH_2.N{:}C_4H_8{:}N.NH_2$, which crystallises in needles [c. 100°] (228°), and yields B'HCl, $B'C_6H_3N_3O_7$, an amorphous di-benzoyl derivative, and reacts with benzoic aldehyde, forming $CHPh{:}N.N{:}C_4H_8{:}N.N{:}CHPh$ [205°], which crystallises in pearly plates.

PYRAZOLE $C_3H_4N_2$ *i.e.* $\begin{matrix}\mathrm{CH{:}N}\\ \mathrm{CH{:}CH}\end{matrix}{>}\mathrm{NH}$. [70°]. **(187°). Formed by heating the tri-carboxylic acid produced by saponification of the product of direct addition of diazoacetic ether and** acetylene dicarboxylic ether (Buchner, *B.* 22, 2165). Formed also by heating hydrazine hydrate (10·8 g.) with epichlorhydrin (10 g.) and $ZnCl_2$ (11 g.) (Balbiano, *B.* 23, 1103). Needles, v. sol. cold water, forming a neutral solution, sol. alcohol and ether. Gives a white pp. with $HgCl_2$, and also with ammoniacal $AgNO_3$.

Salts.—B'HCl. Hygroscopic prisms.—$B'_2H_2PtCl_6$ 2aq. At 210° it is split up into HCl and $(C_3H_3N_2)_2PtCl_2$, a light-yellow powder.—$AgC_3H_3N_2$: sl. sol. water.—$B'C_6H_3N_3O_7$. [160°].

PYRAZOLE BLUE $C_{20}H_{16}N_4O_2$ *i.e.*



Formed by oxidation of di-oxy-di-phenyl-di-methyl-dipyrazyl (Knorr, *A.* 238, 172; *B.* 25, 765). Sol. chloroform, conc. H_2SO_4 and HOAc. Its spectrum resembles that of bodies of the indigo group. Decomposes about 230°. Its sulphonic acid, got by the action of Br on di-oxy-di-phenyl-di-methyl-dipyrazyl disulphonic acid, is destroyed by excess of bromine (Möllenhoff, *B.* 25, 1949).

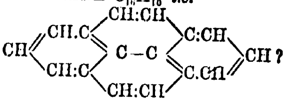
o-**PYRAZYL-BENZOIC ACID** $C_{10}H_8N_2O_2$ *i.e.* $\begin{matrix}\mathrm{CH{:}N}\\ \mathrm{CH{:}CH}\end{matrix}{>}\mathrm{N.C_6H_4.CO_2H}$. [139° cor.]. Formed by oxidising *o*-tolyl-pyrazole with $KMnO_4$ (Balbiano, *G.* 19, 123). Yellow needles (from dilute alcohol).—BaA'_2.

Ethyl ether EtA'. (309° i.V.).

p-**Pyrazyl-benzoic acid.** [265°]. Got in like manner from *p*-tolyl-pyrazole.—NaA'.—BaA'_2.

Ethyl ether EtA'. [62°]. Tables.

PYRENE $C_{16}H_{10}$ *i.e.*



? Mol. w. 202. [149°]. (above 360°). S. (alcohol) 1·87 at 16°; 3·08 at 78°; S. (toluene) 16·5 at 18° (Bechi, *B.* 12, 1978). Occurs in coal tar (Graebe, *A.* 158, 285). Monoclinic tables (Fittig a. Hintz, *B.* 10, 2143), v. e. sol. CS_2 and ether. Yields pyrene-quinone and pyrenic acid on oxidation. $SbCl_5$ at 360° forms CCl_4, $C_{15}Cl_{10}$ [above 300°], $C_{14}Cl_{10}$ [above 300°], and other bodies (Merz a. Weith, *B.* 16, 2880). Bromine forms crystalline $C_{16}H_8Br_4$ and $C_{16}H_7Br_3$ (Graebe).

Picric acid compound $C_{16}H_{10}C_6H_3N_3O_7$. [222°]. Red needles (from alcohol), v. sl. sol. cold alcohol, m. sol. ether, v. sol. benzene.

Hexahydride $C_{16}H_{16}$. [127°]. Formed by heating pyrene with HIAq and P at 200°. Needles, v. e. sol. ether and boiling alcohol. Its alcoholic solution is not ppd. by picric acid.

Chloropyrenes. The following chloro-pyrenes are formed by passing Cl into a solution of pyrene in chloroform. They are separated by fractional crystallisation from alcohol, chloroform, and xylene (Goldschmiedt a. Wegscheider, *M.* 4, 237).

$C_{16}H_9Cl$. [119°]. Golden needles, forming in H_2SO_4 a solution with violet fluorescence. Yields $C_{16}H_9ClC_6H_3N_3O_7$. [177°].

$C_{16}H_8Cl_2$. Two di-chloro-pyrenes [156°] and [196°].

$C_{16}H_7Cl_3$. [257°]. White needles.

$C_{16}H_6Cl_4$. [above 330°]. Needles.

Nitropyrene $C_{16}H_9NO_2$. [150°]. Formed by slowly adding H_2SO_4 to aqueous KNO_3 under an ethereal solution of pyrene (Goldschmiedt, *M.* 2, 580). Yellow needles (from alcohol), sl. sol. cold alcohol.

Di-nitro-pyrene $C_{16}H_8(NO_2)_2$. Formed from pyrene and HNO_3 (S.G. 1·45). Yellow needles (from HOAc). Reduced by tin and HCl to di-amido-pyrene (Jahoda, *M.* 8, 449).

Tetra-nitro-pyrene $C_{16}H_6(NO_2)_4$. [above 300°]. Yellow needles (from HOAc), nearly insol. alcohol.

Amido-pyrene $C_{16}H_9.NH_2$. [116°]. Got by reducing nitropyrene. Needles, sl. sol. water.—$B'_2H_2SO_4$ (dried at 100°).—B'HCl. Its solution dyes fir-wood red.

PYRENE CARBOXYLIC ACID $C_{16}H_9.CO_2H$. [267°]. Formed by fusing its nitrile with potash (Goldschmiedt a. Wegscheider, *M.* 4, 256). Needles, sl. sol. water. Resolved by heat into pyrene and CO_2.—CaA'_2 aq.—BaA'_2 2½aq.

Nitrile $C_{16}H_9.CN$. [150°]. Formed, together with the nitrile of the dicarboxylic acid, by heating potassium pyrene disulphonate with KCy or K_4FeCy_6. Needles (from alcohol). The solutions of this body show green fluorescence.—$(C_{17}H_9N)_2C_6H_3N_3O_7$. [134°]. Red needles, decomposed by alcohol.

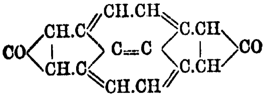
Pyrene dicarboxylic acid $C_{16}H_8(CO_2H)_2$. [above 300°].

Nitrile [above 300°]. $C_{16}H_8(CN)_2$. Formed as above. Yellow powder. Its solutions show green fluorescence.

PYRENE-KETONE $C_{13}H_8O$ *i.e.*

[1:1']
$C_{16}H_8<\substack{CH\\CH}>CO$. [142°]. Formed by distilling pyrenic acid with slaked lime (Bamberger a. Philip, *B.* 19, 1996, 3040; 20, 371; *A.* 240, 178). Golden tables (from dilute alcohol), volatile with steam. Reduced by zinc and HCl to $C_{12}H_8(CH.OH)$. Oxidised by $KMnO_4$ to naphthalene (1,1')-dicarboxylic acid.

PYRENE-QUINONE $C_{16}H_8O_2$ *i.e.*

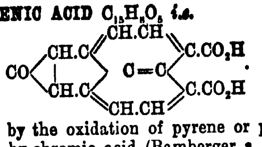


(Bamberger a. Philip, *B.* 20, 369; *A.* 240, 166). [c. 282°]. Formed by oxidation of pyrene by chromic acid mixture (Graebe, *A.* 158, 295; Goldschmiedt, *M.* 4, 309). Red needles (from HOAc), sol. aqueous $NaHSO_3$, v. sl. sol. alcohol and ether. Yields pyrene on distillation with zinc-dust. Bromine forms $C_{16}H_6Br_2O_2$ and $C_{16}H_5Br_3O_2$. Its alcoholic solution is turned claret-colour by a little NaOH. Reduced by zinc-dust and ammonia to hydropyrenequinone or pyrene-hydroquinone $C_{16}H_{10}O_2$, which forms golden crystals exhibiting a dark-blue fluorescence in alcoholic solution, and yielding $C_{16}H_8Ac_2O_2$ [167°].

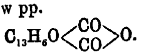
PYRENE SULPHONIC ACID $C_{16}H_9.SO_3H$. Got by fusing the disulphonic acid with potash (Goldschmiedt a. Wegscheider, *M.* 4, 242).—KA'aq: minute needles (from dilute alcohol).

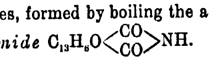
PYRENE DISULPHONIC ACID $C_{16}H_8(SO_3H)_2$. Formed by heating pyrene with H_2SO_4. Sticky mass, v. sol. water, sl. sol. alcohol, insol. ether.—K_2A'' 2½aq.—BaA″ 3½aq.—CaA″2aq: yellow powder.

PYRENIC ACID $C_{15}H_8O_5$ *i.e.*



Formed by the oxidation of pyrene or pyrene-quinone by chromic acid (Bamberger a. Philip, *B.* 19, 1427, 1995, 3036; 20, 369; *A.* 240, 168). Pale-yellow plates, blackened above 250°. V. sl. sol. alcohol. H_2SO_4 forms an orange solution. Oxidised by $KMnO_4$ to naphthalene tetra-carboxylic acid. Reacts with hydroxylamine. Phenyl-hydrazine forms $C_{15}H_6O_4(N_2HPh)$ 2aq, crystallising in yellow prisms.—BaA″aq.—Ag_2A'': amber-yellow pp.

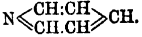
Anhydride 
$C_{13}H_6O<\substack{CO\\CO}>O$. Yellow needles, formed by boiling the acid with HOAc.

Imide 
$C_{13}H_6O<\substack{CO\\CO}>NH$. Yellow plates, got by dissolving the acid in NH_3Aq.

PYRENOLINE $C_{19}H_{11}N$. [153°]. Formed by heating amido-pyrene hydrochloride with nitrobenzene, glycerin, and H_2SO_4 (Jahoda, *M.* 8, 442). Golden scales (from alcohol), v. sol. water, forming solutions which exhibit green fluorescence.—B'HCl. [270°].—$B'_2H_2PtCl_6$. [above 290°]. — $B'H_2SO_4$ ½aq. [246°]. — $B'C_6H_3N_3O_7$. Decomposes at 260°.—B'MeI. [212°].

PYRIDANTHRILIC ACID $C_{13}H_{10}N_2O_7$ *i.e.* [2:1]$CO_2H.C_6H_4.NH.CO.C_5H_2N(CO_2H)_2$. [265°]. Formed by the action of alkaline $KMnO_4$ on cyclothraustic acid derived from α-diquinoline (Weidel a. Strache, *M.* 7, 289; 8, 197). Micaceous plates, sl. sol. hot water. Yields isocinchomeronic and anthranilic acids on oxidation.

PYRIDAZINE. The ring
$CH\lll\substack{N{=}N\\CH.CH}\ggg CH$ (Ach, *A.* 253, 46; *cf.* Knorr, *A.* 236, 295).

PYRIDINE C_5H_5N *i.e.* 
$N\lll\substack{CH{:}CH\\CH.CH}\ggg CH$.

Mol. w. 79. (116°) (Schiff, *B.* 19, 566); (114°) (Ladenburg, *A.* 247, 4); (116·5°) (Perkin, *C. J.* 55, 701). S.G. $\frac{0}{4}$ 1·0033 (L.); $\frac{15}{15}$ ·9855; $\frac{25}{25}$ ·9778 (P.). M.M. 8·761. H.F.p. −19,370 (Thomsen); 7,117 (Ramsay, *C. J.* 35, 696). H.F.v. −20,530 (Thomsen, *Th.*). S.H. ·418 (Colson, *A. Ch.* [6] 19, 408). S.V. 89·4 (Schiff); 91·6 (Ramsay). Occurs in bone oil, in coal-tar, and in tar got by distilling bituminous shale and peat (Anderson, *Tr. E.* 16, 4; 20 [2] 247; *P. M.* [4] 2, 257; *A.* 80, 55; 96, 200; 105, 335; Greville Williams, *P. M.* [4] 8, 24; Church a. Owen, *C. N.* 2, 146; *P. M.* [4] 20, 110; Schulze, *B.* 20, 409). Occurs also in tobacco smoke, and, in small quantity, in fusel oil (Haitinger, *M.* 3, 688).

Formation.—1. By heating isoamyl nitrate with P_2O_5 (Chapman a. Smith, *A. Suppl.* 6, 329). 2. By distilling its carboxylic acids with lime.—3. By distilling oxytrialdine and oxytetraldine with soda-lime (Schiff, *A. Suppl.* 6, 21).—4. With other bases by heating glycerin with ammonium phosphate (Stöhr, *J. pr.* [2] 45, 23).—5. By passing ethyl-allyl-amine over PbO at 450° (Koenigs, *B.* 12, 2344).—6. By heating piperidine with H_2SO_4 at 300° (K.), with nitro-benzene (4½ pts.) at 260° (Lellmann a. Geller, *B.* 21, 1921), or with AgOAc and 10 p.c. HOAc at 180° (Tafel, *B.* 25, 1621).—7. Together with mono- and di-substitution products by the action of Br on acetyl-piperidine (Hofmann, *B.* 16, 587).—8. By heating sodium-pyrrole with NaOMe and CH_2I_2 in sealed tubes at 200° (Dennstedt a. Zimmermann, *B.* 18, 3316).—9. From anhydroecgonine, by treatment with conc. HCl and distillation of the product with zinc-dust (Einhorn, *B.* 22, 1365).

Purification.—By ppg. the crude base (20 g.) dissolved in (100 g. of) a 10 p.c. solution of HCl by adding $HgCl_2$ (135 g.) dissolved in hot water (1,000 g.). The crystalline double salt is distilled with NaOHAq (Ladenburg, *A.* 247, 4).

Properties.—Colourless liquid with powerful odour, miscible with water. Fumes with HCl. Strong poison. Should not be inhaled (Marcus a. Oechsner, *Bl.* [2] 38, 97; *cf.* Kendrick a. Dewar, *Pr.* 22, 432; 23, 290). Forms a hydrate B′3aq, (93°), S.G. 1·0219, V.D. 1·17, which is a colourless liquid (Goldschmidt a. Constam, *B.* 16, 2976). Not attacked by boiling HNO_3 or CrO_3. Pyridine ppts. the hydroxides of Fe, Al, and Cr from their salts. With $CuSO_4$ it gives a pale-blue pp. dissolving in excess, forming a deep-blue liquid. Pyridine passes unchanged into the urine (O. de Coninck, *Compt. rend. Soc. Biol.* 4, 755). Pyridine does not mix with liquid CO_2 (Ditte, *C. R.* 105, 612). It gives no reaction with hot alkaline NaOBr (Denigès, *C. R.* 107, 662).

Reactions.—1. Dry *chlorine* forms di-chloro-pyridine [72°]. Chlorine passed into a solution of pyridine in $CHCl_3$ forms $B'Cl_2$, a white powder (Bally, *B.* 21, 1772). Chlorine-water ppts. a white powder. KOCl completely decomposes pyridine, forming N, CO_2, $CHCl_3$, and chloro-acetic acid (Keiser, *Am.* 8, 308).—2. *Bromine* added to a solution of the hydrochloride ppts. $C_5H_5NBr_2$, which is split up by heat into pyridine and bromine. Bromine acting in the cold on pyridine and water gives rise to $(C_5H_5NBr_2)_2HBr$ [126°] (Grimaux, *Bl.* [2] 38, 127). Pyridine hydrochloride heated with Br at 200° forms mono- and di-bromo-pyridine.—3. HIAq at 300° yields *n*-pentane and NH_3 (Hofmann, *B.* 16, 590).—4. *Sodium* at 80° yields (γ)-dipyridyl $C_{10}H_8N_2$, dipyridine $C_{10}H_{10}N_2$, iso-nicotine $C_{10}H_{14}N_2$, and two nitrogenous oils (240°-260°) and (300°-310°) (Weidel a. Russo, *M.* 3, 884).—5. Its *alkylo-iodides* are converted by distillation with solid KOH into volatile bases.—6. Excess of AcCl forms dehydracetic acid (Dennstedt a. Zimmermann, *B.* 19, 75).—7. Unites with $CH_2Cl.OH$ (the product of the union of formic aldehyde and HCl), and the product in aqueous solution gives with $HgCl_2$ a pp. of $(C_5H_5N)(CH_2ClOH)HgCl_2$ [162°], with platinic chloride a pp. of $(C_5H_5N)_2(CH_2ClOH)_2PtCl_4$ [216°], and with picric acid the compound $(C_5H_5N)CH_2(OH).C_6H_2(NO_2)_3O$ [c. 200°]. Treatment with $AgNO_3$ forms $(C_5H_5N)CH_2(OH)NO_3$ crystallising from alcohol-ether in prisms (Hemmelmayr, *M.* 12, 533).—8. *Alloxan* and aqueous SO_2 form triclinic crystals of $B'C_4H_2N_2O_4H_2SO_3$ (Pellizzari, *A.* 248, 150).—9. *Glycollic chlorhydrin* forms the base C_7H_9NO (Coppola, *G.* 15, 331). *Glycerin chlorhydrin* reacts with formation of $C_5H_5NCl.C_3H_5(OH)_2$ [107°] separating from alcohol in hexagonal crystals and yielding $(C_8H_{12}NO_2Cl)_2PtCl_4$ [180°] and $C_8H_{12}NO_2ClAuCl_3$ [122°] (Krüger, *J. pr.* [2] 44, 130).—10. *Chloro-acetic acid* at 100° forms $C_5H_5NCl.CH_2.CO_2H$ [202°] which may be viewed as the hydrochloride of 'pyridine-betaïne' $C_5H_5N\left\langle\begin{smallmatrix}CH_2\\O\end{smallmatrix}\right\rangle CO$ (von Gerichten, *B.* 15, 1253; Krüger, *B.* 23, 2609; *J. pr.* [2] 43, 279, 297; 44, 136). The pyridine-betaïne hydrochloride is also got by oxidising $C_5H_5NCl.CH_2.CH(OH).CH_2OH$ with chromic acid and is decomposed at 240° into CO_2, MeCl, and pyridine. Pyridine betaïne $C_7H_7NO_2$, got by the action of moist Ag_2O on the hydrochloride, forms hygroscopic tables (containing aq) and yields the salts $B'_2H_2PtCl_6$ [211°], B′HCl [202°], B'_2HCl aq [159°], B'_2HHgCl_3 aq [134°], B'_2HBr aq, an auro-chloride $B'HAuCl_4$ [165°] (Jahns, *B.* 20, 2841), B′HBr, [200°], $B'HNO_3$, [145°], $B'_2H_2SO_4$ [175°], $B'CrO_3$ [c. 166°], $B'C_6H_3N_3O_7$ [143°], $B'AgNO_3$ [171·5°], and $B'HBiI_4$ 2aq. On reduction by sodium-amalgam, pyridine-betaïne yields $C_5H_5NCl.CH_2.CH_2OH$.—11. *Chloro-acetic ether* yields the compound $C_5H_5NCl.CH_2.CO_2Et$, a crystalline powder [100°] (Krüger, *J. pr.* [2] 43, 274). This ether, $C_9H_{10}NO_2Cl$, forms the salts B'_2PtCl_4 [213°], $B'AuCl_3$ [117°], $B'HgCl_2$ [123°], $B'CdCl_2$ [141°], and B'_2CdCl_2 [107°].

Salts. — B′HCl. Deliquescent mass. — $B'_2H_2PtCl_6$. [242°]. Orange triclinic prisms. The aqueous solution is converted by long boiling into crystalline $B'_4H_2Cl_22PtCl_4$ and B'_2PtCl_4, a yellow insoluble powder.—B'_2PtCl_2. Yellow tables, almost insol. cold water (Jörgensen, *J. pr.* [2] 33, 504). An isomeride crystallises in needles. —B'_4PtCl_2 3aq.—$B'_4Pt_2Cl_4$. — $B'_2(NH_3)_2PtCl_2$. — $B'(NH_3)PtCl_2$.—$B'_2(NH_3)_2Pt_2Cl_6$.— $B'(NH_3)PtCl_4$. —$B'_2(NH_3)PtCl_2$.—$B'_2(NH_3)_2PtCl_2$ aq. Minute colourless prisms.—$B'HHg_2Cl_5$. [178°]. Needles (from water).—B'_23HgCl_2.—$B'HAuCl_4$. [285°]. Prisms, sl. sol. water.—$B'C_6H_3N_3O_7$. [162°] Needles, sl. sol. water.—B'_2ZnCl_2: short prisms, very soluble in cold water (Lang, *B.* 21, 1578).—B'_2ZnCl_2 2aq (Lachovitch, *M.* 9, 516).— B'_2ZnBr_2: prisms, v. sol. pyridine.—$B'_2H_2ZnCl_4$. — B'_2CuCl_2 [180°-190°]. — $B'CuSO_4$ 3aq. — $B'_4Cu_2Cl_2$. — $B'_6Cu_2Cl_2$. — B'_6CuBr_2. — $B'_4Cu_2I_2$. — $B'_4Cu_2Cy_2$. — $B'_2H_2CuCl_4$. — B'_2CdCl_2: needles, almost insol. alcohol, sol. water.—B'_6CdBr_2.— B'_2CdI_2.—$B'CdI_2$ (Monari, *J.* 1884, 629). — $B'HgCl_2$.—B'_2HgCy_2.—B'_3CaCl_2: white powder.— B'_4NiBr_2.—B′AgBr: white needles, sol. cold pyridine.—B′AgI.—B′AgCy: prisms (Varet, *Bl.* [3] 5, 843).—B'_2CuCy: yellow lamellæ, v. sol. warm pyridine (Varet, *C. R.* 112, 391). Loses pyridine on warming.—$B'H_2SO_4$: deliquescent mass.—B′HI: tables, v. sol. water, but not deliquescent. — $B'HI_3$. [89°]. Green crystalline powder (Dafert, *M.* 4, 508). — B′HBr. Deliquescent needles. — B'_2HBr_3. [126°]. Red tables.—B'_2Cl_2. Waxy mass (Keiser, *Am.* 8, 312). —$B'HNO_3$.—B'_2AgNO_3. [87°] (Jörgensen, *J. pr.* [2] 33, 502).—B'_3AgNO_3.—B'_4CuSO_4.—$B'CuSO_4$ 3aq. — $B'_4CuS_2O_6$.—B'_2SiCl_4. Amorphous (Harden, *C. J.* 51, 47).—B'_2SiF_4 (Corney a. Smith, *Am.* 10, 294).—B'_32SiF_4.—$B'_2H_4FeCy_6$ 2aq: monoclinic prisms (Mohler, *B.* 21, 1015).—B′ICl. [132°]. Needles (Pictet a. Krafft, *Bl.* [3] 7, 72).— B′IClHCl. [180°]. Long yellow needles (from water).—B'_2RhCl_3HCl 2aq (Jörgensen, *J. pr.* [2] 27, 478).—B'_4RhCl_3.—$B'_8Rh_2PtCl_{10}$.—B'_4RhCl_2Br. —$B'_4RhCl_2(NO_3)$ (dried at 100°).—$B'_8Rh_2Cl_4SO_4$ (dried at 100°).

Acetate B'_23HOAc. (140°). Miscible with

water, forming an acid solution (Gardner, *B.* 23, 1588).—**Formate** $B'3CH_2O_2$. (149°). Liquid, v. sol. water.—**Propionate** $B'3C_3H_6O_2$. (149°). Liquid. — **Cupric oxalate compound** $B'_2CuC_2O_4$: minute prisms (Seubert a. Rauter, *B.* 25, 2825).

Methylo-chloride $B'MeCl$. White needles (Ostermeyer, *B.* 18, 591). Converted by a hot aqueous solution of picric acid into $B'MeOC_6H_2(NO_2)_3\frac{1}{2}aq$, which crystallises in greenish-yellow explosive needles [34°]. — $B'_2Me_2PtCl_6$. [188°] (O.); [207°] (B.). — $B'MeAuCl_4$. [253°].—$B'MeClICl$. [82°] (O.); [90°] (B.). Yellow plates.—$B'MeClICl_3$. [180°]. Unstable yellow crystals (Bally, *B.* 21, 1774).

Methylo-perbromide $B'MeBr_3$. [48°].

Methylo-iodide $B'MeI$. Converted at 290° into methyl-pyridine hydriodides. On heating with alcoholic potash at 45° it yields a brown resin, forming a deep-red solution in alcohol, turned bright-red by HCl, orange-red by acetic acid, and ruby-red by ammonia (O. de Coninck, *C. R.* 102, 1479). Chlorine forms $B'MeICl_2$ [90°] (*v. supra*). Oxidised by alkaline K_3FeCy_6 to oxy-methyl-pyridine or ν-methyl-pyridone $CH{<}\genfrac{}{}{0pt}{}{CH.CO}{CH:CH}{>}NMe$ (250°), a liquid miscible with water (Decker, *J. pr.* [2] 47, 28; *cf.* Pechmann, *B.* 24, 3144).

Ethylo-iodide $B'EtI$. Silvery tables (Anderson, *A.* 94, 364). At 300° it yields pyridine, NH_3, (*a*) and (γ)- ethyl-pyridine, and di-ethyl-pyridine (Ladenburg, *B.* 16, 2059; 18, 2961). Yields $B'_2Et_2PtCl_6$. Oxidised by alkaline K_3FeCy_6 to $CH{<}\genfrac{}{}{0pt}{}{CH.CO}{CH:CH}{>}NEt$ (250°).

Ethyleno-iodide $B'C_2H_4I_2$. Prisms (Coppola, *G.* 15, 332). Ag_2O yields a base C_7H_9NO. By heating pyridine with ethylene bromide and some alcohol at 100° there is found $B'_2C_2H_4Br_2$, which yields $B'_2C_2H_4PtCl_6$ (Davidson, *A.* 121, 254).

Benzylo-chloride $B'PhCH_2Cl$. Reduced by sodium-amalgam to the unstable $C_{24}H_{24}N_2$ (Hofmann, *B.* 14, 1503).—$(B'PhCH_2Cl)_2PtCl_4$.

Nitro-benzylo-chlorides $B'C_6H_4(NO_2).CH_2Cl$. *o* [c. 76°], *m* [70°–100°], *p* [90°–100°]. These bodies are reduced by tin and HClAq to $B'C_6H_4(NH_3Cl).CH_2Cl$, which are split up by heat into pyridine hydrochloride and $C_6H_4{<}\genfrac{}{}{0pt}{}{NH_2Cl}{CH_2}$ (Lellmann a. Pekrun, *A.* 259, 54).

Phenacylo-bromide $B'BzCH_2Br$. Prisms (Bamberger, *B.* 20, 3344).—$B'_2(BzCH_2)_2Cr_2O_7$.

References.—BROMO-, CHLORO-, OXY-AMIDO-, and OXY- PYRIDINE.

Dipyridine $C_{10}H_{10}N_2$ *v.* DIPYRIDYL DIHYDRIDE.

Dipyridine $C_{10}H_{10}N_2$. (275°). S.G. $\frac{13}{}$ 1·124. Is probably a dipyridyl dihydride. Formed by heating nicotine with KOH and K_3FeCy_6, and also by heating the product of the action of S on nicotine at 150° with finely-divided copper (Cahours a. Etard, *Bl.* [2] 34, 452). Inactive liquid.—$B'HHgCl_3$.—$B'_2H_2PtCl_6$ 2aq.—$B'_2H_4FeCy_6$ 2aq: brownish-green tables.

(a)-PYRIDINE CARBOXYLIC ACID

$C_6H_5NO_2$ *i.e.* $\begin{array}{l}CH:CH.C.CO_2H\\CH:CH.N\end{array}$. *Picolinic acid.* [136°]. Formed by oxidation of (*a*)-methyl-pyridine with $KMnO_4$ (Weidel, *B.* 12, 1994), and by oxidation of (*a*)-phenyl-pyridine (Skraup, *M.* 4, 477). **Obtained also, together with its hexahydride,** from comenamic acid by successive treatment with PCl_5 and H_2SO_4, the resulting di-chloro-picolinic acid being reduced by heating for three days at 155° with HI dissolved in HOAc (Ost, *J. pr.* [2] 27, 285).

Preparation.—The three acids got by oxidation of crude methyl-pyridine from animal oil are converted into copper salts. Cupric pyridine (*a*)-carboxylate is extracted by hot water. The residue is treated with H_2S, and the difficultly-soluble (γ)- acid separated from the (β)- acid (Ost, *J. pr.* [2] 27, 286).

Properties.—Needles, v. sol. water and alcohol, almost insol. ether, benzene, $CHCl_3$, and CS_2. May be sublimed. $FeSO_4$ gives a red colouration with picolinic acid and with all the carboxylic acids of pyridine that contain CO_2H in the (*a*)- position (Skraup, *M.* 7, 210). The absorption of the ultra-violet spectrum has been studied by Hartley (*C. J.* 41, 45).

Reactions.—1. Yields pyridine on distillation with *lime* or with *alcoholic potash* at 240°. The Cu salt on distillation gives pyridine and (*a*)-dipyridyl [70°] (Blau, *M.* 10, 375; *B.* 21, 1077).—2. *Sodium-amalgam* forms δ-oxy-adipic acid (Weidel, *M.* 11, 522).—3. Fuming HI at 170° forms (*a*)-methyl-pyridine and piperidine (Seyfferth, *J. pr.* [2] 34, 241).—4. *Zinc-dust* and HOAc reduce it to (*a*)-methyl-pyridine.

Constitution.—This may be deduced from its formation from (β)-naphthoquinoline *viâ* (β)-phenyl-pyridine carboxylic acid (Skraup a. Cobenzl, *M.* 4, 436).

Salts. — $HA'HCl$: unstable crystals. — $H_2A'_2H_2PtCl_6$ 2aq: orange-red crystals.—NH_4A': triclinic tables.—KA'.—$BaA'_2\frac{1}{2}aq$.—CaA'_2 aq.—MgA'_2 2aq.

Hexahydride $C_5H_{10}N.CO_2H$. *Piperidine (a)-carboxylic acid.* The chief product of the action of HI at 160° on mono- or di- chloro-picolinic acid (Ost, *J. pr.* [2] 27, 287). Got also by reducing picolinic acid (Ladenburg, *B.* 24, 640). Syrup, v. sol. water. **Salts.**—$B'HCl$. [264°]. Nodules.—$B'_2H_2PtCl_6$. [184°] (L.).—$B'_2H_2PtCl_6$ 2aq.—$B'MeCl$. [191°]. Needles.

Pyridine (β)-carboxylic acid

$\begin{array}{l}CH:CH.C.CO_2H\\CH:\ N\ .CH\end{array}$. *Nicotinic acid.* [230°].

Formation.—1. By oxidising nicotine with HNO_3 (Weidel, *A.* 165, 330), CrO_3 (Huber, *A.* 141, 271; *B.* 3, 849), or $KMnO_4$ (Laiblin, *A.* 196, 129).—2. A product of oxidation of coal-tar bases (Weidel; Mohler, *B.* 21, 1009).—3. By heating quinolinic acid at 160° or with HCl at 180° (Ost, *J. pr.* [2] 27, 286; Lippmann a. Fleissner, *M.* 8, 315).—4. By oxidation of (β)-methyl-pyridine (Weidel, *B.* 12, 2004), (β)-ethyl-pyridine (Stoehr, *J. pr.* [2] 43, 155) or (β)-phenyl-pyridine (Skraup, *M.* 4, 453).—5. By saponification of its nitrile, which is got by distilling sodium-pyridine sulphonate with KCy (Fischer, *B.* 15, 63).—6. By heating three of the pyridine dicarboxylic acids (Hoogewerff a. Van Dorp, *R. T. C.* 1, 1, 107; *A.* 204, 117; 207, 226; Weidel a. Herzig, *M.* 1, 16).—7. By heating berberonic acid at 215° (Fürth, *M.* 2, 420).—8. By the action of Zn and HClAq on chloro-nicotinic acid (Pechmann a. Welsh, *C. J.* 47, 145).

Properties.—Needles, sl. sol. cold water, sol. alcohol, nearly insol. ether. May be sublimed.

Reactions.—1. Yields pyridine on distillation with lime.—2. *Sodium-amalgam* yields a mixture of δ-oxy-α-methyl-glutaric acid and its lactone, which, on treatment with alcohol and HCl, yields a mixture of two ethers. One of these, $C_{10}H_{17}ClO_4$, is converted by sodium-amalgam into α-methyl-glutaric acid, and the other, $C_8H_{14}O_4$, is also converted by successive treatment with PI_2 and with Zn and dilute H_2SO_4 into α-methyl-glutaric acid (Weidel, *M.* 11, 502).—3. *Bromine* and water at 120° yield CO_2, pyridine, and bromoform.—4. The K salt heated with MeI at 150° forms $C_5H_4NMeI.CO_2Me$, which on saponification yields $C_5H_4NMe(OH).CO_2H$ [130°], converted at 100° into trigonellin $C_5H_4NMe\left\langle\begin{matrix}CO\\ O\end{matrix}\right.$ [218°], which occurs in the seeds of *Trigonella fœnum græcum* (Jahns, *B.* 18, 2521; Hantzsch, *B.* 19, 31). This anhydride forms the salts $C_7H_7NO_2HCl$, $B'_2H_2PtCl_6aq$, $B'HAuCl_4$ [198°], and $B'_4 3HAuCl_4$ [186°].

Constitution.—This may be deduced from its formation from (α)-naphthaquinoline *viâ* (α)-phenyl-pyridine carboxylic acid.

Salts. — HA'HCl. Colourless prisms.—$H_2A'_2H_2PtCl_6$ 2aq.—$B'_2H_2AuCl_5$.—$B'HNO_3$ aq.—NH_4A': needles.—KA'.—MgA'_2: needles.—CaA'_2 5aq: monoclinic crystals; $a:b:c = 1{\cdot}537:1:{\cdot}629$; $\beta = 62°\ 50'$. — Cu(OH)A' (De Coninck, *Bl.* [2] 42, 100).—AgA': needles (from hot water).

Nitrile $C_5H_4N.Cy$. [49°]. Formed by distilling sodium pyridine sulphonate with KCy (Fischer, *B.* 15, 63). Needles or prisms, sol. water. — B'HCl. — $B'_2H_2PtCl_6$: yellow soluble needles. Tables (by sublimation). Converted by means of hydroxylamine into the amidoxim $C_5H_4N.C(NH_2){:}NOH$ [128°], which yields an acetyl derivative [143°] and a benzoyl derivative [190°], and is converted by phenyl cyanate into $C_5H_4N.C(NOH).NH.CO.NHPh$ [167°], by phenyl thiocarbimide into $C_5H_4N.C\left\langle\begin{matrix}N.S\\ N\end{matrix}\right\rangle C.NHPh$ [241°], and by succinic anhydride at 100° into $C_5H_4N\left\langle\begin{matrix}N.O\\ N\end{matrix}\right\rangle C.CH_2.CH_2.CO_2H$ [178°]. The acetyl and benzoyl derivatives are converted by heating into $C_5H_4N\left\langle\begin{matrix}N.O\\ N\end{matrix}\right\rangle CMe$ [109°] and $C_5H_4N\left\langle\begin{matrix}N.O\\ N\end{matrix}\right\rangle CPh$ [139°] respectively (Michaelis, *B.* 24, 3439).

Hexahydride $C_5H_{10}N(CO_2H)$. *Nipecotinic acid.* [250°]. Got by reducing nicotinic acid in alcoholic solution by Na (Ladenburg, *B.* 25, 2763). Crystals, v. e. sol. water, insol. alcohol and ether.—HA'HCl. [240°].—$H_2A'_2H_2PtCl_6$. [213° cor.]. — $HA'HAuCl_4$. [197° cor.].—$HA'HCl5HgCl_2$. [231°].—MeA'HCl [208°].—$Me_2A'_2H_2PtCl_6$. — Nitrosamine $C_6H_{10}N_2O_3$. [112°].

Pyridine (γ)-carboxylic acid

$N\left\langle\begin{matrix}CH.CH\\ CH{:}CH\end{matrix}\right\rangle C.CO_2H$. *Isonicotinic acid.* [305°] (S.); [306°] (B. a. H.); [309·5°] (W. a. H.).

Formation.—1. By heating pyridine *s*-tricarboxylic acid (Skraup, *B.* 12, 2331) and three of the pyridine di-carboxylic acids (Hoogewerff a. Van Dorp, *A.* 204, 112; Weidel a. Herzig, *M.* 1, 28; Böttinger, *B.* 14, 68).—2. By the action of $KMnO_4$ on (γ)-methyl-pyridine (Behrmann a. Hofmann, *B.* 17, 2696; Ladenburg, *B.* 21, 287). 3. By heating di-chloro-pyridine carboxylic acid [210°] with HI (B. a. H.).

Properties.—Needles, sl. sol. cold water, insol. alcohol. Yields pyridine on distilling with lime and δ-oxy-ethyl-succinic acid on reduction with sodium-amalgam (Weidel, *M.* 11, 517).

Salts.—NH_4A': needles.—CaA'_2 4aq: silky needles, m. sol. water.—HA'HCl: monoclinic prisms.—$H_2A'_2H_2PtCl_6$ 2aq: monoclinic crystals.

Hexahydride $C_5H_{10}N(CO_2H)$. Got by reducing the acid in alcoholic solution by Na (Ladenburg, *B.* 25, 2773). Branching groups of needles, v. e. sol. water, insol. alcohol. Blackens at 300°, but is not melted at 320°.—HA'HCl. [228°]. Trimetric crystals; $a:b:c = {\cdot}922:1:{\cdot}979$. —$H_2A'_2H_2PtCl_6$. [239°]. — Aurochloride: [197°]. Nitrosamine $C_6H_{10}N_2O_3$. [101°].

Pyridine (αα)-dicarboxylic acid

$CH\left\langle\begin{matrix}CH.C(CO_2H)\\ CH{:}C(CO_2H)\end{matrix}\right\rangle N$. *Dipicolinic acid.* [226°] (L. a. R.; S.); [237°] (E.); [236° cor.] (Collie, *C. J.* 59, 179). Formed by oxidation of (αα)-di-methyl-pyridine [145°] (derived from aceto-acetic ether or from coal-tar) by $KMnO_4$ (Epstein, *A.* 231, 26; Ladenburg a. Roth, *B.* 18, 52; 19, 790; 20, 130; *A.* 247, 32; Lange a. Rosenberg, *B.* 20, 132; *cf.* Dewar, *C. N.* 23, 18). Got also by oxidation of (α)-methyl-(α)-ethyl-pyridine by dilute (2 p.c.) $KMnO_4$ (Schultz, *B.* 20, 2724).

Properties.—Hair-like needles (containing 1½aq) or anhydrous scales; sl. sol. cold alcohol, water, and ether. On heating at 245° in a current of H it yields pyridine and pyridine (α)-carboxylic acid. PCl_5 forms a chloride [61°], (284°). $FeSO_4$ gives a reddish-yellow colour.

Salts. — CaA'' 2aq: minute prisms. — CuA'' 2aq: dark-blue prisms.

Pyridine (αβ)-dicarboxylic acid

$\left.\begin{matrix}C(CO_2H).C(CO_2H)\\ CH—\!—CH{=}CH\end{matrix}\right\rangle N$. *Quinolinic acid.* [231°]. S. ·55 at 6·5°. Formed by the oxidising action of $KMnO_4$ on quinoline (Hoogewerff a. van Dorp, *B.* 12, 747; *R. T. C.* 1, 107; *A.* 204, 117), on cinchonine (H. a. D.), on *o*- and *p*- methyl-quinoline (Skraup, *M.* 2, 157), on *o*-oxy-quinoline, on quinoline *o*-sulphonic acid (O. Fischer a. Renouf, *B.* 17, 755), and on (α)-oxy-quinoline carboxylic acid (La Coste a. Valeur, *B.* 20, 103).

Properties. — Monoclinic needles, $a:b:c = {\cdot}542:1:{\cdot}607$; $\beta = 64°\ 54'$; sl. sol. water and alcohol, insol. ether. Begins to decompose at 140°, and forms nicotinic acid. Yields pyridine when distilled with lime. Reduced by sodium-amalgam to the δ-lactone of butane αβγ-tricarboxylic acid $\begin{matrix}CH_2.CH_2.CH.CO_2H\\ CO\ .\ O\ \ .CH.CO_2H\end{matrix}$ (Perlmutter, *M.* 13, 840).

Salts.—KHA'' 2aq: triclinic plates (Lippmann a. Fleissner, *M.* 8, 311).—K_2A'' 2aq.—BaA'' aq.—Ag_2A'': crystalline.—AgHA'' aq.

Anhydride $C_5H_3N\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle O$. [135°]. Got from the acid and Ac_2O (Bernthsen a. Mettegang, *B.* 20, 1208). Prisms. Converted by benzene and $AlCl_3$ into $C_5H_3BzN.CO_2H$ [147°], converted by heat into the ketone C_5H_4BzN (307° uncor.), which yields a crystalline phenyl-hydrazide [143·5°].

Pyridine (αγ)-dicarboxylic acid

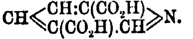
$CO_2H.C\left\langle\begin{matrix}CH{:}C(CO_2H)\\ CH—\!—\!—CH\end{matrix}\right\rangle N$. *Lutidinic acid.*

[240°] (V.); [235°] (B.; L. a. R.). **Formed by** the oxidising action of $KMnO_4$ on (αγ)-di-methyl-pyridine (Ramsay, *P. M.* [5] 4, 241; 6, 19; Weidel a. Herzig, *M.* 1, 20; Ladenburg a. Roth, *B.* 18, 915; *A.* 247, 37), on (α)-methyl-(γ)-ethyl-pyridine (Schultz, *B.* 20, 2726), on di-ethyl-pyridine, on (αα)-di-methyl-dipyridyl (Heuser a. Stoehr, *J. pr.* [2] 44, 409), and on the methyl-pyridine carboxylic acid obtained from uvitonic acid (Böttinger, *B.* 14, 68; 17, 93; Voigt, *A.* 228, 54).

Properties.—Needles (containing aq), m. sol. cold water, sol. alcohol, insol. ether. Gives a blood-red colour with $FeSO_4$. Yields pyridine on distillation with lime. Converted by heat into CO_2 and isonicotinic acid. PCl_5 yields a chloride [203°].

Salts.—$KHA''\frac{1}{2}aq$. Crystals.—$(NH_4)_2A''$.—$(NH_4)HA''aq$: hygroscopic needles.—$CaA''3aq$. $CaA''aq$.—$CaA''\frac{1}{2}aq$.—$CaH_2A''_2 2aq$.—$BaA''aq$.—$BaA''1\frac{1}{2}aq$ (B.). — $BaA''3aq$. — $CdA''4aq$ (Waage, *M.* 4, 727).—$MgA''5aq$.—$CuA''3aq$.—$CuA''4aq$ (B.).—$Ag_2A''2aq$: white pp.

Pyridine (αβ')-dicarboxylic acid



$CH\left\langle\begin{matrix}CH{:}C(CO_2H)\\C(CO_2H).CH\end{matrix}\right\rangle N$. *Isocinchomeronic acid.* [236°].

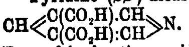
Formation.—1. By oxidation of lutidine (150°-170°) with $KMnO_4$ (Ramsay, *P. M.* [5] 4, 246; Weidel a. Herzig, *M.* 1, 1; Lange a. Rosenberg, *B.* 20, 135).—2. By oxidising (β')-methyl-(α)-ethyl-pyridine (Ladenburg, *A.* 247, 44).—3. By oxidation of quinine (Ramsay a. Dobbie, *C. J.* 33, 102; *B.* 11, 324).—4. By heating the dihydride of potassium pyridine tricarboxylate (Weiss, *B.* 19, 1311).—5. By the action of alkaline $KMnO_4$ on cyclothraustic acid and on pyridanthrilic acid (Weidel a. Strache, *M.* 7, 290).—6. By oxidising (β)-ethyl-(α)-stilbazole (Plath, *B.* 22, 1062).

Properties.—Small prisms (containing aq), almost insol. cold water, alcohol, and benzene, sol. hot HClAq. On heating with HOAc at 220° it is split up into CO_2 and nicotinic acid [230°]. On heating with lime it gives pyridine. PCl_5 yields a chloride [61°] converted by NH_3 into an amide [297°]. $FeSO_4$ gives a reddish colour.

Salts.—$(NH_4)HA''aq$. [253°]. Triclinic prisms, sl. sol. cold water.—$(NH_4)_2A''$.—$KHA''\frac{1}{2}aq$: needles.—$K_2A''aq$.—$CaA''2aq$.—$Ca(HA'')_2 3aq$.—$MgA''5aq$.—$CuA''aq$.—Ag_2A''.

Methyl ether Me_2A''. [117·5°] (R.).

Pyridine (ββ')-dicarboxylic acid

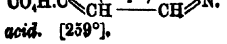


$CH\left\langle\begin{matrix}C(CO_2H).CH\\C(CO_2H){:}CH\end{matrix}\right\rangle N$. *Dinicotinic acid.* [322°]. Formed by heating pyridine (2,3,5)-tri-carboxylic acid and pyridine (2,3,5,6)-tetra-carboxylic acid (Riedel, *B.* 16, 1613; Hantzsch a. Weiss, *B.* 19, 286; Weber, *A.* 241, 12). Formed also by heating di-chloro-pyridine di-carboxylic acid with conc. HIAq at 180° (Guthzeit, *A.* 262, 130).

Properties.—Small prisms (from HOAc), split up by heat into CO_2 and nicotinic acid.

Salts.—$PbA''2aq$.—$Ag_2A''aq$.—$Ag_2A''1\frac{1}{2}aq$.—$HA'HCl 2aq$: needles, decomposed by water.—$H_2A'_2H_2PtCl_6$: orange-red needles.

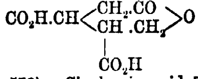
Pyridine (βγ)-dicarboxylic acid



$CO_2H.C\left\langle\begin{matrix}C(CO_2H){:}CH\\CH\text{——}CH\end{matrix}\right\rangle N$. *Cinchomeronic acid.* [259°].

Formation.—1. By oxidation of cinchonine or cinchonidine by HNO_3 of S.G. 1·4 (Weidel, *A.* 173, 76).—2. By oxidation of quinine by HNO_3, the yield being 28 p.c. (Weidel a. Schmidt, *B.* 12, 1146).—3. By heating apophyllenic acid with conc. HClAq at 240° (Von Gerichten, *B.* 13, 1635).—4. By heating pyridine tricarboxylic acid (formed from cinchonic acid) at 190° (Hoogewerff a. van Dorp, *B.* 13, 61; Skraup, *M.* 1, 184; Weidel a. Brix, *M.* 3, 604).—5. By the action of $KMnO_4$ on methyl-pyridine carboxylic acid and on isoquinoline (Hoogewerff a. van Dorp, *R. T. C.* 2, 23; 4, 285).—6. By heating pyridine pentacarboxylic acid (Weber, *A.* 241, 16).—7. By oxidation of methyl-nicotinic acid, derived from (β)-collidine (Oechsner de Coninck, *Bl.* [2] 43, 106).—8. By boiling berberonic acid with HOAc (2 pts.) and Ac_2O (1 pt.) for six hours (Mayer, *M.* 13, 344; *cf.* Fürth, *M.* 2, 426).

Properties.—Prisms (from HClAq), v. sl. sol. water and ether, sl. sol. alcohol. Yields isonicotinic and some nicotinic acid on heating (Hoogewerff a. van Dorp, *A.* 207, 217). Gives pyridine on distillation with lime. Sodium-amalgam yields NH_3 and cinchonic acid $C_7H_8O_6$,



i.e. $CO_2H.CH\left\langle\begin{matrix}CH_2.CO\\CH.CH_2\end{matrix}\right\rangle O$, with CO_2H attached below the CH (Weidel a. Hoff, *M.* 13, 578). Cinchonic acid [169°] forms monoclinic crystals, v. sol. hot water and alcohol, and yields $BaC_7H_6O_6 3aq$, $Ba_3(C_7H_7O_7)_2 3aq$, $CaA''2aq$, $Ca_3(C_7H_7O_7)_2$ (dried at 190), and oily Et_2A'', whence PCl_5, followed by alcohol, yields $CO_2Et.CH(CH_2Cl).CH(CO_2Et).CH_2.CO_2Et$, which is a heavy oil. Cinchonic acid is reduced by HI to butane tricarboxylic acid $C_7H_{10}O_6$ [184°], whence $Ca_3A'''_2 8aq$, accompanied by an isomeric butane tricarboxylic acid [133°]. $FeSO_4$ gives no colour.

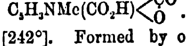
Salts.—$Na_2A''2aq$: tables.—$NaHA''$.—$BaA''1\frac{1}{2}aq$: needles, sl. sol. water.—$CaA''3\frac{1}{2}aq$: prisms. — $CaA''3aq$. — $CuA''3\frac{1}{2}aq$: small blue crystals.—Ag_2A'': white pp.—$AgHA''$.—$HA'HCl$: monoclinic prisms, decomposed by water.—$H_2A'_2H_2PtCl_6$: golden prisms.

Anhydride $(C_5H_3N)_2C_2O_3$. [77°]. Formed by boiling the acid with Ac_2O (Goldschmiedt a. Strache, *M.* 10, 156). Plates. May be sublimed. Converted by NH_3 gas into $C_5H_3N(CO_2NH_4).CONH_2$ [229°], which is converted by heat into a yellow powder [130°], and which yields the amic acid $C_5H_3N(CO_2H).CONH_2$ [237°], crystallising in needles.

Mono-ethyl ether $HEtA''$. [133°]. Formed from the anhydride and EtOH. Plates (from benzene).—$AgEtA''$: long needles.

Mono-methyl ether $HMeA''$. [154°].

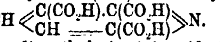
Anhydride of the Methylo-hydroxide



$C_8H_7NO_4$ *i.e.* $C_5H_3NMe(CO_2H)\left\langle\begin{matrix}CO\\O\end{matrix}\right.$. *Apophyllenic acid* [242°]. Formed by oxidation of cotarnine by HNO_3 (Wöhler, *A.* 50, 24; Anderson, *Tr. E.* 23, 347; *C. J.* 5, 257; Gerichten, *B.* 13, 1635). Formed also by heating cinchomeronic acid with MeI and MeOH at 100° (Roser, *A.* 234, 116). Needles (anhydrous) or octahedra (containing aq), sol. hot water, insol. alcohol and ether. HClAq at 250° decomposes it, forming cinchomeronic acid and MeCl. — BaA'_2. — AgA'.—$Ag_2A'(NO_3)$.—$H_2A'_2H_2PtCl_6 aq$.

Bromo-apophyllenic acid $C_8H_8BrNO_4 2aq$. [205°]. Formed by oxidation of bromo-tarconine. Yields $BaA'_2 3aq$ and $H_2A'_2H_2PtCl_6$ (Gerichten, *A.* 210, 91).

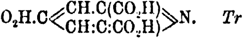
Pyridine (αα'β)-tricarboxylic acid



$$CH\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\CH = C(CO_2H)\end{array}\right>N.$$

Formed by oxidising di-methyl-nicotinic acid with $KMnO_4$ (Weiss, *B.* 19, 1309). Crystallises from alcohol in plates (containing 2aq), v. e. sol. water. Decomposes at 160° into CO_2 and isocinchomeronic acid. $FeSO_4$ colours its neutral solution red. — $KH_8A'''_2 5aq$: needles.—$Ca_3A'''_2 4aq$.—$Pb_3A'''_2 5aq$.

Pyridine (αα'γ)-tricarboxylic acid



$$CO_2H.C\left<\begin{array}{l}CH.C(CO_2H)\\CH:C:CO_2H)\end{array}\right>N.$$

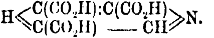
Trimesitic acid. Carbolutidinic acid. [244°]. Formed by oxidation of uvitonic acid (Böttinger, *B.* 13, 2048; 14, 69), and by oxidation of the tri-methyl-pyridine obtained from acetoacetic ether and aldehyde-ammonia (Voigt, *A.* 228, 31). Tables or spheroidal groups of needles (containing 2aq), sol. hot water, sl. sol. alcohol and ether. Yields isonicotinic acid on sublimation. $FeSO_4$ gives a violet-red colour.

Salts.—$K_3A''' 5aq$: needles.—$Ca_3A'''_2 4aq$.—$Ba_3A'''_2 6aq$. — $BaH_4A'''_2 4aq$. —$Mg_3A'''_2 12aq$.—$Cu_3A'''_2 12aq$. $Ag_3A''' 1\frac{1}{2}aq$.

Ethyl ether Et_3A'''. [127·5°].

Amide. [above 280°].

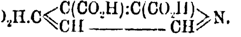
Pyridine (αββ')-tri-carboxylic acid



$$CH\left<\begin{array}{l}C(CO_2H):C(CO_2H)\\C(CO_2H) — CH\end{array}\right>N.$$

Carbodinicotinic acid. [323°]. Formed by oxidation of quinoline (*Py.* 2)-carboxylic acid (Riedel, *B.* 16, 1615), of methyl-pyridine (ββ')-dicarboxylic acid (Weber, *A.* 241, 11), and of the parvoline got by heating propionic aldehyde-ammonia with propionic aldehyde at 200° (Dürkopf, *B.* 21, 832, 2707; 23, 689). Spherical aggregates (containing 1½aq), v. sol. hot water. At 155° it is split up into CO_2 and dinicotinic acid.—$Ba_3A'''_2 5aq$.—$Ag_2HA''' 1\frac{1}{2}aq$: rosettes of plates.

Pyridine (αβγ)-tri-carboxylic acid



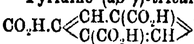
$$CO_2H.C\left<\begin{array}{l}C(CO_2H):C(CO_2H)\\CH ——— CH\end{array}\right>N.$$

[250°] (H. a. D.; S.); [257°] (D. a. R.). S. 1·2 at 15°.

Formation.—1. By the action of $KMnO_4$ on quinine, cinchonine, cinchonidine, quinoïdine, and cinchonic acid (Dobbie a. Ramsay, *C. J.* 35, 189; Hoogewerff a. van Dorp, *B.* 12, 158; 13, 152; *A.* 204, 84; Skraup, *A.* 201, 312; Strache, *M.* 10, 642).—2. By oxidation of cinchonine by HNO_3 (Weidel, *A.* 173, 101; *B.* 12, 415).—3. By oxidation of methyl-pyridine (αβ)-dicarboxylic acid (Hoogewerff a. van Dorp, *R. T. C.* 2, 18), of di-methyl-pyridine carboxylic acid (Michael, *B.* 18, 2027), of (α)-oxy-cinchonic acid (Weidel a. Cobenzl, *M.* 1, 865).—4. By oxidation of papaverine (Goldschmiedt, *M.* 6, 397). Trimetric plates (containing 1½aq), v. sol. hot water, m. sol. alcohol, nearly insol. ether. Blackens at 200°. $FeSO_4$ gives a reddish colour. H_2S forms a red amorphous body (D. a. R.). Decomposed by long heating at 180°, or by boiling with HOAc into CO_2 and cinchomeronic acid. Yields pyridine on distilling with lime. MeI and MeOH at 100° form CO_2 and apophyllenic acid. Sodium-amalgam gives NH_3 and cinchonic acid. PCl_5 forms a chloride (206° at 40 mm.).

Salts. — $K_3A''' 3aq$. — $Ba_3A'''_2 16aq$. — $Ba_3A'''_2 12aq$. — $Ca_3A'''_2 14aq$. — $Ca_3A'''_2 13aq$.— $CaHA''' 2\frac{1}{2}aq$. — $Cu_3A'''_2 9aq$: light-blue pp.— $CuHA''' 3\frac{1}{2}aq$: hexagonal prisms. - $CuH_4A'''_2 2aq$. —$Cd_3A'''_2 6aq$.—$Ag_2HA'''aq$.—$Ag_3A''' 2aq$; amorphous pp.—$AgH_5A'''_2 2\frac{1}{2}aq$.—$H_3A'''HCl$: crystalline powder (Roser, *A.* 234, 125).

Pyridine (αβ'γ)-tricarboxylic acid

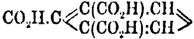


$$CO_2H.C\left<\begin{array}{l}CH.C(CO_2H)\\C(CO_2H):CH\end{array}\right>N.$$

Berberonic acid. [243°]. Formed by oxidising berberine with nitric acid (Weidel, *B.* 12, 410; Fürth, *M.* 2, 416). Triclinic prisms (containing 2aq), sol. hot water, v. sl. sol. hot alcohol, insol. ether. Yields pyridine on distillation with lime. $FeSO_4$ gives a red colour. At 215° it is split up into CO_2 and nicotinic acid; above 243° it yields isonicotinic acid.

Salts. — $K_3A''' 4\frac{1}{2}aq$. — $K_2HA''' 3aq$. — $KH_2A''' 1\frac{1}{2}aq$. — $Ca_3A'''_2 8aq$. — $Cd_3A'''_2 4aq$. — Ag_3A''' : white pp., insol. water.

Pyridine (ββ'γ)-tricarboxylic acid

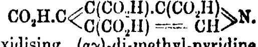


$$CO_2H.C\left<\begin{array}{l}C(CO_2H).CH\\C(CO_2H):CH\end{array}\right>N.$$

(β) - *Carbocinchomeronic acid.* [261°]. Formed by heating di-potassium pyridine pentacarboxylate at 220° (Weber, *A.* 241, 17). Plates (containing 3aq), v. sol. hot water. Yields cinchomeronic acid when heated. Gives no colour with $FeSO_4$. — $Cu_5H_2A'''_4 24aq$.—$Ag_3A''' 2aq$: crystalline pp.

Pyridine (αββ'γ)-tetra-carboxylic acid

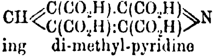
$C_9H_5NO_8$ i.e.



$$CO_2H.C\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\C(CO_2H) = CH\end{array}\right>N.$$

Formed by oxidising (αγ)-di-methyl-pyridine (ββ')-dicarboxylic acid (Weber, *A.* 241, 23). Prisms (containing 2aq or 3aq). At 120° it loses CO_2, forming (β)-carbocinchomeronic acid. $FeSO_4$ gives a dark-red colour.—$Ba_2A^{iv} 4aq$.—$Ag_7HA^{iv}_2 aq$: crystalline.

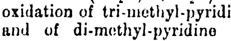
Pyridine (αα'ββ')-tetracarboxylic acid



$$CH\left<\begin{array}{l}C(CO_2H).C(CO_2H)\\C(CO_2H):C(CO_2H)\end{array}\right>N.$$

Formed by oxidising di-methyl-pyridine dicarboxylic acid (Hantzsch, *B.* 19, 286; Weber, *A.* 241, 4). Needles (containing 2aq), v. sol. water. Decomposes at 150° into CO_2 and dinicotinic acid.—$CaH_2A^{iv} 2aq$: needles, v. sol. water.—$Cu_2A^{iv} 5aq$. —$Ag_4A^{iv} 2aq$: bulky pp.

Pyridine (αα'β'γ)-tetra-carboxylic acid



$$CO_2H.C\left<\begin{array}{l}CH —— C(CO_2H)\\C(CO_2H):C(CO_2H)\end{array}\right>N.$$

Formed by oxidation of tri-methyl-pyridine carboxylic acid and of di-methyl-pyridine di-carboxylic acid (Michael, *A.* 225, 142). Formed also by oxidation of flavenol by alkaline $KMnO_4$ (Fischer a. Täuber, *B.* 17, 2927). Slender needles (containing 2aq), v. sol. water, v. sl. sol. alcohol and ether. Not decomposed at 150°. $FeSO_4$ gives a brownish-red colour.—$Ba_2A^{iv} 2\frac{1}{2}aq$.—$Ba_2A^{iv} aq$. —$Cu_2A'' 2\frac{1}{2}aq$.—$Ag_4A^{iv} aq$.

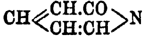
Pyridine penta-carboxylic acid $NC_5(CO_2H)_5$. Formed from potassium tri-methyl-pyridine dicarboxylate and $KMnO_4$ (Hantzsch, *A.* 215, 62; Weber, *A.* 241, 15). Crystalline mass of minute needles (containing 2aq), extremely sol. water, v. sl. sol. ether. Acid to litmus and to taste. Loses 2aq at 120° and decomposes, without having melted, at 220°. The neutral alkaline salts are very soluble, but the acid alkaline salts are sl. sol. water. The acid does not combine with HCl. Distilled with lime it gives pyridine. $FeSO_4$ gives a dark-red colour.

water, forming an acid solution (Gardner, *B.* 23, 1588).—Formate $B'3CH_2O_2$. (149°). Liquid, v. sol. water.—Propionate $B'3C_3H_6O_2$. (149°). Liquid. — Cupric oxalate compound $B'_2CuC_2O_4$: minute prisms (Seubert a. Rauter, *B.* 25, 2825).

Methylo-chloride B'MeCl. White needles (Ostermeyer, *B.* 18, 591). Converted by a hot aqueous solution of picric acid into $B'MeOC_6H_2(NO_2)_3\frac{1}{2}aq$, which crystallises in greenish-yellow explosive needles [34°]. — $B'_2Me_2PtCl_6$. [188°] (O.); [207°] (B.). — $B'MeAuCl_4$. [253°].—B'MeClICl. [82°] (O.); [90°] (B.). Yellow plates.—$B'MeClICl_3$. [180°]. Unstable yellow crystals (Bally, *B.* 21, 1774).

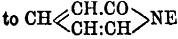
Methylo-perbromide $B'MeBr_3$. [48°].

Methylo-iodide B'MeI. Converted at 290° into methyl-pyridine hydriodides. On heating with alcoholic potash at 45° it yields a brown resin, forming a deep-red solution in alcohol, turned bright-red by HCl, orange-red by acetic acid, and ruby-red by ammonia (O. de Coninck, *C. R.* 102, 1479). Chlorine forms $B'MeICl_2$ [90°] (*v. supra*). Oxidised by alkaline K_3FeCy_6 to oxy-methyl-pyridine or ν-methyl-pyridone



$\mathrm{CH}\ll\begin{matrix}\mathrm{CH.CO}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{NMe}$ (250°), a liquid miscible with water (Decker, *J. pr.* [2] 47, 28; *cf.* Pechmann, *B.* 24, 3144).

Ethylo-iodide B'EtI. Silvery tables (Anderson, *A.* 94, 364). At 300° it yields pyridine, NH_3, (α) and (γ)- ethyl-pyridine, and di-ethyl-pyridine (Ladenburg, *B.* 16, 2059; 18, 2961). Yields $B'_2Et_2PtCl_6$. Oxidised by alkaline K_3FeCy_6 to

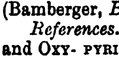


$\mathrm{CH}\ll\begin{matrix}\mathrm{CH.CO}\\ \mathrm{CH{:}CH}\end{matrix}>\mathrm{NEt}$ (250°).

Ethyleno-iodide $B'C_2H_4I_2$. Prisms (Coppola, *G.* 15, 332). Ag_2O yields a base C_7H_9NO. By heating pyridine with ethylene bromide and some alcohol at 100° there is found $B'_2C_2H_4Br_2$, which yields $B'_2C_2H_4PtCl_6$ (Davidson, *A.* 121, 254).

Benzylo-chloride $B'PhCH_2Cl$. Reduced by sodium-amalgam to the unstable $C_{24}H_{24}N_2$ (Hofmann, *B.* 14, 1503).—$(B'PhCH_2Cl)_2PtCl_4$.

Nitro-benzylo-chlorides $B'C_6H_4(NO_2).CH_2Cl$. *o* [c. 76°], *m* [70°–100°], *p* [90°–100°]. These bodies are reduced by tin and HClAq to $B'C_6H_4(NH_3Cl).CH_2Cl$, which are split up by heat into pyridine hydrochloride and



$C_6H_4<\begin{matrix}NH_2Cl\\ \dot{C}H_2\end{matrix}$ (Lellmann a. Pekrun, *A.* 259, 54).

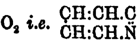
Phenacylo-bromide $B'BzCH_2Br$. Prisms (Bamberger, *B.* 20, 3344).—$B'_2(BzCH_2)_2Cr_2O_7$.

References.—Bromo-, Chloro-, Oxy-amido-, and Oxy- pyridine.

Dipyridine $C_{10}H_{10}N_2$ *v.* Dipyridyl dihydride.

Dipyridine $C_{10}H_{10}N_2$. (275°). S.G. $\frac{13}{}$ 1·124. Is probably a dipyridyl dihydride. Formed by heating nicotine with KOH and K_3FeCy_6, and also by heating the product of the action of S on nicotine at 150° with finely-divided copper (Cahours a. Etard, *Bl.* [2] 34, 452). Inactive liquid.—$B'HHgCl_3$.—$B'_2H_2PtCl_6$ 2aq.—$B'_2H_2FeCy_6$2aq: brownish-green tables.

(α)-PYRIDINE CARBOXYLIC ACID



$C_6H_5NO_2$ *i.e.* $\begin{matrix}\mathrm{CH{:}CH.C.CO_2H}\\ \mathrm{CH{:}CH.N}\end{matrix}$. *Picolinic acid.* [136°]. Formed by oxidation of (α)-methyl-pyridine with $KMnO_4$ (Weidel, *B.* 12, 1994), and by oxidation of (α)-phenyl-pyridine (Skraup, *M.* 4, 477). **Obtained also, together with its hexahydride,** from comenamic acid by successive treatment with PCl_5 and H_2SO_4, the resulting di-chloro-picolinic acid being reduced by heating for three days at 155° with HI dissolved in HOAc (Ost, *J. pr.* [2] 27, 285).

Preparation.—The three acids got by oxidation of crude methyl-pyridine from animal oil are converted into copper salts. Cupric pyridine (α)-carboxylate is extracted by hot water. The residue is treated with H_2S, and the difficultly-soluble (γ)- acid separated from the (β)- acid (Ost, *J. pr.* [2] 27, 286).

Properties.—Needles, v. sol. water and alcohol, almost insol. ether, benzene, $CHCl_3$, and CS_2. May be sublimed. $FeSO_4$ gives a red colouration with picolinic acid and with all the carboxylic acids of pyridine that contain CO_2H in the (α)- position (Skraup, *M.* 7, 210). The absorption of the ultra-violet spectrum has been studied by Hartley (*C. J.* 41, 45).

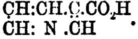
Reactions.—1. Yields pyridine on distillation with *lime* or with *alcoholic potash* at 240°. The Cu salt on distillation gives pyridine and (α)-dipyridyl [70°] (Blau, *M.* 10, 375; *B.* 21, 1077). —2. *Sodium-amalgam* forms δ-oxy-adipic acid (Weidel, *M.* 11, 522).—3. Fuming HI at 170° forms (α)-methyl-pyridine and piperidine (Seyfferth, *J. pr.* [2] 34, 241).—4. *Zinc-dust* and HOAc reduce it to (α)-methyl-pyridine.

Constitution.—This may be deduced from its formation from (β)-naphthoquinoline *viâ* (β)-phenyl-pyridine carboxylic acid (Skraup a. Cobenzl, *M.* 4, 436).

Salts. — HA'HCl: unstable crystals. — $H_2A'_2H_2PtCl_6$ 2aq: orange-red crystals.—NH_4A': triclinic tables.—KA'.—$BaA'_2\frac{1}{2}aq$.—CaA'_2 aq.—MgA'_2 2aq.

Hexahydride $C_5H_{10}N.CO_2H$. *Piperidine (α)-carboxylic acid.* The chief product of the action of HI at 160° on mono- or di-chloro-picolinic acid (Ost, *J. pr.* [2] 27, 287). Got also by reducing picolinic acid (Ladenburg, *B.* 24, 640). Syrup, v. sol. water. Salts.—B'HCl. [264°]. Nodules.—$B'_2H_2PtCl_6$. [184°] (L.).—$B'_2H_2PtCl_6$ 2aq.—B'MeCl. [191°]. Needles.

Pyridine (β)-carboxylic acid



$\begin{matrix}\mathrm{CH{:}CH.C.CO_2H}\\ \mathrm{CH{:}\ N\ .CH}\end{matrix}$. *Nicotinic acid.* [230°].

Formation.—1. By oxidising nicotine with HNO_3 (Weidel, *A.* 165, 330), CrO_3 (Huber, *A.* 141, 271; *B.* 3, 849), or $KMnO_4$ (Laiblin, *A.* 196, 129).—2. A product of oxidation of coal-tar bases (Weidel; Mohler, *B.* 21, 1009).—3. By heating quinolinic acid at 160° or with HCl at 180° (Ost, *J. pr.* [2] 27, 286; Lippmann a. Fleissner, *M.* 8, 315).—4. By oxidation of (β)-methyl-pyridine (Weidel, *B.* 12, 2004), (β)-ethyl-pyridine (Stoehr, *J. pr.* [2] 43, 155) or (β)-phenyl-pyridine (Skraup, *M.* 4, 453).—5. By saponification of its nitrile, which is got by distilling sodium-pyridine sulphonate with KCy (Fischer, *B.* 15, 63).—6. By heating three of the pyridine dicarboxylic acids (Hoogewerff a. Van Dorp, *R. T. C.* 1, 1, 107; *A.* 204, 117; 207, 226; Weidel a. Herzig, *M.* 1, 16).—7. By heating berberonic acid at 215° (Fürth, *M.* 2, 420).—8. By the action of Zn and HClAq on chloro-nicotinic acid (Pechmann a. Welsh, *C. J.* 47, 145).

Properties.—Needles, sl. sol. cold water, sol. alcohol, nearly insol. ether. May be sublimed.

Reactions.—1. Yields pyridine on distillation with lime.—2. *Sodium-amalgam* yields a mixture of δ-oxy-α-methyl-glutaric acid and its lactone, which, on treatment with alcohol and HCl, yields a mixture of two ethers. One of these, $C_{10}H_{17}ClO_4$, is converted by sodium-amalgam into α-methyl-glutaric acid, and the other, $C_8H_{14}O_4$, is also converted by successive treatment with PI_2 and with Zn and dilute H_2SO_4 into α-methyl-glutaric acid (Weidel, *M.* 11, 502).—3. *Bromine* and water at 120° yield CO_2, pyridine, and bromoform.—4. The K salt heated with MeI at 150° forms $C_5H_4NMeI.CO_2Me$, which on saponification yields $C_5H_4NMe(OH).CO_2H$ [130°], converted at 100° into trigonellin $C_5H_4NMe\left\langle\begin{array}{l}CO\\O\end{array}\right.$ [218°], which occurs in the seeds of *Trigonella fœnum græcum* (Jahns, *B.* 18, 2521; Hantzsch, *B.* 19, 31). This anhydride forms the salts $C_7H_7NO_2HCl$, $B'_2H_2PtCl_6$ aq, $B'HAuCl_4$ [198°], and $B'_43HAuCl_4$ [186°].

Constitution.—This may be deduced from its formation from (α)-naphthaquinoline *viâ* (α)-phenyl-pyridine carboxylic acid.

Salts. — HA'HCl. Colourless prisms.—$H_2A'_2H_2PtCl_6$ 2aq.—$B'_2H_2AuCl_5$.—$B'HNO_3$ aq.—NH_4A': needles.—KA'.—MgA'_2: needles.—CaA'_2 5aq: monoclinic crystals; *a:b:c* = 1·537:1:·629; β = 62° 50'. — Cu(OH)A' (De Coninck, *Bl.* [2] 42, 100).—AgA': needles (from hot water).

Nitrile $C_5H_4N.Cy$. [49°]. Formed by distilling sodium pyridine sulphonate with KCy (Fischer, *B.* 15, 63). Needles or prisms, sol. water. — B'HCl. — $B'_2H_2PtCl_6$: yellow soluble needles. Tables (by sublimation). Converted by means of hydroxylamine into the amidoxim $C_5H_4N.C(NH_2):NOH$ [128°], which yields an acetyl derivative [143°] and a benzoyl derivative [190°], and is converted by phenyl cyanate into $C_5H_4N.C(NOH).NH.CO.NHPh$ [167°], by phenyl thiocarbimide into $C_5H_4N.C\left\langle\begin{array}{c}N.S\\N\end{array}\right\rangle C.NHPh$ [241°], and by succinic anhydride at 100° into $C_5H_4N\left\langle\begin{array}{c}N.O\\N\end{array}\right\rangle C.CH_2.CH_2.CO_2H$ [178°]. The acetyl and benzoyl derivatives are converted by heating into $C_5H_4N\left\langle\begin{array}{c}N.O\\N\end{array}\right\rangle CMe$ [109°] and $C_5H_4N\left\langle\begin{array}{c}N.O\\N\end{array}\right\rangle CPh$ [139°] respectively (Michaelis, *B.* 24, 3439).

Hexahydride $C_5H_{10}N(CO_2H)$. *Nipecotinic acid.* [250°]. Got by reducing nicotinic acid in alcoholic solution by Na (Ladenburg, *B.* 25, 2768). Crystals, v. e. sol. water, insol. alcohol and ether.—HA'HCl. [240°].—$H_2A'_2H_2PtCl_6$. [213° cor.]. — $HA'HAuCl_4$. [197° cor.].—$HA'HCl5HgCl_2$. [231°].—MeA'HCl [208°].—$Me_2A'_2H_2PtCl_6$. — Nitrosamine $C_6H_{10}N_2O_3$. [112°].

Pyridine (γ)-carboxylic acid

$N\left\langle\begin{array}{l}CH.CH\\CH:CH\end{array}\right\rangle C.CO_2H$. *Isonicotinic acid.* [305°] (S.); [306°] (B. a. H.); [309·5°] (W. a. H.).

Formation.—1. By heating pyridine *s*-tricarboxylic acid (Skraup, *B.* 12, 2331) and three of the pyridine di-carboxylic acids (Hoogewerff a. Van Dorp, *A.* 204, 112; Weidel a. Herzig, *M.* 1, 28; Böttinger, *B.* 14, 68).—2. By the action of $KMnO_4$ on (γ)-methyl-pyridine (Behrmann a. Hofmann, *B.* 17, 2696; Ladenburg, *B.* 21, 287). 3. By heating di-chloro-pyridine carboxylic acid [210°] with HI (B. a. H.).

Properties.—Needles, sl. sol. cold water, insol. alcohol. Yields pyridine on distilling with lime and δ-oxy-ethyl-succinic acid on reduction with sodium-amalgam (Weidel, *M.* 11, 517).

Salts.—NH_4A': needles.—CaA'_2 4aq: silky needles, m. sol. water.—HA'HCl: monoclinic prisms.—$H_2A'_2H_2PtCl_6$ 2aq: monoclinic crystals.

Hexahydride $C_5H_{10}N(CO_2H)$. Got by reducing the acid in alcoholic solution by Na (Ladenburg, *B.* 25, 2773). Branching groups of needles, v. e. sol. water, insol. alcohol. Blackens at 300°, but is not melted at 320°.—HA'HCl. [228°]. Trimetric crystals; *a:b:c* = ·922:1:·979. —$H_2A'_2H_2PtCl_6$. [239°]. — Aurochloride: [197°]. Nitrosamine $C_6H_{10}N_2O_3$. [101°].

Pyridine (αα)-dicarboxylic acid

$CH\left\langle\begin{array}{l}CH.C(CO_2H)\\CH:C(CO_2H)\end{array}\right\rangle N$. *Dipicolinic acid.* [226°] (L. a. R.; S.); [237°] (E.); [236° cor.] (Collie, *C. J.* 59, 179). Formed by oxidation of (αα)-dimethyl-pyridine [145°] (derived from aceto-acetic ether or from coal-tar) by $KMnO_4$ (Epstein, *A.* 231, 26; Ladenburg a. Roth, *B.* 18, 52; 19, 790; 20, 130; *A.* 247, 32; Lange a. Rosenberg, *B.* 20, 132; *cf.* Dewar, *C. N.* 23, 18). Got also by oxidation of (α)-methyl-(α)-ethyl-pyridine by dilute (2 p.c.) $KMnO_4$ (Schultz, *B.* 20, 2724).

Properties.—Hair-like needles (containing 1½aq) or anhydrous scales; sl. sol. cold alcohol, water, and ether. On heating at 245° in a current of H it yields pyridine and pyridine (α)-carboxylic acid. PCl_5 forms a chloride [61°], (284°). $FeSO_4$ gives a reddish-yellow colour.

Salts. — CaA'' 2aq: minute prisms. — CuA'' 2aq: dark-blue prisms.

Pyridine (αβ)-dicarboxylic acid

$\left.\begin{array}{l}C(CO_2H).C(CO_2H)\\CH \text{———} CH{=}CH\end{array}\right\rangle N$. *Quinolinic acid.* [231°]. S. ·55 at 6·5°. Formed by the oxidising action of $KMnO_4$ on quinoline (Hoogewerff a. van Dorp, *B.* 12, 747; *R. T. C.* 1, 107; *A.* 204, 117), on cinchonine (H. a. D.), on *o*- and *p*- methyl-quinoline (Skraup, *M.* 2, 157), on *o*-oxy-quinoline, on quinoline *o*-sulphonic acid (O. Fischer a. Renouf, *B.* 17, 755), and on (α)-oxy-quinoline carboxylic acid (La Coste a. Valeur, *B.* 20, 103).

Properties. — Monoclinic needles, *a:b:c* = ·542:1:·607; β = 64° 54'; sl. sol. water and alcohol, insol. ether. Begins to decompose at 140°, and forms nicotinic acid. Yields pyridine when distilled with lime. Reduced by sodium-amalgam to the δ-lactone of butane αβγ-tricarboxylic acid $\begin{array}{l}CH_2.CH_2.CH.CO_2H\\CO\;.\;O\;\;.CH.CO_2H\end{array}$ (Perlmutter, *M.* 13, 840).

Salts.—KHA'' 2aq: triclinic plates (Lippmann a. Fleissner, *M.* 8, 311).—K_2A'' 2aq.—BaA'' aq.—Ag_2A'': crystalline.—AgHA'' aq.

Anhydride $C_5H_3N\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle O$. [135°]. Got from the acid and Ac_2O (Bernthsen a. Mettegang, *B.* 20, 1208). Prisms. Converted by benzene and $AlCl_3$ into $C_5H_3BzN.CO_2H$ [147°], converted by heat into the ketone C_5H_4BzN (307° uncor.), which yields a crystalline phenyl-hydrazide [143·5°].

Pyridine (αγ)-dicarboxylic acid

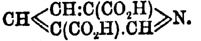
$CO_2H.C\left\langle\begin{array}{l}CH:C(CO_2H)\\CH \text{———} CH\end{array}\right\rangle N$. *Lutidinic acid.*

[240°] (V.); [235°] (B.; L. a. R.). Formed by the oxidising action of $KMnO_4$ on (αγ)-di-methyl-pyridine (Ramsay, *P. M.* [5] 4, 241; 6, 19; Weidel a. Herzig, *M.* 1, 20; Ladenburg a. Roth, *B.* 18, 915; *A.* 247, 87), on (α)-methyl-(γ)-ethyl-pyridine (Schultz, *B.* 20, 2726), on di-ethyl-pyridine, on (αα)-di-methyl-dipyridyl (Heuser a. Stoehr, *J. pr.* [2] 44, 409), and on the methyl-pyridine carboxylic acid obtained from uvitonic acid (Böttinger, *B.* 14, 68; 17, 93; Voigt, *A.* 228, 54).

Properties.—Needles (containing aq), m. sol. cold water, sol. alcohol, insol. ether. Gives a blood-red colour with $FeSO_4$. Yields pyridine on distillation with lime. Converted by heat into CO_2 and isonicotinic acid. PCl_5 yields a chloride [203°].

Salts.—KHA″ ½aq. Crystals.—$(NH_4)_2A''$.—$(NH_4)HA''$aq: hygroscopic needles.—CaA″ 3aq. CaA″ aq.—CaA″ ½aq.—$CaH_2A''_2$ 2aq.—BaA″ aq.—BaA″ 1½aq (B.).—BaA″ 3aq.—CdA″ 4aq (Waage, *M.* 4, 727).—MgA″ 5aq.—CuA″ 3aq.—CuA″ 4aq (B.).—Ag_2A'' 2aq: white pp.

Pyridine (αβ′)-dicarboxylic acid


$CH\left<\begin{matrix}CH{:}C(CO_2H)\\C(CO_2H).CH\end{matrix}\right>N$. *Isocinchomeronic acid.* [236°].

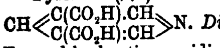
Formation.—1. By oxidation of lutidine (150°–170°) with $KMnO_4$ (Ramsay, *P. M.* [5] 4, 246; Weidel a. Herzig, *M.* 1, 1; Lange a. Rosenberg, *B.* 20, 135).—2. By oxidising (β′)-methyl-(α)-ethyl-pyridine (Ladenburg, *A.* 247, 44).—3. By oxidation of quinine (Ramsay a. Dobbie, *C. J.* 33, 102; *B.* 11, 324).—4. By heating the dihydride of potassium pyridine tricarboxylate (Weiss, *B.* 19, 1311).—5. By the action of alkaline $KMnO_4$ on cyclothraustic acid and on pyridanthrilic acid (Weidel a. Strache, *M.* 7, 290).—6. By oxidising (β)-ethyl-(α)-stilbazole (Plath, *B.* 22, 1062).

Properties.—Small prisms (containing aq), almost insol. cold water, alcohol, and benzene, sol. hot HClAq. On heating with HOAc at 220° it is split up into CO_2 and nicotinic acid [230°]. On heating with lime it gives pyridine. PCl_5 yields a chloride [61°] converted by NH_3 into an amide [297°]. $FeSO_4$ gives a reddish colour.

Salts.—$(NH_4)HA''$aq. [253°]. Triclinic prisms, sl. sol. cold water.—$(NH_4)_2A''$.—KHA″ ½aq: needles.—K_2A'' aq.—CaA″ 2aq.—$Ca(HA'')_2$ 3aq.—MgA″ 5aq.—CuA″ aq.—Ag_2A''.

Methyl ether Me_2A''. [117·5°] (R.).

Pyridine (ββ′)-dicarboxylic acid

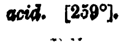

$CH\left<\begin{matrix}C(CO_2H).CH\\C(CO_2H){:}CH\end{matrix}\right>N$. *Dinicotinic acid.* [322°].

Formed by heating pyridine (2,3,5)-tri-carboxylic acid and pyridine (2,3,5,6)-tetra-carboxylic acid (Riedel, *B.* 16, 1613; Hantzsch a. Weiss, *B.* 19, 286; Weber, *A.* 241, 12). Formed also by heating di-chloro-pyridine di-carboxylic acid with conc. HIAq at 180° (Guthzeit, *A.* 262, 130).

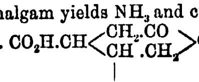
Properties.—Small prisms (from HOAc), split up by heat into CO_2 and nicotinic acid.

Salts.—PbA″ 2aq.—Ag_2A'' aq.—Ag_2A'' 1½aq.—HA′HCl 2aq: needles, decomposed by water.—$H_2A'_2H_2PtCl_6$: orange-red needles.

Pyridine (βγ)-dicarboxylic acid


$CO_4H.C\left<\begin{matrix}C(CO_2H){:}CH\\CH\text{——}CH\end{matrix}\right>N$. *Cinchomeronic acid.* [259°].

Formation.—1. By oxidation of cinchonine or cinchonidine by HNO_3 of S.G. 1·4 (Weidel, *A.* 173, 76).—2. By oxidation of quinine by HNO_3, the yield being 28 p.c. (Weidel a. Schmidt, *B.* 12, 1146).—3. By heating apophyllenic acid with conc. HClAq at 240° (Von Gerichten, *B.* 13, 1635).—4. By heating pyridine tricarboxylic acid (formed from cinchonic acid) at 190° (Hoogewerff a. van Dorp, *B.* 13, 61; Skraup, *M.* 1, 184; Weidel a. Brix, *M.* 3, 604).—5. By the action of $KMnO_4$ on methyl-pyridine carboxylic acid and on isoquinoline (Hoogewerff a. van Dorp, *R. T. C.* 2, 23; 4, 285).—6. By heating pyridine pentacarboxylic acid (Weber, *A.* 241, 16).—7. By oxidation of methyl-nicotinic acid, derived from (β)-collidine (Oechsner de Coninck, *Bl.* [2] 43, 106).—8. By boiling berberonic acid with HOAc (2 pts.) and Ac_2O (1 pt.) for six hours (Mayer, *M.* 13, 344; *cf.* Fürth, *M.* 2, 426).

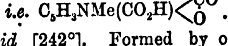

Properties.—Prisms (from HClAq), v. sl. sol. water and ether, sl. sol. alcohol. Yields isonicotinic and some nicotinic acid on heating (Hoogewerff a. van Dorp, *A.* 207, 217). Gives pyridine on distillation with lime. Sodium-amalgam yields NH_3 and cinchonic acid $C_7H_8O_6$, *i.e.* $CO_2H.CH\left<\begin{matrix}CH_2.CO\\\underset{\substack{|\\CO_2H}}{CH}.CH_2\end{matrix}\right>O$ (Weidel a. Hoff, *M.* 13, 578). Cinchonic acid [169°] forms monoclinic crystals, v. sol. hot water and alcohol, and yields $BaC_7H_6O_6$ 3aq, $Ba_3(C_7H_7O_7)_2$ 3aq, CaA″ 2aq, $Ca_3(C_7H_7O_7)_2$ (dried at 190°), and oily Et_2A'', whence PCl_5, followed by alcohol, yields $CO_2Et.CH(CH_2Cl).CH(CO_2Et).CH_2.CO_2Et$, which is a heavy oil. Cinchonic acid is reduced by HI to butane tricarboxylic acid $C_7H_{10}O_6$ [184°], whence $Ca_3A'''_2$ 8aq, accompanied by an isomeric butane tricarboxylic acid [133°]. $FeSO_4$ gives no colour.

Salts.—Na_2A'' 2aq: tables.—NaHA″.—BaA″ 1½aq: needles, sl. sol. water.—CaA″ 3½aq: prisms.—CaA″ 3aq.—CuA″ 3½aq: small blue crystals.—Ag_2A'': white pp.—AgHA″.—HA′HCl: monoclinic prisms, decomposed by water.—$H_2A'_2H_2PtCl_6$: golden prisms.

Anhydride $(C_5H_3N)_2C_2O_3$. [77°]. Formed by boiling the acid with Ac_2O (Goldschmiedt a. Strache, *M.* 10, 156). Plates. May be sublimed. Converted by NH_3 gas into $C_5H_3N(CO_2NH_4).CONH_2$ [229°], which is converted by heat into a yellow powder [130°], and which yields the amic acid $C_5H_3N(CO_2H).CONH_2$ [237°], crystallising in needles.

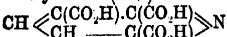
Mono-ethyl ether HEtA″. [133°]. Formed from the anhydride and EtOH. Plates (from benzene).—AgEtA″: long needles.

Mono-methyl ether HMeA″. [154°].


Anhydride of the Methylo-hydroxide $C_8H_7NO_4$ *i.e.* $C_5H_3NMe(CO_2H)\left<\begin{matrix}CO\\O\end{matrix}\right.$. *Apophyllenic acid* [242°]. Formed by oxidation of cotarnine by HNO_3 (Wöhler, *A.* 50, 24; Anderson, *Tr. E.* 23, 347; *C. J.* 5, 257; Gerichten, *B.* 13, 1635). Formed also by heating cinchomeronic acid with MeI and MeOH at 100° (Roser, *A.* 234, 116). Needles (anhydrous) or octahedra (containing aq), sol. hot water, insol. alcohol and ether. HClAq at 250° decomposes it, forming cinchomeronic acid and MeCl.—BaA'_2.—AgA′.—$Ag_2A'(NO_3)$.—$H_2A'_2H_2PtCl_6$ aq.

Bromo-apophyllenic acid $C_8H_6BrNO_4$ 2aq. [205°]. Formed by oxidation of bromo-tarconine. Yields BaA'_2 3aq and $H_2A'_2H_2PtCl_6$ (Gerichten, *A.* 210, 91).

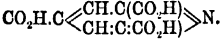
Pyridine (αα'β)-tricarboxylic acid



$CH{<}\begin{matrix}C(CO_2H).C(CO_2H)\\CH=C(CO_2H)\end{matrix}{>}N.$

Formed by oxidising di-methyl-nicotinic acid with $KMnO_4$ (Weiss, *B.* 19, 1309). Crystallises from alcohol in plates (containing 2aq), v. e. sol. water. Decomposes at 160° into CO_2 and isocinchomeronic acid. $FeSO_4$ colours its neutral solution red. — $KH_8A'''_3$ 5aq: needles.—$Ca_3A'''_2$ 4aq.—$Pb_3A'''_2$ 5aq.

Pyridine (αα'γ)-tricarboxylic acid



$CO_2H.C{<}\begin{matrix}CH.C(CO_2H)\\CH:C:CO_2H)\end{matrix}{>}N.$

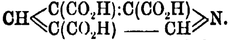
Trimesitic acid. Carbolutidinic acid. [244°]. Formed by oxidation of uvitonic acid (Böttinger, *B.* 13, 2048; 14, 69), and by oxidation of the tri-methyl-pyridine obtained from acetoacetic ether and aldehyde-ammonia (Voigt, *A.* 228, 31). Tables or spheroidal groups of needles (containing 2aq), sol. hot water, sl. sol. alcohol and ether. Yields isonicotinic acid on sublimation. $FeSO_4$ gives a violet-red colour.

Salts.—K_3A''' 5aq: needles.—$Ca_3A'''_2$ 4aq.—$Ba_3A'''_2$ 6aq. — $BaH_4A'''_2$ 4aq. —$Mg_3A'''_2$ 12aq.—$Cu_3A'''_2$ 12aq. - Ag_3A''' 1½aq.

Ethyl ether Et_3A'''. [127·5°].

Amide. [above 280°].

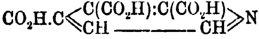
Pyridine (αββ')-tri-carboxylic acid



$CH{<}\begin{matrix}C(CO_2H):C(CO_2H)\\C(CO_2H)-CH\end{matrix}{>}N.$

Carbodinicotinic acid. [323°]. Formed by oxidation of quinoline (*Py.* 2)-carboxylic acid (Riedel, *B.* 16, 1615), of methyl-pyridine (ββ')-dicarboxylic acid (Weber, *A.* 241, 11), and of the parvoline got by heating propionic aldehyde-ammonia with propionic aldehyde at 200° (Dürkopf, *B.* 21, 832, 2707; 23, 689). Spherical aggregates (containing 1½aq), v. sol. hot water. At 155° it is split up into CO_2 and dinicotinic acid.—$Ba_3A'''_2$ 5aq.—Ag_2HA''' 1½aq: rosettes of plates.

Pyridine (αβγ)-tri-carboxylic acid



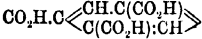
$CO_2H.C{<}\begin{matrix}C(CO_2H):C(CO_2H)\\CH-CH\end{matrix}{>}N.$

[250°] (H. a. D.; S.); [257°] (D. a. R.). S. 1·2 at 15°.

Formation.—1. By the action of $KMnO_4$ on quinine, cinchonine, cinchonidine, quinoïdine, and cinchonic acid (Dobbie a. Ramsay, *C. J.* 35, 189; Hoogewerff a. van Dorp, *B.* 12, 158; 13, 152; *A.* 204, 84; Skraup, *A.* 201, 312; Strache, *M.* 10, 642).—2. By oxidation of cinchonine by HNO_3 (Weidel, *A.* 173, 101; *B.* 12, 415).—3. By oxidation of methyl-pyridine (αβ)-dicarboxylic acid (Hoogewerff a. van Dorp, *R. T. C.* 2, 18), of di-methyl-pyridine carboxylic acid (Michael, *B.* 18, 2027), of (α)-oxy-cinchonic acid (Weidel a. Cobenzl, *M.* 1, 865).—4. By oxidation of papaverine (Goldschmiedt, *M.* 6, 397). Trimetric plates (containing 1½aq), v. sol. hot water, m. sol. alcohol, nearly insol. ether. Blackens at 200°. $FeSO_4$ gives a reddish colour. H_2S forms a red amorphous body (D. a. R.). Decomposed by long heating at 180°, or by boiling with HOAc into CO_2 and cinchomeronic acid. Yields pyridine on distilling with lime. MeI and MeOH at 100° form CO_2 and apophyllenic acid. Sodium-amalgam gives NH_3 and cinchonic acid. PCl_5 forms a chloride (206° at 40 mm.).

Salts. — K_3A''' 3aq. — $Ba_3A'''_2$ 16aq. — $Ba_3A'''_2$ 12aq. — $Ca_3A'''_2$ 14aq. — $Ca_3A'''_2$ 13aq.—$CaHA'''$ 2½aq. — $Cu_3A'''_2$ 9aq: light-blue pp.—$CuHA'''$ 3½aq: hexagonal prisms.—$CuH_4A'''_2$ 2aq.—$Cd_3A'''_2$ 6aq.—Ag_2HA'''aq.—Ag_3A''' 2aq; amorphous pp.—$AgH_5A'''_2$ 2½aq.—$H_3A'''HCl$: crystalline powder (Roser, *A.* 234, 125).

Pyridine (αβ'γ)-tricarboxylic acid

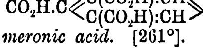


$CO_2H.C{<}\begin{matrix}CH.C(CO_2H)\\C(CO_2H):CH\end{matrix}{>}N.$

Berberonic acid. [243°]. Formed by oxidising berberine with nitric acid (Weidel, *B.* 12, 410; Fürth, *M.* 2, 416). Triclinic prisms (containing 2aq), sol. hot water, v. sl. sol. hot alcohol, insol. ether. Yields pyridine on distillation with lime. $FeSO_4$ gives a red colour. At 215° it is split up into CO_2 and nicotinic acid; above 243° it yields isonicotinic acid.

Salts. — K_3A''' 4½aq. — K_2HA''' 3aq. — KH_2A''' 1½aq. — $Ca_3A'''_2$ 8aq. — $Cd_3A'''_2$ 4aq. — Ag_3A''': white pp., insol. water.

Pyridine (ββ'γ)-tricarboxylic acid

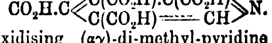


$CO_2H.C{<}\begin{matrix}C(CO_2H).CH\\C(CO_2H):CH\end{matrix}{>}N.$

(β) - *Carbocinchomeronic acid.* [261°]. Formed by heating di-potassium pyridine pentacarboxylate at 220° (Weber, *A.* 241, 17). Plates (containing 3aq), v. sol. hot water. Yields cinchomeronic acid when heated. Gives no colour with $FeSO_4$. — $Cu_5H_2A'''_4$ 24aq.—Ag_3A''' 2aq: crystalline pp.

Pyridine (αββ'γ)-tetra-carboxylic acid

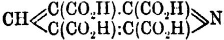
$C_9H_5NO_8$ *i.e.*



$CO_2H.C{<}\begin{matrix}C(CO_2H).C(CO_2H)\\C(CO_2H)=CH\end{matrix}{>}N.$

Formed by oxidising (αγ)-di-methyl-pyridine (ββ')-dicarboxylic acid (Weber, *A.* 241, 23). Prisms (containing 2aq or 3aq). At 120° it loses CO_2, forming (β)-carbocinchomeronic acid. $FeSO_4$ gives a dark-red colour.—Ba_2A^{iv} 4aq.—$Ag_7HA^{iv}_2$ aq: crystalline.

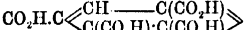
Pyridine (αα'ββ')-tetracarboxylic acid



$CH{<}\begin{matrix}C(CO_2H).C(CO_2H)\\C(CO_2H):C(CO_2H)\end{matrix}{>}N.$

Formed by oxidising di-methyl-pyridine dicarboxylic acid (Hantzsch, *B.* 19, 286; Weber, *A.* 241, 4). Needles (containing 2aq), v. sol. water. Decomposes at 150° into CO_2 and dinicotinic acid.—CaH_2A^{iv} 2aq: needles, v. sol. water.—Cu_2A^{iv} 5aq.—Ag_4A^{iv} 2aq: bulky pp.

Pyridine (αα'β'γ)-tetra-carboxylic acid



$CO_2H.C{<}\begin{matrix}CH-C(CO_2H)\\C(CO_2H):C(CO_2H)\end{matrix}{>}N.$

Formed by oxidation of tri-methyl-pyridine carboxylic acid and of di-methyl-pyridine di-carboxylic acid (Michael, *A.* 225, 142). Formed also by oxidation of flavenol by alkaline $KMnO_4$ (Fischer a. Täuber, *B.* 17, 2927). Slender needles (containing 2aq), v. sol. water, v. sl. sol. alcohol and ether. Not decomposed at 150°. $FeSO_4$ gives a brownish-red colour.—Ba_2A^{iv} 2½aq.—Ba_2A^{iv} aq.—Cu_2A'' 2½aq.—Ag_4A^{iv} aq.

Pyridine penta-carboxylic acid $NC_5(CO_2H)_5$. Formed from potassium tri-methyl-pyridine dicarboxylate and $KMnO_4$ (Hantzsch, *A.* 215, 62; Weber, *A.* 241, 15). Crystalline mass of minute needles (containing 2aq), extremely sol. water, v. sl. sol. ether. Acid to litmus and to taste. Loses 2aq at 120° and decomposes, without having melted, at 220°. The neutral alkaline salts are very soluble, but the acid alkaline salts are sl. sol. water. The acid does not combine with HCl. Distilled with lime it gives pyridine. $FeSO_4$ gives a dark-red colour.

Salts.—KH_4A^v 2 or 3aq. When heated swells up like Pharaoh's serpent.—$K_2H_3A^v$ $3\frac{1}{2}$aq. — K_5A^v. — $Ba_5A^v_2$ 11aq. — $Ca_5A^v_2$ 12aq. — CaH_3A^v $\frac{1}{2}$aq.—$Mg_5A^v_2$ 12aq.—$Ca_2(NH_4)A^v$ 5aq.—Ag_4HA^v 2aq.

Double salt with oxalic acid $KH_4A^vKHC_2O_4$ 5aq.

References.—BROMO- and OXY-PYRIDINE CARBOXYLIC ACID.

PYRIDINE TETRAHYDRIDE C_5H_9N *i.e.* $CH_2<\begin{smallmatrix}CH:CH\\CH_2.CH_2\end{smallmatrix}>NH$. *Piperideïn.* Formed by heating amido-valeric aldehyde with solid KOH (Wolffenstein, *B.* 25, 2782).—$B'HAuCl_4$. [141°].—$B'_2H_2PtCl_6$.—B'HCl. [230°].—B'HBr. [178°].

Pyridine hexahydride *v.* PIPERIDINE.

PYRIDINE (β)-SULPHONIC ACID $C_5H_4N.SO_3H$. Formed by heating pyridine (1 pt.) with H_2SO_4 (3 pts.) at 320° (O. Fischer, *B.* 15, 62; 16, 1183). Small needles or plates, sol. water, sl. sol. alcohol, insol. ether. Br added to its boiling aqueous solution forms dibromopyridine. Potash-fusion gives oxy-pyridine [123°]. On distillation with KCy it yields the nitrile of nicotinic acid. The K salt, heated with MeI at 150° forms crystalline $C_5H_4NMe<\begin{smallmatrix}SO_2\\O\end{smallmatrix}$ (Hantzsch, *B.* 19, 36).—BaA'_2 4aq : needles.

Pyridine sulphonic acid? $C_5H_5NSO_3$. [155°]. Formed from pyridine and $ClSO_3H$ (Wagner, *B.* 19, 1157). Crystalline, decomposed by water into pyridine and H_2SO_4.

Pyridine disulphonic acid $C_5H_3N(SO_3H)_2$. Formed by heating piperidine (1 pt.) with H_2SO_4 (10 pts.) (Königs, *B.* 16, 735; 17, 592). Needles (from HOAc), v. sol. water, nearly insol. alcohol and ether. PCl_5 at 200° forms tri-chloropyridine [48°]. — Na_2A'' 4aq. — K_2A'' 3aq. — PbA'' $4\frac{1}{2}$aq.

PYRIDONE *v.* OXY-PYRIDINE.

(αα)-DIPYRIDYL $C_{10}H_8N_2$ *i.e.* $C_5H_4N.C_5H_4N$. [70°]. (272·5°). V.D. 5·6. Formed by distilling cupric picolinate (Blau, *B.* 21, 1077; *M.* 10, 875). Crystals (from water), m. sol. water, v. sol. alcohol. Not hygroscopic. Strong base. $FeSO_4$ colours its aqueous solution red. Oxidised by $KMnO_4$ to picolinic acid.—$B''H_2PtCl_6$.—$B''H_4FeCy_6$.—$B''C_6H_3N_3O_7$. [155·5°]. Needles

Hexahydride. Formed by reducing the base with zinc and HClAq. Alkaline oil.

Dodecahydride $C_{10}H_{20}N_2$. *Dipiperidyl.* (259° cor.). Formed by reducing the base, dissolved in isoamyl alcohol, by Na. Powerful base. Very deliquescent. Not poisonous. Forms with CS_2 a compound [93°], and yields a nitrosamine [159°].—$B''H_2PtCl_6$ $2\frac{1}{2}$aq.

(ββ)-Dipyridyl $C_{10}H_8N_2$. [68°]. (287°) (L. a. O.); (292° at 736 mm.) (S. a. V.). Formed by distilling its dicarboxylic acid with KOH (Skraup a. Vortmann, *M.* 4, 591), and by the dry distillation of pyridine disulphonic acid (Leone a. Oliveri, *G.* 15, 276). Extremely deliquescent needles, miscible with water and alcohol, sl. sol. ether. Yields nicotinic acid on oxidation.—$B''_2H_2PtCl_6$.—$B''2C_6H_3N_3O_7$. [232°].

Hexahydride $C_{10}H_{14}N_2$. *Nicotidine.* (288°). Got by warming the base with tin and conc. HClAq. Poisonous oil, v. e. sol. water and alcohol, m. sol. ether.—$B''_2H_2PtCl_6$: orange-red pp.—**Picrate**: [202°].

(γγ)-Dipyridyl $C_{10}H_8N_2$. [114°]. (305° cor.). V.D. 5·9 (calc. 5·5). Formed by boiling pyridine with sodium (Anderson, *A.* 154, 274; Weidel a. Russo, *M.* 3, 854). Formed also by heating its (αα)-dicarboxylic acid with HOAc at 180° (Heuser a. Stoehr, *J. pr.* [2] 44, 407). Tables, sl. sol. cold water, v. sol. alcohol. Crystallises from water in tables (containing 2aq). [73°]. Tastes bitter. Yields isonicotinic acid on oxidation. Br forms $C_{10}H_6Br_2N_2$ crystallising from alcohol in needles. MeI and EtI form crystalline B''2MeI and B''2EtI respectively.

Salts. — $B''H_2Cl_2$. Monoclinic crystals; $a:b:c = 1·064:1:·595$. $\beta = 112°\ 33'$.—$B''H_2ZnCl_4$. — $B''H_2HgCl_4$. Monoclinic tables; $a:b:c = ·673:1:·341$; $\beta = 91°\ 3'$. — $B''H_2PtCl_6$. — $B''2HNO_3$. [256°]. Trimetric prisms; $a:b:c = ·841:1:·397$.—$B''HNO_3AgNO_3$.—$B''H_2SO_4$ 2aq.

Dihydride $C_{10}H_{10}N_2$. *Dipyridine.* (290°) at 735 mm. V.D. 5·0 (calc. 5·5). Formed by the action of Na on pyridine (Anderson, *C. J.* 22, 406; Weidel, *M.* 3, 879). Liquid, sol. water and alcohol.—$B''H_2PtCl_6$. — B''2MeI. — $B''Me_2PtCl_6$ (Ramsay, *C. J.* 36, 264).

Hexahydride $C_{10}H_{14}N_2$. *Isonicotine.* [78°]. (above 260°). Formed by reducing (γγ)-dipyridyl with tin and HClAq (W. a. R.). Deliquescent needles, sol. water, alcohol, and benzene. Has hardly any smell. Strongly alkaline and caustic. Poisonous, acting somewhat like curari. Its salts are much less poisonous. Oxidised by $KMnO_4$ to isonicotinic acid.—$B''2HNO_3$. Deliquescent needles. — $B''H_2PtCl_6$ aq. — $B''_2H_4Hg_3Cl_{10}$. — B''2MeI: triclinic prisms (from MeOH).

Dodecahydride $C_{10}H_{20}N_2$. [122°]. Formed by reducing (γγ)-dipyridyl in alcohol by Na (Ahrens, *B.* 21, 2929). Needles, insol. water, v. sol. alcohol and ether.—$B''H_2PtCl_6$.—$B''HAuCl_4$. **Picrate**: needles, blackening when heated.

Dipyridyl $C_{10}H_8N_2$. (281°). Formed by passing pyridine vapour through a red-hot tube (Roth, *B.* 19, 360). Oil.—B''2HCl: hygroscopic needles.—$B''H_2PtCl_6$.—**Picrate**: [208°].

(αβ)-Dipyridyl $C_{10}H_8N_2$. (296° cor.). Formed by heating its carboxylic acid with lime (Skraup a. Vortmann, *M.* 3, 599; Blau, *B.* 24, 326). Oil, sol. alcohol and ether. — $B''H_2PtCl_6$ $\frac{1}{2}$aq. — $B''C_6H_3N_3O_7$. [149·5°]. Yellow needles.

Dodecahydride $C_{10}H_{20}N_2$. [69°]. (269° cor.). Formed by reducing the base with isoamyl alcohol and Na (Blau, *M.* 13, 332). Hygroscopic crystalline mass. Not identical with nicotine hexahydride. Strongly alkaline, absorbing CO_2 from the air. V. e. sol. water, but much water gives a turbidity. V. sol. alcohol, m. sol. ether. CS_2 forms a compound [205°].—$B''H_2Cl_2$. V. e. sol. water, sl. sol. alcohol and ether.—$B''H_2PtCl_6$ 2aq. [238°]. — $B''2HAuCl_4$. [212°]. — $B''2C_6H_3N_3O_7$. [215°].

Benzene sulphonyl derivative. [157°].

Nitrosamine $C_{10}H_{18}N_2(NO)_2$. [88°].

Dipyridyl *dodecahydride?* $C_{10}H_{20}N_2$? (251°). S.G. ^{4} ·956. Is perhaps (αβ)-dipyridyl hexa-hydride (Blau). Formed by the action of Na on nicotine in alcoholic solution (Liebrecht, *B.* 18, 2970; 19, 2590). Lævorotatory liquid, v. sol. water, alcohol, and ether. Alkaline in reaction. Smells like piperidine. Readily unites with CS_2. Forms an oily nitrosamine and an oily di-acetyl derivative (c. 405°).—B''2HCl. Sol. alcohol.—$B''H_2PtCl_6$. [202°].—$B''H_2I_6$: brown needles.—

$B''2HAuCl_4$. [182°].—$B''H_2Hg_3Cl_{12}$.—$B''Me_2PtCl_6$.—$C_{10}H_{12}MeN_2Me_2PtCl_6$. Blau (*M.* 13, 341) by reducing nicotine obtained a mixture of bases (235°-265°) yielding a sparingly soluble platinochloride [218°], which gave a base (244°), possibly methyl-nicotine hexahydride $C_{11}H_{22}N_2$.

(α)-**PYRIDYL-ACRYLIC ACID** $C_8H_7NO_2$ *i.e.* $C_5H_4N.CH:CH.CO_2H$. [203°]. Formed by heating α-oxy-tri-ω-chloro-propyl-pyridine with alcoholic potash (Einhorn, *B.* 20, 1593; 23, 220; *A.* 265, 215). Got also by heating α-oxy-pyridyl-propionic acid. Small transparent needles, v. sl. sol. cold water, v. sol. alcohol.

Reactions.—1. Br in HOAc forms $C_5H_4N.CHBr.CHBr.CO_2H$ [127°], which melts at 146·5° when containing HOAc of crystallisation.—2. Hydrogen bromide in HOAc forms $(C_5H_4N.CHBr.CH_2.CO_2H)HBr$ [164°], crystallising in needles.—3. MeI yields HA'MeI [220°] converted by AgBr into HA'MeBr [242°].

Salts.—HA'HCl. [220°].—$H_2A'_2H_2PtCl_6$. [210°]. Red prisms.—$HA'HAuCl_4$. [195°].—HA'HBr. [223°].—CaA'_2.—AgA': needles.

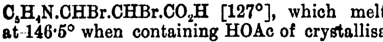
Methyl ether MeA'.—MeA'HCl. [186°].—MeA'HBr. [242°]. MeA'HI. [220°].

Ethyl ether EtA'. Needles.

(α)-**PYRIDYL-BUTYLENE** $C_9H_{11}N$ *i.e.* $C_5H_4N.CH:CHEt$. (148° at 75 mm.). By distilling oxybutyl-pyridine $C_5H_4N.CH_2.CH(OH).C_2H_5$ with KOH *in vacuo* or by heating it with HClAq at 165° (Matzdorff, *B.* 23, 2711). Colourless oil, smelling like conyrin.—Platinochloride: [140°].—$B'HAuCl_4$. [130°]. Small needles.

(αβ)-**DIPYRIDYL (β)-CARBOXYLIC ACID** $C_{11}H_8N_2O_2$ *i.e.* $C_5H_4N.C_5H_3N.CO_2H$. [183°]. Formed by heating the dicarboxylic acid at 200° (Skraup, *B.* 15, 896; *M.* 3, 597). Needles (containing $1\frac{1}{2}$aq), sl. sol. cold water and alcohol. Gives a yellow colour with $FeCl_3$.—CaA'_2 2aq.—AgA' $\frac{1}{2}$aq: prismatic needles.

(αβ)-Dipyridyl (βγ)-dicarboxylic acid



$$CH\Big\langle\begin{matrix}CH:C(CO_2H)\\N\text{———}CH\end{matrix}\Big\rangle C.C\Big\langle\begin{matrix}C(CO_2H):CH\\N\text{———}CH\end{matrix}\Big\rangle CH.$$

[215°]. Formed by oxidation of phenanthroline by $KMnO_4$ (Skraup a. Vortmann, *B.* 15, 896; *M.* 3, 587). Triclinic prisms (containing 2aq), sl. sol. cold water, v. sol. alcohol. $FeSO_4$ colours its aqueous solution red. Salts.—KHA'' $\frac{1}{2}$aq.—CaA'' 3aq.—CuA'' 3aq.—BaA'' $1\frac{1}{2}$aq. Crystals.—AgHA'' 4aq.—H_2A'' 2HCl.—$H_2A''H_2PtCl_6$ 3aq.—$(H_2A'')_2H_2PtCl_6$ 6aq: golden prisms.

(ββ)-Dipyridyl (αα)-dicarboxylic acid $C_{12}H_8N_2O_4$. [213°]. Formed by oxidation of pseudo-phenanthroline by $KMnO_4$ (Skraup a. Vortmann, *M.* 4, 583). Thick prisms (containing $\frac{1}{2}$aq), sl. sol. cold water, alcohol, and ether. $FeSO_4$ gives an orange-yellow colour.—K_2A'' 5aq.—KHA'' 2aq.—CaA'' 5aq.—CuA'' $3\frac{1}{2}$aq.—Ag_2A'' $\frac{1}{2}$aq.—$Ag_2A''AgNO_3$.—H_2A''HCl aq. Monoclinic prisms; $a:b:c = 1·27:1:2·29$; $\beta = 110°\ 16'$.—H_2A 'H_2PtCl_6 8aq: orange crystalline pp.

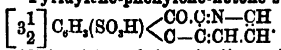
(γγ)-Dipyridyl (αα)-dicarboxylic acid. [247·5°]. Formed by oxidising (αα)-di-methyl-dipyridyl by $KMnO_4$ (Heuser a. Stoehr, *J. pr.* [2] 44, 405). Needles, v. sl. sol. water and alcohol. $FeSO_4$ gives a reddish-yellow colour. AcOH at 180° gives (γγ)-dipyridyl.

Dipyridyl tetracarboxylic acid? [96°]. Got by oxidising diquinolyl (Claus, *B.* 14, 1942). Needles (from hot water).—Pb_2A^{iv}.—Ag_4A^{iv}.

PYRIDYLENE-PHENYLENE-KETONE

PHENYLENE PYRIDYL KETONE.

Pyridylene-phenylene-ketone sulphonic acid



$$\left[3\tfrac{1}{2}\right]C_6H_3(SO_3H)\Big\langle\begin{matrix}CO.C:N\text{—}CH\\C\text{—}C:CH.CH\end{matrix}$$

Formed by oxidising (β)-naphthoquinoline sulphonate with alkaline $KMnO_4$ (Immerheiser, *B.* 22, 408). Yellow plates (from water), v. sl. sol. alcohol and ether. Yields an oxim crystallising in yellow flakes and a phenyl-hydrazide crystallising in minute orange needles.—KA' aq.—BaA'_2 2aq.—PbA'_2 3aq.—AgA' aq.

PYRIDYL-ETHYLENE $C_5H_4N.CH:CH_2$. (160°). Formed by the action of NaOHAq on the hydrochloride of β-bromo-β-pyridyl-propionic acid (Einhorn, *B.* 23, 221; *A.* 265, 229). Liquid.—$B'HAuCl_4$. [144°]. Yellow needles.

(α)-**PYRIDYL ETHYL KETONE** C_8H_9NO *i.e.* $C_5H_4N.CO.C_2H_5$. (205°). Formed by distilling calcium picolinate with calcium propionate (Engler a. Bauer, *B.* 24, 2530). Oil, sol. alcohol. Sodium-amalgam forms a pinacone [136°]. Phenyl-hydrazine sulphonic acid yields a crystalline compound [268°].—$B'HgCl_2$: crystalline.—B'EtI. [160°].

Oxim $C_5H_4N.C(NOH).C_2H_5$. [106°]. Needles. Yields an acetyl derivative [46°] and a benzoyl derivative [69°].

(β)-Pyridyl ethyl ketone $C_5H_4N.CO.C_2H_5$. Formed by distilling calcium nicotinate with calcium propionate (Engler, *B.* 24, 2539). Yields a phenyl hydrazide [145°] and a phenyl-hydrazide sulphonate [235°] which forms $B'_2H_2PtCl_6$. $B'C_6H_3N_3O_7$, and $B'HgCl_2$ [130°].

Oxim $C_5H_4N.C(NOH).C_2H_5$. [115°].

(α)-**PYRIDYL METHYL KETONE** $C_5H_4N.CO.CH_3$. (192°). Formed by distilling calcium picolinate with calcium acetate (Engler a. Rosumoff, *B.* 24, 2527). V. sol. alcohol and ether. Readily volatile with steam. Yields an oxim [120°], a phenyl-hydrazide [155°], and a phenyl-hydrazide sulphonate which is not melted at 300°.—$B'C_6H_3N_3O_7$. [131°].—$B'HgCl_2$. [150°].—B'MeI. [161°].—B'EtI. [205°].

(β)-Pyridyl methyl ketone $C_5H_4N.CO.CH_3$. (220°). Formed by distilling calcium nicotinate with calcium acetate (Engler a. Kiby, *B.* 22, 597). Oil, v. sol. acids. Yields an oxim [112°], which yields B'HCl [204°]. The phenyl-hydrazide [137°] crystallises from alcohol in yellow needles.—$B'HgCl_2$. [158°]. White needles.

DI-(α)-PYRIDYL-PROPANE $C_{13}H_{14}N_2$ *i.e.* $CH_2(CH_2.C_5H_4N)_2$. (323°). S.G. ^{0} 1·0281. Formed by heating picoline with methylal and $ZnCl_2$ for 10 hours at 290° (Ladenburg, *B.* 21, 3100). Yellow oil, v. sol. alcohol and ether.—Salts: $B''H_2PtCl_6$. [215°].—$B''2HAuCl_4$ $1\frac{1}{2}$aq.—$B''H_2Hg_4Cl_{10}$. [161°]. Large plates.

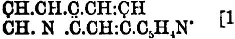
Dodecahydride $C_{13}H_{26}N_2$. *Dipipecolyl-methane.* [54°]. (195° at 26 mm.). Formed by reducing the base with Na and alcohol. Crystalline mass, sl. sol. water.—B''2HCl: very hygroscopic needles.—B''2MeCl. [171°].—$C_{13}H_{24}Me_2N_2$2MeI. Crystals, v. e. sol. water.

(α)-**PYRIDYL PROPYL KETONE** $C_5H_4N.CO.Pr$. (216°-220°). Formed by distilling calcium picolinate with calcium butyrate (Engler a. Majmon, *B.* 24, 2536). Oil. Yields an oxim [48°] which forms a benzoyl derivative [57°]. Forms a phenyl-hydrazide [82°] and a phenyl-hydrazide sulphonic acid [251°]. The ketone is reduced, in dilute alcoholic solution, by sodium-amalgam to a pinacone $C_{18}H_{21}N_2O_2$ [146°]. The chloro-iodide melts at 85°.

Salts.—$B'_2H_2PtCl_6$.—$B'HgCl_2$. [c. 78°].—B'MeI. [79°].

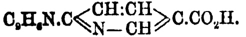
(*β*)-**Pyridyl propyl ketone** $C_5H_4N.CO.Pr$. (246°-252°). Formed by distilling calcium nicotinate with calcium butyrate (Engler, *B.* 24, 2541). Yellow needles, sol. alcohol. Yields a phenyl-hydrazide [182°], a phenyl-hydrazide sulphonate [283°], a crystalline oxim, and an ethylo-iodide [192°]. — $B'HgCl_2$. [173°]. — $B'C_6H_3N_3O_7$.

(*B*.3)-(*a*)-**PYRIDYL-QUINOLINE** $C_{14}H_{10}N_2$ *i.e.*



$\begin{matrix}\text{CH.CH.C.CH:CH}\\ \text{CH. N .C.CH:C.C}_5\text{H}_4\text{N}\end{matrix}$ [104°]. Formed by heating the Ag salt of its carboxylic acid (O. Fischer a. H. van Loo, *B.* 19, 2475). Prisms.—$B'_2H_2PtCl_6$.

Carboxylic acid $C_{15}H_{10}N_2O_2$ *i.e.*



$C_9H_6N.C\begin{matrix}\text{CH:CH}\\ \text{N—CH}\end{matrix}C.CO_2H$. [273°]. Formed by oxidising (*β*)-diquinolyl with CrO_3. Needles, v. sl. sol. water.—AgA': pale yellow pp.

PYRO-. *Use of this prefix applied to inorganic compounds*; for *pyro- compounds v.* the compounds to the names of which *pyro-* is prefixed. Thus *pyro-phosphoric acid* will be found under PHOSPHORIC ACID, and *pyro-phosphates* under PHOSPHATES.

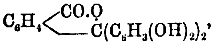
PYROCATECHIN $C_6H_6O_2$ *i.e.* $C_6H_4(OH)_2$[1:2]. *Catechol. o-Di-oxy-benzene. Oxyphenic acid.* [104°] (F. a. M.); [111°] (Mortinon). (240°-245°). H.C.p. 685,200. H.C.v. 684,900. H.F. 85,800 (Stohmann, *J. pr.* [2] 45, 334). Occurs in urine, especially after administration of benzene or phenol (Baumann, *H.* 1, 244; 3, 157; Nencki a. Giacosa, *H.* 4, 335; Schmiedeberg, *H.* 6, 189). Occurs in the green leaves of the Virginia creeper (*Ampelopsis hederacea*) (Gorup-Besanez, *B.* 4, 905) and in the sap of the plants from which kino is prepared (Flückiger, *B.* 5, 1). Occurs sometimes in raw beet sugar (Lippmann, *B.* 20, 3298). Occurs in wood-tar (Béhal a. Desvignes, *Bl.* [3] 9, 141).

Formation.—1. By dry distillation of catechin, moritannic acid, and all varieties of tannin that turn green with $FeCl_3$ (Zwenger, *A.* 37, 327; Wagner, *J. pr.* 52, 450; 55, 65; Eissfeldt a. Uloth, *A.* 92, 101; 111, 215).—2. By the dry distillation of wood (Buchner, *A.* 96, 188).—3. By heating cellulose, starch, or cane sugar with water at 200°-280° (Hoppe-Seyler, *B.* 4, 15).—4. By potash-fusion from *o*-iodo-phenol (Körner, *Bull. Acad. Belg.* [2] 24, 166; Lautemann, *A.* 120, 315).—5. By the action of HI on guaiacol (Gorup-Besanez, *J.* 1867, 688; Baeyer, *B.* 8, 155).—6. By the dry distillation of protocatechuic acid and of quinic acid (Strecker, *A.* 118, 285; Hlasiwetz a. Barth, *J.* 1864, 405; Tiemann a. Haarmann, *B.* 7, 617).—7. By potash-fusion from *o*-phenol sulphonic acid (Kekulé, *Z.* 1867, 643), benzoic acid, gum guaiacum (Hlasiwetz a. Barth, *A.* 130, 352; 134, 282), and, together with resorcin, from *o*- and *m*- bromo-phenol (Fittig, *B.* 8, 364).—8. By soda-fusion from phenol (Barth a. Schreder, *B.* 12, 419).—9. From phenol and H_2O_2 (Martinon, *Bl.* [2] 43, 157).—10. By passing a rapidly alternating electric current through a solution of phenol.—11. A product of the action of water at 200° on benzene hexachloride (Meunier, *C. R.* 100, 1591).

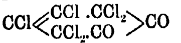
Preparation.—1. From HIAq and guaiacol at 200° or by heating guaiacol with conc. HClAq for 4 hours at 175° (Perkin, jun., *C. J.* 57, 587). 2. By fusing *o*-phenol sulphonic acid with potash at 350° (Degener, *J. pr.* [2] 20, 308).

Properties.—Large plates (from benzene) or needles (from water), v. sol. water, alcohol, and ether, m. sol. benzene and chloroform, insol. ligroïn. Gives an acid reaction in presence of borax (Lambert, *C. R.* 108, 1017). $FeSO_4$ gives no colour. $FeCl_3$ colours the aqueous solution green, turned violet-red by alkalis (Ebstein a. Müller, *Fr.* 15, 465). The alkaline solution absorbs oxygen, becoming brown. It reduces $AgNO_3$, $AuCl_3$, and platinic chloride. Ppts. a conc. solution of egg-albumen. Does not ppt. gelatin. Lead acetate gives a white pp. Quinone in ethereal solutions forms $C_6H_4O_2C_6H_6O_2$, crystallising in deep-green needles with violet lustre [153°] (Clermont a. Chautard, *C. R.* 102, 1072). Ppts. a solution of quinine sulphate, forming $C_{20}H_{24}N_2O_2\ H_2SO_4\ C_6H_6O_2$ aq, which separates from alcohol in yellow crystals [167°], v. sl. sol. cold water.

Reactions.—1. *Nitric acid* acts violently, forming oxalic acid.—2. *Phthalic anhydride* and $ZnCl_2$ at 150° form 'pyrocatechin phthaleïn'



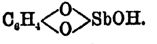
$C_6H_4\begin{matrix}\text{CO.O}\\ \text{C(C}_6\text{H}_3\text{(OH)}_2)_2\end{matrix}$, a yellow mass forming a blue solution in alkalis and yielding a tetra-benzoyl derivative [202°] (Baeyer a. Kochendörfer, *B.* 22, 2196).—3. *Phenyl cyanate* at 100° forms $C_6H_4(O.CO.NHPh)_2$ [165°] crystallising in needles, v. sol. alcohol (Snape, *C. J.* 47, 772).—4. The disodium compound $C_6H_4(ONa)_2$ treated with CO_2 in the cold forms $C_6H_4(O.CO_2Na)_2$, which at 100° changes to the compound $C_6H_3(O.CO_2Na)(OH).CO_2Na$ and at 210° to $C_6H_2(OH)_2(CO_2Na)_2$ (Schmitt a. Hähle, *J. pr.* [2] 44, 2).—5. *Ammonium carbonate* and water at 140° react forming protocatechuic acid and $C_6H_3(OH)(CO_2H)_2$[1:2:3].—6. $K_2S_2O_7$ acting on K salt forms crystalline $C_6H_4(O.SO_3K)_2$ and $C_6H_4(OH)(O.SO_3K)$ (Baumann, *B.* 11, 1913).—7. $Cl.CONH_2$ forms $C_6H_4(O.CONH_2)_2$ [178°] crystallising from alcohol in needles.—8. *Chlorine* passed into its solution in acetic acid forms



$CCl\begin{matrix}\text{CCl .CCl}_2\\ \text{CCl}_2\text{.CO}\end{matrix}CO$ crystallising (with 2aq) from ether-ligroïn, and from ligroïn (with aq), melting at 94° (Zincke a. Klein, *B.* 21, 2719).—9. KOH and $ClCO_2Et$ form $C_6H_4CO_3$ [118°] (Bender, *B.* 13, 697), (225°-230°) (M. Wallach, *A.* 226, 84).

Estimation. — By extracting its acidified aqueous solution with ether, evaporating the ether, dissolving the residue in water, and precipitating with lead acetate. The pp. is dried at 100° and weighed (Degener, *J. pr.* [2] 20, 303).

Salts.—$C_6H_4O_2Pb$. White pp.—$C_6H_5O_3Sb$ or



$C_6H_4\begin{matrix}\text{O}\\ \text{O}\end{matrix}SbOH$. Formed by adding $SbCl_3$ to a solution of pyrocatechin saturated with NaCl (Causse, *Bl.* [3] 7, 245). Prisms, insol. water, alcohol, and ether, sol. alkalis and mineral acids. Ac_2O at 125° forms $C_6H_4(OAc)_2$ and $Sb(OH)(OAc)_2$.

Di-acetyl derivative $C_6H_4(OAc)_2$. Needles (Nachbauer, *A.* 107, 248).

Di-benzoyl derivative $C_6H_4(OBz)_2$. [84°]. Plates (Doebner, *A.* 210, 261; Hinsberg, *A.* 254, 254).

Mono-methyl ether $C_6H_4(OH)(OMe)$. *Guaiacol.* Mol. w. 124. [28·5°]. (205°) (Tiemann a. Koppe, *B.* 14, 2016; Béhal a. Choay, *Bl.* [3] 9, 142). S.G. $\frac{16}{}$ 1·125 (V.); $\frac{0}{}$ 1·153; $\frac{15}{}$ 1·143 (B. a. C.). A product of distillation of gum guaiacum (Sobrero, *A.* 48, 19; Deville a. Pelletier, *A.* 52, 403; Völckel, *A.* 89, 349). Occurs among the products of the distillation of wood (Hlasiwetz, *A.* 106, 362; Gorup-Besanez, *A.* 143, 151). Prepared by heating calcium vanillate with slaked lime (Tiemann, *B.* 8, 1123) and by heating pyrocatechin with MeI and $KMeSO_4$ (Gorup-Besanez, *A.* 147, 248, or with NaOMe, MeOH, and MeI). Liquid, with peculiar odour, sol. alcohol and ether, sl. sol. water, sol. dry glycerin and ligroïn. $FeCl_3$ gives a green colour in its alcoholic solution. Dissolves in alkalis. Yields $C_6H_5.OMe$ on heating with zinc-dust (Marasso, *A.* 152, 64). PCl_5 forms $C_6H_4Cl.OMe$ (Fischli, *B.* 11, 1463). I and KOHAq give a coffee-brown pp. [125°–130°] (Messinger a. Vortmann, *B.* 22, 2320). The K salt is converted by acetochlorhydrose into $C_6H_4(OMe)(O.C_6H_{11}O_5)$ [157°] (Michael, *Am.* 6, 339). Phthalic anhydride and $SnCl_4$ at 115° form 'guaiacol-phthaleïn,' which yields a crystalline benzoyl derivative (Baeyer, *B.* 22, 2199). H_2SO_4 forms two sulphonic acids (Tikmann a. Koppe, *B.* 14, 2019).—$C_6H_4(OK)(OMe)$ 2aq.—KHA'_2 aq: prisms (from alcohol), decomposed by water.—$Pb(OH)A'$: flocculent pp. — $C_6H_4(O.SO_3K)(OMe)$: white needles.—$C_6H_4(OAc)(OMe)$. (235°–240°). V.D. 82·7 (obs.). Colourless liquid.

Di-methyl ether $C_6H_4(OMe)_2$. *Veratrole.* (205°). V.D. 68·6 (obs.; H = 1). S.G. $\frac{15}{}$ 1·086. Formed by heating veratric acid with baryta (Merk, *A.* 108, 60; Koelle, *A.* 159, 243; Tiemann, *B.* 14, 2016). It is obtained also from $C_6H_4(OK)(OMe)$ and MeI (Marasse). Solidified at 15°.

Methyl ethyl ether $C_6H_4(OMe)(OEt)$. (213°). V.D. (H = 1) 75·6 (obs.). Liquid.

Methyl propyl ether $C_6H_4(OMe)(OPr)$. (240°–245°). Liquid (Cahours, *Bl.* [2] 29, 270).

Di-ethyl ether $C_6H_4(OEt)_2$. [44°]. Formed from pyrocatechin, EtI, and alcoholic potash (Herzog a. Zeisel, *M.* 10, 152).

Di-benzyl derivative $C_6H_4(OC_7H_7)_2$. [61°]. Yellowish needles (from alcohol). Forms a nitro- derivative crystallising in needles [98°].

The *mono-benzyl derivative* is liquid, but its nitro- derivative forms yellow needles (from alcohol) [129°] (Schiff a. Pellizzari, *A.* 221, 378; *G.* 13, 507).

Sulphonic acid $C_6H_3(OH)_2(SO_3H)$[4:3:1]. Formed by fusing phenol (α)-disulphonic acid with KOH at 300° (Barth a. Schmidt, *B.* 12, 1260). Deliquescent needles, v. sol. water and alcohol, insol. ether.—KA′.—NaA′aq.—BaA'_2.

References.—Amido-, Bromo-, Chloro-, and Nitro- Pyrocatechin, and Tri-bromo-guaiacol.

PYROCINCHONIC ACID *v.* Di-methyl-maleïc acid.

PYROCOLL $C_{10}H_6N_2O_2$ (Magnanini, *B.* 22, 2502). [269°]. A product of the distillation of gelatin when free from fat but containing albumen, caseïn, or gluten (Weidel a. Ciamician, *M.* 1, 279; 2, 29). Formed also, together with HOAc, by heating the acetyl derivative of pyrrole (α)-carboxylic acid (Ciamician a. Silber, *B.* 17, 103; *G.* 14, 162, 563). Colourless plates, insol. water and cold alcohol, sl. sol. ether. Sublimes before fusion.

Reactions.—1. Boiling KOHAq converts it into pyrrole carboxylic acid.—2. Alcoholic NH_3 forms the amide of pyrrole carboxylic acid.—3. PCl_5 forms $C_{10}Cl_6N_2O_2$ [above 320°] insol. ether and $C_{10}Cl_{10}N_2O$ [197°] sol. ether (Ciamician a. Dancsi, *G.* 13, 28). The perchloro-pyrocoll $C_{10}Cl_6N_2O_2$ is converted by boiling KOHAq into tri-chloro-pyrrole carboxylic acid, and by PCl_5 into $C_{10}Cl_{14}N_2O_2$ [147°].—4. *Bromine* forms $C_{10}H_5BrN_2O_2$ [192°], $C_{10}H_4Br_2N_2O_2$ [290°], and $C_{10}H_2Br_4N_2O_2$, which is converted by KOHAq into di-bromo-pyrrole carboxylic acid (Ciamician, *G.* 11, 330; 12, 29; *B.* 16, 2388).

Reference.—Chloro-, Bromo-, and Nitro-Pyrocoll.

PYROCRESOL. $C_{15}H_{14}O$? An inappropriate name given by Schwarz (*B.* 15, 2201; 16, 2141; *M.* 3, 726; *cf.* Armstrong, *C. J. Proc.* 3, 114) to some neutral substances found in coal-tar.

(α)-**Pyrocresol** [195°]. Thin silvery plates, yielding crystalline $C_{28}H_{22}Br_3O_2$? and oxidised by CrO_3 in HOAc to $C_{15}H_{12}O_2$ [168°] which yields $C_{15}H_{10}(NO_2)_2O_2$ [235°], $C_{15}H_8(NO_2)_4O_2$ and $C_{15}H_8(NH_2)_4O_2$ [300°]? (Bott a. Miller, *C. J.* 55, 52). Chlorine acting on a solution of (α)-pyrocresol in chloroform gives $C_{15}H_{11}Cl_3O$ [225°]? HI reduces (α)-pyrocresol to a hydrocarbon $C_{15}H_{22}$? (Bott, *C. J. Proc.* 3, 114).

(β)-**Pyrocresol** [c. 124°]. Yields, on oxidation, '(β)-Pyrocresol oxide' $C_{15}H_{12}O_2$ [95°].

(γ)-**Pyrocresol** [165°]. Yields '(γ)-pyrocresol oxide' [77°] on oxidation. Bromine forms $C_{28}H_{22}Br_3O_2$? crystallising in trimetric plates.

PYROGALLIC ACID *v.* Pyrogallol.

PYROGALLOL $C_6H_6O_3$ *i.e.* $C_6H_3(OH)_3$[1:2:3]. *c-Tri-oxy-benzene. Pyrogallic acid.* Mol. w. 126. [131°] (Etti, *B.* 11, 1882; *cf.* Stenhouse, *A.* 179, 236); [134°] (Stohmann). (210°). S. 40 at 12°. H.C.p. 633,300 (Berthelot a. Louguinine, *A. Ch.* [6] 13, 339; *C. R.* 104, 1577). H.F. (from diamond) 137,700 (B. a. L.); 132,000 (Stohmann, *J. pr.* [2] 45, 336). Occurs in wood-tar as dimethyl ether.

Formation.—1. By heating gallic acid (alone or mixed) with pumice stone (2 pts.) (Braconnot, *A.* 1, 26; Pelouze, *A.* 10, 159; Liebig, *A.* 101, 47).—2. By heating di-iodo-*o*-oxy-benzoic acid with KOHAq (Lautemann, *A.* 120, 299).—3. By heating (α)- or (β)- chloro-phenol sulphonic acid with KOH at 190° (Petersen a. Baehr, *A.* 157, 136).—4. By heating gallic acid (10 g.) with glycerin (30 c.c.) at 200° as long as CO_2 comes off (Thorpe, *Ph.* [3] 11, 990).—5. By heating gallic acid (1 pt.) with aniline (2 pts.) at 120° (Cazeneuve, *Bl.* [3] 7, 549). The product is aniline pyrogallate $C_6H_6O_32NPhH_2$ [56°], which gives off aniline when exposed to air, or when shaken with benzene.

Properties.—Prisms, v. sol. water, m. sol. alcohol and ether. Tastes bitter. Poisonous (Personne, *Z.* [2] 5, 728). Its alkaline solution rapidly absorbs oxygen, turning brown, and giving off a little CO in bulk about $\frac{1}{30}$th of the oxygen absorbed (Calvert a. Cloez, *A.* 130, 248). Reduces $KMnO_4$ (Monier, *C. R.* 46, 577) and salts of mercury, Ag, Au, and Pt. $FeSO_4$ gives a white milkiness, but if a ferric salt is present, or the pyrogallol solution has become slightly oxidised by keeping, $FeSO_4$ gives an indigo-blue colour, changing to brownish-red on standing and on adding HCl (Jacquemin, *C. R.* 77, 593; Cazeneuve, *Bl.* [2] 44, 114; *C. R.* 101, 56). $FeCl_3$, in absence of air, gives a transient blue colour, restored by cautious addition of alkali. A solution of pyrogallol renders borax slightly acid (Lambert, *C. R.* 108, 1017). Nitrous acid colours the aqueous solution brown (Schönbein, *Fr.* 1, 319). K_2CrO_4 and H_2SO_4 give a dark colour. Reduces $CuSO_4$ and, on addition of alkalis, gives a black colour changed by NH_3 to red. $Cu(OAc)_2$ gives at once a black colour. Pyrogallol fused with ammonium oxalate yields ammonium rufigallate, which dissolves in water with red colour and gives with K_3FeCy_6 and $K_2Cr_2O_7$ a dark-brown pp. insol. alcohol (Kliebahn, *Fr.* 26, 641). A solution of iodine in presence of Na_2SO_4 gives a purple colour (Nasse, *B.* 17, 1166). A solution of $HgCl_2$ and pyrogallol in alcohol gives a black pp. with alkaloids but not with glucosides (Schlagdenhaufen, *Ph.* [3] 4, 772). An alkaline solution of pyrogallol absorbs about 50 vols. of NO in 12 hours, but no N_2O (Russell a. Lapraik, *C. J.* 32, 35). Pyrogallol does not react with hydroxylamine (Baeyer, *B.* 19, 163). A solution of potassium pyrogallate which is absorbing oxygen in contact with alumina gives out a feeble light, especially in presence of Na_2S (Lenard a. Wolf, *P.* [2] 34, 918).

Reactions.—1. Fuming HNO_3 forms oxalic acid.—2. *Bromine* forms tri-bromo-pyrogallol.—3. *Chlorine* in presence of HOAc forms mairogallol (vol. iii. p. 165) and crystalline leucogallol $C_{18}H_6Cl_{12}O_{12}2aq$, which yields tri-chloro-pyrogallol when boiled with water and zinc-dust (Stenhouse a. Groves, *C. J.* 28, 706; Webster, *C. J.* 45, 208; Hantzsch a. Schniter, *B.* 20, 2033).—4. *Ozone* passed through a solution of pyrogallol (1 mol.) and KOH (3 mols.) in water forms a syrupy acid $C_6H_6O_7$, which yields $BaC_6H_4O_7$ (Boeke, *B.* 6, 486).—5. Purpurogallin or pyrogalloquinone is formed by *oxidation* by alcoholic $AgNO_3$, by $KMnO_4$ and H_2SO_4, or by excess of $FeCl_3$ (Girard, *C. R.* 69, 865). It is also got from pyrogallol and quinone (Wichelhaus, *B.* 5, 847; Nietzki, *B.* 20, 1278). It forms garnet-red needles (by sublimation), sl. sol. water, m. sol. alcohol and ether, forming yellow solutions. Alkalis impart a transient blue colour. Purpurogallin dyes cotton mordanted with alumina violet-blue. When an aqueous solution of pyrogallol is mixed with gum arabic and exposed to the air, purpurogallin $C_{20}H_{16}O_9$ separates, the yield in the course of two months being 67 p.c. of the pyrogallol used (Struve, *A.* 163, 160; De Clermont a. Chautard, *C. R.* 94, 1189, 1254). A solution of pyrogallol and Na_2HPO_4 also yields pyrogalloquinone on exposure to air (Loew, *J. pr.* [2] 15, 322). Purpurogallin forms $C_{20}H_{12}Ac_4O_9$ and $C_{20}H_{12}Br_4O_9$.—6. An ammoniacal solution exposed to the air forms brown pyrogalleïn $C_{18}H_{20}N_6O_{10}$ (Rösing, *J.* 1858, 259).—7. *Ammonium carbonate* at 130° forms pyrogallol carboxylic acid $C_7H_6O_5$ (*v.* TRI-OXY-BENZOIC ACID) and pyrogallol dicarboxylic acid $C_8H_6O_7$ [270°] (Senhofer a. Brünner, *M.* 1, 468).—8. Distillation over zinc-dust yields benzene.—9. $ClCO_2Et$ acting on the K salt forms $C_9H_8O_4$ [105°] converted by aniline into di-phenyl-urea and the mono-ethyl ether of pyrogallol (Bender, *B.* 13, 698).—10. A few drops of $POCl_3$ added to a mixture of pyrogallol (2 pts.) and acetone (1 pt.) react violently, forming gallacetonin $C_9H_{10}O_3$, which crystallises from 15 p.c. alcohol in whetstone-shaped crystals, insol. water, decomposing about 250°, and yielding $C_9H_9AcO_3$ (Wittenberg, *J. pr.* [2] 26, 76). Its solutions are turned purple by $FeCl_3$ and reduce $AgNO_3$.—11. A few drops of H_2SO_4 added to a mixture of pyrogallol (12 g.) and acetoacetic ether (8 g.) form di-oxy-methyl-coumarin $C_{10}H_8O_4$, which crystallises from water in needles [235°] and yields $C_{10}H_6Ac_2O_4$ [176°] (Wittenberg, *J. pr.* [2] 26, 68; Pechmann, *B.* 16, 2127; 17, 2188).—12. *Phthalic anhydride* forms, on heating, $C_{20}H_{10}O_7$ (Baeyer, *B.* 4, 457, 663; *A.* 209, 261).—13. *Phenyl cyanate* at 100° forms $C_6H_3(O.CO.NHPh)_3$ [173°] crystallising in minute needles (Snape, *C. J.* 47, 774).—14. *Cyanogen* passed into an aqueous solution forms $C_6H_6O_3Cy$, or a polymeride thereof, as an unstable crystalline pp. (Loew, *J. pr.* [2] 15, 326).—15. *Chloro-acetic acid* (2½ pts.) followed by NaOHAq forms $C_6H_3(O.CH_2.CO_2H)_3$ crystallising in needles [198°], S. 1·3 at 14·5° and yielding K_3A''' and $KH_2A'''aq$ (Giacosa, *J. pr.* [2] 19, 398).—16. *Benzotrichloride* at 160° yields 'pyrogallol-benzeïn' $C_{38}H_{24}O_{11}$, crystallising in minute red plates with green lustre forming a blue solution in alkalis and a bluish-violet solution in alcohol. Zinc and HOAc reduce it to the anhydride of hexa-oxy-diphenyl-methane. Pyrogallol-benzeïn yields $C_{38}H_{20}Ac_4O_{11}$ [208°], $C_{38}H_{20}Bz_4O_{11}$ [251°], $C_{38}H_{20}O_{11}(C_5H_9O)_4$ [228°] (Döbner a. Förster, *A.* 257, 60).—17. *Benzoic acid* and $ZnCl_2$ at 145° form tri-oxy-benzophenone (*Alizarin yellow A*) $C_6H_2(OH)_3.CO.C_6H_5$ [141°], which crystallises with aq. The same body is got by heating pyrogallol with benzotrichloride (*G. P.* 50,451 [1889] and 54,661 [1890]; Graebe a. Eichengrün, *A.* 269, 297).—18. On heating pyrogallol with *salicylic acid* and zinc chloride tetra-oxy-benzophenone $C_6H_4(OH).CO.C_6H_2(OH)_3$ [149°] is formed (G. a. E.). 19. Ac_2O forms $C_{10}H_{10}O_4$ [280°] crystallising in white prisms (Causse, *Bl.* [3] 3, 867). Fuming HClAq at 170° forms $C_{21}H_{14}O_7$ as a black powder, sol. NaOHAq (Böttinger, *A.* 202, 280).—20. *Benzene sulphonic chloride* added to a solution of pyrogallol kept slightly alkaline forms $C_6H_3(O.SO_2Ph)_3$ [142°], sol. alcohol, sl. sol. ether (Georgesen, *B.* 24, 418).—21. *Formic aldehyde* and dilute HClAq form $CH_2(C_6H_2(OH)_3)_2$, a microcrystalline powder, insol. water, sol. alcohol (Caro, *B.* 25, 947).—22. *Aldehyde* and dilute H_2SO_4 mixed with Na_2SO_4 added slowly at 60° gives colourless crystals of $C_8H_8O_3\,2aq$, which when dried at 30° over H_2SO_4 leaves violet $C_8H_8O_3\,aq$ (Causse, *Bl.* [3] 3, 865; *cf.* Michael a. Ryder, *Am.* 9, 133).—23. *Benzoic aldehyde* and a large quantity of HClAq form amorphous $C_{26}H_{22}O_7$ (Baeyer, *B.* 5, 280). Benzoic aldehyde, alcohol, and a little conc. HClAq form a pp. of $C_{26}H_{20}O_6$, which yields $C_{26}H_{14}Ac_6O_6$ (Michael a. Ryder, *Am.* 9, 130). On heating with benzoic acid alone pyrogallol forms resinous $C_{26}H_{22}O_7$ and red $C_{26}H_{16}O_7$, which may be reduced to colourless $C_{26}H_{22}O_7$ (Baeyer, *B.* 5, 25). 24. KOH (33 pts.) and $K_2S_2O_8$ (70 pts.) heated

with water (33 pts.) and pyrogallol (25 pts.) at 70° form $C_6H_3(OH)_2(O.SO_3K)$, crystallising in needles, v. e. sol. water (Baumann, *B.* 11, 1913).—25. $ClCONH_2$ forms $C_6H_3(O.CO.NH_2)_3$. [178°], crystallising from alcohol in plates.

Salts.—$C_6H_3(OH)_2(ONH_4)$. Crystals, got by passing NH_3 into an ethereal solution of pyrogallol (De Luynes, *A. Suppl.* 6, 252).—$C_6H_3(OH)(O_2Pb)$ aq. Crystalline pp. got by adding lead nitrate to ammonium pyrogallol. Converted by conc. NH_3Aq into $C_6H_6O_3 3PbO$.—$(C_6H_5O_3)Pb.OAc$. Ppd. by adding lead acetate to a solution of pyrogallol (Deering, *C. J.* 26, 702).—$C_6H_5(SbO)O_3$. Plates, got by ppg. pyrogallol solution with tartar-emetic (Rösing). $SbCl_3$ (100 g.) dissolved in a saturated solution (250 c.c.) of NaCl, filtered, and slowly added to pyrogallol (50 g.) dissolved in saturated NaClAq (250 g.), forms a white pp. which changes to crystals of $C_6H_3(OH){<}\substack{O\\O}{>}SbOH\,2aq$, insol. water and alcohol, sol. mineral acids (Causse a. Bayard, *Bl.* [3] 7, 794). At 100° the above liquids on mixing yield $C_6H_3O_3Sb$, which is also crystalline, whence Ac_2O at 100° forms $C_6H_3O_3Ac_3$. AcCl in Ac_2O converts both antimonites into $C_6H_3(OAc)_3$.—$C_6H_6O_3 2NPhH_2$. [56°] (Mylius, *B.* 19, 1003).

Acetyl derivative $C_6H_3(OAc)_3$. Got from pyrogallol and AcCl (Nachbauer, *A.* 107, 244).

Benzoyl derivative $C_6H_3(OBz)_3$. [90°]. Got, together with a mono- or di- benzoyl derivative [131·5°], from pyrogallol and BzCl (Skraup, *M.* 10, 391).

Di-methyl ether $C_6H_3(OH)(OMe)_2$. [52°]. (253°). Occurs in beech-wood creosote (Hofmann, *B.* 11, 333; 12, 1373). Formed from pyrogallol (1 mol.), KOH, and MeI (2 mols.) at 160°. Prisms (from water). Its alkaline solution does not turn brown in air. Oxidised by means of $K_2Cr_2O_7$ and HOAc to cœrulignone $C_{12}H_4O_2(OMe)_4$. Yields $C_6H_3(OAc)(OMe)_2$ as a sticky mass, and $C_6H_3(OBz)(OMe)_2$ [118°].

Tri-methyl ether $C_6H_3(OMe)_3$. [47°]. (235°). Formed by the action of MeI and KOH on pyrogallol dissolved in MeOH (Will, *B.* 21, 607). Needles, insol. water and alkalis, v. sol. alcohol and ether. Yields $C_6Br_3(OMe)_3$ [81°]. Conc. HNO_3 forms $C_6H_2(NO_2)(OMe)_3$ [100°] and the di-methyl derivative of dioxyquinone.

Mono-ethyl ether $C_6H_3(OH)_2(OEt)$. [95°]. Formed, together with the di- and tri-ethyl ethers, by heating pyrogallol with KOH and $KEtSO_4$ at 100° (Benedikt, *B.* 9, 125; *M.* 2, 212; Hofmann, *B.* 11, 797). Needles, m. sol. water, v. e. sol. alcohol and ether. $FeSO_4$ gives a bluish-violet colour. Volatile with steam.

Di-ethyl ether $C_6H_3(OH)(OEt)_2$. [79°]. (262°). Crystals (from dilute alcohol). Oxidised by $K_2Cr_2O_7$ and HOAc to ethyl-cœrulignone. Nitrous acid passed into an ethereal solution forms $C_{20}H_{24}O_6HNO_3$, which forms a brown solution in water.

Tri-ethyl ether $C_6H_3(OEt)_3$. [89°]. Got from pyrogallol, alcoholic potash, and EtI (Herzig a. Zeisel, *M.* 10, 151). Needles, insol. KOHAq.

Ethylene ether $C_6H_3(OH):O_2:C_2H_4$. (267°). Formed from pyrogallol, alcoholic potash, and ethylene bromide (Magatti, *B.* 12, 1860). Yields $C_6H_3(OBz):O_2C_2H_4$ [109°].

References.—Amido-, Bromo-, Chloro-, and Nitro- pyrogallol.

PYROGALLOL CARBOXYLIC ACID *v.* Gallic acid.

Pyrogallol dicarboxylic acid $C_6H(OH)_3(CO_2H)_2[1:2:3:4:5]$. *Gallocarboxylic acid.* [270°]. S. ·05 at 0°. H.C. 633,700. H.F. 231,300 (Stohmann, *J. pr.* [2] 40, 128). Formed by heating pyrogallol or gallic acid with ammonium carbonate at 130° (Senhofer a. Brunner, *M.* 1, 468). Needles (containing 3aq), sl. sol. cold water. Gives a violet colour with $FeCl_3$.—K_2A'' 2aq: needles. — BaA''aq. — CaA'' 6aq. — Ag_2A''.

PYROGALLOL SULPHONIC ACID $C_6H_6SO_6$ *i.e.* $C_6H_2(OH)_3.SO_3H$ ½aq. Formed by dissolving pyrogallol in H_2SO_4 (Personne, *Bl.* [2] 12, 169; 20, 531; Schiff, *A.* 178, 179). Hygroscopic crystals.—KA' 2aq: prisms, v. sol. water. Converted by heating with $POCl_3$ into $C_{12}H_{10}S_2O_{11}$, a flocculent mass, v. sol. alcohol, which is converted by warming with HOAc and Ac_2O into crystalline $C_{12}H_5Ac_5S_2O_{11}$ and $C_{12}H_6Ac_4S_2O_{11}$.

PYROGALLOQUINONE *v.* Pyrogallol, *Reaction* 5, and Purpurogallin.

PYROGENTISIC ACID is Hydroquinone.

PYROGLUTAMIC ACID is Oxy-tetramethenyl dihydride carboxylic acid.

PYROGLYCERIN *v.* Diglycerin.

PYROGUAIACIN $C_{18}H_{18}O_3$ *i.e.* $C_{18}H_{16}O(OH)_2$. [180·5°]. (258°) at 80–90 mm. V.D. 9·53 (calc. 9·76). A product of the distillation of gum guaiacum (Pelletier a. Deville, *C. R.* 17, 1143; Ebermaier, *J. pr.* 62, 291; Nachbauer, *A.* 106, 382; Hlasiwetz, *A.* 106, 381; 119, 277; Wieser, *M.* 1, 594). Plates, v. sl. sol. hot water, sl. sol. alcohol and ether. Forms a blue solution in H_2SO_4. On distillation with zinc-dust it yields guaiene $C_{12}H_{12}$ [100°], which is converted by oxidation into a lemon-yellow quinone $C_{12}H_{10}O_2$ [121°]. Potash-fusion forms $C_{12}H_{12}O_2$ [202°], which is reduced by zinc-dust to guaiene. Pyroguaiacin yields $C_{18}H_{16}Ac_2O_3$ [122°], $C_{18}H_{16}Bz_2O_3$ [179°], $C_{18}H_{15}Br_3O_3$ [172°], and the salt $C_{18}H_{16}K_2O_3$.

PYROLIC ACID *v.* Sebacic acid.

PYRO-MECAZONIC ACID $C_5H_5NO_3$. Formed by heating oxycomenic acid, with NH_3Aq and also, in small quantity, along with the isomeric amido-pyro-meconic acid, by the reduction of nitro-pyromeconic acid. Prepared from oxy-pyro-mecazonic acid by reducing with HI (Ost, *J. pr.* [2] 19, 203; 23, 441; 27, 258).

Properties.—Streaked trimetric tablets. Combines with mineral acids, but not with acetic acid. Gives rise to a di-acetyl derivative [155°] and a bromo- derivative $C_5H_4BrNO_3$. Is stable in acid solutions, but soon turns brown in alkaline solution. Gives a blue colour with $FeCl_3$. $BaCl_2$ and NH_3 give a pp. which turns bright blue in air.

Reactions.—1. Suspended in ether and mixed with HNO_3 forms 'pyromecazone' $C_5H_3NO_3$. Pyromecazone is a brick-red powder, insol. ether, v. sol. water, gives no colour with $FeCl_3$, and turns the skin violet. With $BaCl_2$ and NH_3 it gives, on exposure to air, a crimson pp. Crystallises from alcohol as $C_5H_3NO_3$,EtOH. Aqueous SO_2 converts pyromecazone back into pyromecazonic acid. These properties resemble those of a quinone.—2. Suspended in HOAc and treated with HNO_3 it forms yellowish prisms of nitro-pyromecazone $C_5H_4(NO_2)NO_3$ aq. This body is decomposed by water at 30° into nitro-pyro-mecazonic acid $C_5H_4(NO_2)NO_3$, CO_2 coming off through oxidation of some of the substance. SO_2 rapidly changes nitro-pyromecazone into nitro-pyromecazonic acid, so that the former resembles quinone in its ready reducibility. Nitro-pyromecazonic acid gives a blood-red colour with $FeCl_3$, nitro-pyromecazone gives no colour with $FeCl_3$. It yields the salt $C_5H_3NaN_2O_5$.

Salt.—HA'HClaq: needles.

Oxypyromecazonic acid $C_5H_5NO_4$. Formed by passing SO_2 into an ethereal solution of nitrosopyromeconic acid, and boiling the product (*v. Nitroso*-PYROMECONIC ACID) with $CHCl_3$ (Ost, *J. pr.* [2] 19, 177). Needles (containing aq or 2aq). Coloured dirty-violet by $FeCl_3$.—NaHA'$_2$.—KHA'$_2$.—TlHA'$_2$.—CaA'$_2$.—HA'HCl.

PYROMECONIC ACID $C_5H_4O_3$. [117°]. (225° uncor.).

Preparation.—By distillation of meconic acid in a current of CO_2, some comenic acid being also formed (Ost, *J. pr.* [2] 19, 182; 23, 441; *cf.* Robiquet, *A.* 5, 90; *A. Ch.* [2] 5, 282; 51, 236; Stenhouse, *P. M.* [3] 24, 128; *A.* 49, 18; F. D. Brown, *P. M.* [4] 4, 161; 8, 201; *A.* 84, 32; 92, 321; Ihlée, *A.* 188, 31). The yield is 14 p.c.

Properties.—Glittering prisms from water or alcohol. V. sol. chloroform, much less sol. ether. Gives a blood-red colour with $FeCl_3$. Feeble acid. Does not react with hydroxylamine (Oderheimer, *B.* 17, 2081). Bromine forms $C_5H_3BrO_3$, crystallising in prisms and yielding PbA'$_2$ aq. Excess of Br yields $C_4H_3BrO_3$ aq [109°]. ICl forms $C_5H_3IO_3$ yielding BaA'$_2$ aq and PbA'$_2$.

Salts.—Forms two series of unstable salts, alkaline to litmus: KA'.—HNaA'$_2$.—BaA'$_2$ 3aq.—BaH$_2$A'$_4$.—CaA'$_2$ aq.—CaH$_2$A'$_4$.—MgA'$_2$.—SrA'$_2$ aq.—PbA'$_2$.—FeA'$_3$.—CuA'$_2$.—$C_5H_4O_3$,HCl. Formed by passing HCl into ethereal solution of the acid. Decomposed into its constituents by water or alcohol. **Sulphates** $C_5H_4O_3.H_2SO_4$ and $(C_5H_4O_3)_2H_2SO_4$. Got by adding H_2SO_4 to an ethereal solution (Ost, *J. pr.* [2] 19, 189).

Acetyl derivative $C_5H_3AcO_3$. [91°]. Obtained by warming with AcCl.

Nitroso-pyro-meconic acid $C_5H_3(NO)O_3$. An unstable compound of this body with an equivalent of pyro-meconic acid is formed by passing N_2O_3 into an ethereal solution of that acid (Ost, *J. pr.* [2] 19, 195). An aqueous solution of SO_2 converts this compound by addition of H_2 into $C_5H_5(NO)O_3,C_5H_4O_3$, a compound which is split up by boiling chloroform, leaving so-called *oxy-mecaronic acid*, $C_5H_5NO_4$. This acid gives a violet colour with $FeCl_3$, and a blue pp. with $BaCl_2$ and NH_3. By Sn and HCl it is reduced to *pyro-mecaronic acid* $C_6H_5NO_2$.

References.—AMIDO- and NITRO-PYROMECONIC ACID.

PYROMELLIC ACID $C_{10}H_6O_8$. [238°]. Obtained in the electrolysis of aqueous KOH with carbon electrodes, and got also by oxidation of mellogen by KOCl (Bartoli a. Papasogli, *G.* 12, 113; 13, 51). Crystalline (containing 2aq), sol. water and alcohol. Yields the crystalline salt $C_{10}H_2Na_4O_8$ and an ethyl ether crystallising in colourless needles [below 100°], insol. water.

PYROMELLITIC ACID $C_{10}H_6O_8$ *i.e.* $C_6H_2(CO_2H)_4$[1:2:4:5]. Mol. w. 254. [264°]. S. 14·2 at 16°. H.C.p. 777,400 (Stohmann, *J. pr.* [2] 40, 140; 43, 540). H.C.v. 778,900. H.F. 369,600. Formed by gently distilling mellitic acid (Erdmann, *A.* 80, 281) and by oxidising *s*-durene (Jacobsen, *B.* 17, 2517). Crystallises from water in triclinic tables (containing 2aq), v. sol. hot water. Forms various compounds on heating with (*a*)-naphthol (Grabowski, *B.* 4, 726; 6, 1065).—Ca$_2$A^{iv} 6aq.—Pb$_2$A^{iv}aq.—Ag$_4$A^{iv}: pp.

Methyl ether Me$_4$A^{iv}. [138°]. Plates, sl. sol. hot alcohol (Baeyer, *A.* 166, 339).

Ethyl ether Et$_4$A^{iv}. [53°]. Formed from the Ag salt and EtI (Baeyer, *A. Suppl.* 7, 36). Needles (from alcohol).

Chloride $C_6H_2(COCl)_4$. Got by heating the acid with PCl_5. Crystalline mass, v. sol. ether.

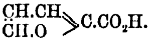
Anhydride $C_6H_2(C_2O_3)_2$. [268°]. Got by distilling the acid. Needles (by sublimation), v. sol. hot water, being re-converted into the acid.

Tetrahydride $C_6H_6(CO_2H)_4$. Formed by the action of sodium-amalgam on the ammonium salt of pyromellitic acid (Baeyer). Amorphous hygroscopic mass, v. sol. water. When heated with H_2SO_4 it yields pyromellitic, trimellitic, and isophthalic acids.

Iso-tetrahydride $C_6H_6(CO_2H)_4$. [above 200°]. Accompanies the preceding acid. Needles (containing 2aq). Behaves like the preceding hydride when heated with H_2SO_4. Yields a methyl ether [156°] which may be distilled.

References.—AMIDO- and NITRO- PYROMELLITIC ACID.

PYROMUCIC ACID $C_5H_4O_3$ *i.e.*



$\begin{matrix}\text{CH.CH}\\\text{CH.O}\end{matrix}\!>\!\text{C.CO}_2\text{H}$. *Furfurane* (*a*)-*carboxylic acid.* Mol. w. 112. [132°]. S. 3·6 at 15°; 25 at 100°. R_∞ 40·18 (in a 2·19 p.c. aqueous solution).

Formation.—1. By the distillation of mucic acid (Houton-Labillardière, *A. Ch.* [2] 9, 365; Pelouze, *A.* 9, 273; Boussingault, *A.* 15, 184; Liès-Bodart, *A.* 100, 327).—2. By distilling dehydromucic acid (Heinzelmann, *A.* 193, 184).—3. By oxidation of furfuraldehyde by Ag_2O (Schwanert, *A.* 114, 63; 116, 257).—4. Together with furfuryl-carbinol by boiling furfuraldehyde with alcoholic potash (Ulrich, *Z.* 1861, 186; Schmelz a. Beilstein, *A. Suppl.* 3, 275; Limpricht, *A.* 165, 279).—5. By distilling iso-saccharic acid in a current of CO_2 (Tiemann a. Haarmann, *B.* 19, 1271).—6. Occurs, together with pyromycuric acid $C_7H_7NO_4$ [165°] which yields BaA'$_2$ 1½aq, in the urine of dogs dosed with furfuraldehyde (Jaffé a. Cohn, *B.* 20, 2311).

Preparation.—By oxidising furfuraldehyde with alkaline $KMnO_4$ below 20° (Volhard, *A.* 261, 379).

Properties.—Long white needles (by sublimation), v. sol. alcohol and ether. $FeCl_3$ gives no colour.

Reactions.—1. *Bromine* in excess forms mucobromic acid. Dry Br gives $C_5H_4Br_4O_3$ [160°], oxidised by dilute CrO_3 to di-bromo-pyromucic acid (Tönnies, *B.* 11, 1086).—2. Distillation with soda-lime yields furfurane.—3. On heating with lime and ammonia-zinc-chloride it yields pyrrole.

Salts.—KA': needles.—NaA'.—BaA'$_2$: crystals, sol. water and alcohol.—CaA'_2: crystalline powder.—CuA'_2 3aq.—PbA'_2 2aq.—AgA': scales.

Ethyl ether EtA'. [34°]. (209°). Laminæ, v. sol. alcohol and ether, insol. water (Malaguti, *A.* 25, 276). Combines with dry chlorine, forming $C_7H_6Cl_4O_3$. S.G. $\underline{19\cdot5}$ 1·496. Dry Br forms $C_7H_6Br_4O_3$ [48°] (Tönnies) and also the ethers of ($\beta\delta$)-di-bromo-pyromucic acid [167°], of ($\beta\gamma$)-di-bromo-pyromucic acid [192°] and of (δ)-bromo-pyromucic acid [183°] (Hill a. Sanger, *A.* 232, 65).

Chloride $C_5H_3O_2Cl$. (170°).

Amide $C_4H_3O.CONH_2$. [143°]. Formed from the ether or chloride and NH_3Aq (Wallach, *B.* 14, 751; 214, 227; Ciamician a. Dennstedt, *B.* 14, 1058; *G.* 11, 294). Large plates, sol. alcohol, sl. sol. ether. Converted by PCl_5 or P_2O_5 into the nitrile.

Ethylamide $C_4H_3O.CONHEt$. [258° cor.). Formed from pyromucic ether and ethylamine solution at 100°. Converted by PCl_5 into crystalline $C_4H_3O.CCl_2.NHEt$. PCl_5 in smaller quantity ($\frac{1}{3}$ pt.) forms the amidine $C_4H_3O.C(NEt).NHEt$, a liquid (240°) which gives $B'_2H_2PtCl_6$.

Anilide $C_4H_3O.CO.NHPh$. [123·5°]. Long needles (Schiff, *B.* 19, 849).

Nitrile $C_4H_3O.CN$. *Furfuryl cyanide.* (148°). Liquid with sweet taste, sl. sol. water, smelling like benzoic aldehyde. On reduction it gives $C_4H_3O.CH_2.NH_2$.

(β)-**Pyromucic acid**, got by oxidation of fucusol, is a mixture of pyromucic acid with methyl-pyromucic acid [108°] (Bieler a. Tollens, *A.* 258, 126).

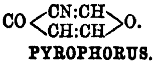
Isopyromucic acid. [82°]. Formed, together with pyromucic acid, in the distillation of mucic acid. It decomposes $BaCO_3$ very slowly, and can be separated by shaking the product with $BaCO_3$ and extracting with ether (Limpricht, *A.* 165, 256). Plates (by sublimation), v. e. sol. water, alcohol, and ether. $FeCl_3$ gives a green colour. Br yields mucobromic acid.

References. — BROMO-, BROMO-SULPHO-, CHLORO-, NITRO-, and SULPHO- PYROMUCIC ACIDS.

PYROMUCIC ALDEHYDE *v.* FURFURALDEHYDE.

PYROMYKURIC ACID $C_7H_7NO_4$. [165°]. Occurs in the urine of rabbits dosed with furfuraldehyde (Jaffé a. Cohn, *B.* 20, 2311). Prisms (from water). Split up by boiling baryta-water into glycocoll and pyromucic acid.—BaA'_2 $1\frac{1}{2}$aq: plates.—A urea compound $(C_7H_7NO_4)CO(NH_2)_2$ [120°] occurs in the urine of dogs fed with meat. It crystallises from benzene in needles, v. sol. water and alcohol, sl. sol. ether, and is decomposed by heating with $BaCO_3$ into urea and pyromykuric acid.

PYRONE. A name given to the ring



$$CO\left\langle\begin{matrix}CN{:}CH\\CH{:}CH\end{matrix}\right\rangle O.$$

PYROPHORUS. Any finely-divided substance which takes fire very easily when exposed to air is called a *pyrophorus*.

PYRORACEMIC ACID is PYRUVIC ACID.

PYROTARTARIC ACID $C_5H_8O_4$ *i.e.* $CO_2H.CHMe.CH_2.CO_2H$.

Methyl-succinic acid. Mol. w. 132. [115°]. S. 66 at 20°. S.H. ·3098 (from 0° to 50°) (Hess, *A. Ch.* [2] 35, 410). H.C.v. and p. 515,200 (Stohmann, *J. pr.* [2] 40, 209); 511,672 (Louguinine, *C. R.* 107, 597). H.F. 230,800 (S.).

Formation.—1. By dry distillation of tartar (Valentin Rose, *Gehlen's Journ.* 3, 598) and of tartaric and racemic acids (Gruver, *N. J. T.* 24, 2, 55; Pelouze, *A. Ch.* [2] 56, 297; Weniselos, *A.* 15, 148; Fourcroy a. Vauquelin, *A. Ch.* 35, 161; 64, 42; Arppe, *A.* 66, 73).—2. By the reduction of ita-, citra-, and mesa- conic acids and of dibromopyrotartaric acid with sodium-amalgam (Kekulé, *A. Suppl.* 1, 342; 2, 95).—3. By saponifying its nitrile with HClAq (Maxwell Simpson, *A.* 121, 161).—4. By heating powdered tartaric acid with HClAq at 180° (Geuther a. Riemann, *Z.* [2] 5, 318).—5. By potash-fusion from gamboge (Hlasiwetz a. Barth, *A.* 138, 73).—6. By heating pyruvic acid alone at 170° or with HClAq at 100°, or by boiling it with baryta. 7. By boiling β-acetyl-α- or β- methyl-succinic ether with potash (Conrad, *A.* 188, 217; Kressner, *A.* 192, 135).—8. By heating allyl iodide (1 mol.) with KCy (2 mols.) and a little alcohol, and boiling the resulting nitrile with KOHAq (Claus, *B.* 5, 612; 8, 100; *A.* 191, 38).—9. By heating propane tricarboxylic acid (Bischoff a. Guthzeit, *B.* 20, 614).—10. By oxidation of β-acetyl-*n*- and *iso*- butyric acid (Bischoff, *A.* 206, 337).

Properties.—Triclinic prisms grouped like frog's feet (from ether), v. sol. water, alcohol, and ether. Begins to boil at 200°, yielding an anhydride together with some butyric acid (Claus, *A.* 191, 48). Its solution is not ppd. by lime-water or lead acetate, but gives a pp. with lead subacetate.

Reactions.—1. *Bromine* acts very slowly in the cold, but when the acid (10 pts.) is heated with Br (24 pts.) and water (10 pts.) at 120° for 6 hours bromocitraconic anhydride is formed (Lagermark, *Z.* 6, 299). When the acid (1 mol.) is heated with Br (4 mols.) at 132° acetylene tetrabromide is formed (Bourgoin, *A. Ch.* [5] 12, 419).—2. The K salt yields, on electrolysis, O, CO, and CO_2 at the positive pole (Reboul a. Bourgoin, *C. R.* 84, 1231).—3. Distillation with P_2S_3 yields methyl-thiophene.—4. On heating the acid (5 pts.) with resorcin (9 pts.) and H_2SO_4 (18 pts.) at 150° there is formed pyrotartryl-fluoresceïn $C_{17}H_{16}O_6$, a brownish-red powder, sl. sol. water, v. sol. dilute acids and alkalis. Its dilute alkaline solutions fluoresce yellowish-green. It yields $C_{17}H_{12}Br_4O_6$ (Hjelt, *B.* 17, 1280).

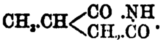
Salts.—K_2A'' aq: deliquescent. — KHA'': monoclinic prisms.—Na_2A'' 6aq: efflorescent laminæ.—$NaHA''$: small prisms.—$(NH_4)_2A''$: deliquescent; gives off NH_3 on evaporation, leaving $(NH_4)HA''$, which crystallises from water in prisms, permanent in the air.—BeA''.—$BeH_2A''_2$. —CaA'' 2aq: powder. S. 1 at 100°.—$CaH_{10}A''_6$ 2aq. — SrA'' aq. — SrA'' 2aq. — $SrH_2A''_2$ 2aq. — BaA'' 2aq. — $BaH_2A''_2$ aq. — $BaH_2A''_2$ 2aq. — $BaH_2A''_2$ 3aq. — $BaH_2A''_2$ 4aq. — MgA'' 3aq. — MgA'' 6aq. — $Al(OH)A''$. — $Bi_4A''_3(HO)_4O$. — CdA'' 3aq.—CdA'' 2aq.—MnA'' 3aq.—CuA'' 2aq. —$Cu_2(OH)_2A''$. —$Fe(OH)A''$ 2aq.—PbA'' 2aq.—$Pb_3A''O_2$.—NiA'' 2aq.—$NiH_4A''_3$ 2aq.—ZnA'' 3aq. —Ag_2A'': white curdy pp., blackened by light.

Ethyl ether Et_2A''. (218° cor.). S.G. $\frac{15}{15}$ 1·0189; $\frac{25}{25}$ 1·0113. M.M. 9·347 at 17·4° (Perkin, *C. J.* 45, 516; *cf.* Malaguti, *A.* 25, 274).

Chloride $C_5H_6O_2Cl_2$. (190°–193°) (Hjelt, *B.* 16, 2624). Reduced in ethereal solution by sodium-amalgam and HOAc to liquid $C_5H_8O_2$, (204°), S. 20, which is the anhydride of an acid $C_5H_{10}O_3$.

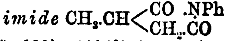
Anhydride $C_5H_6O_3$. (245° cor.) (Lebedeff, *A.* 182, 327). Got by heating the acid at 200° alone or with P_2O_5. Heavy oil, slowly converted by water into the acid.

Amide $CH_3.CH(CO.NH_2).CH_2.CONH_2$. [175°]. S. 7 at 10°. Large plates (Henry, *C. R.* 100, 943).

Imide  $CH_3.CH<\begin{matrix}CO.NH\\CH_2.CO\end{matrix}$. [66°]. Formed by heating acid ammonium pyrotartrate (Arppe, *A.* 87, 228). Six-sided trimetric plates, sol. water, alcohol, and ether.

Di-methylamide $C_3H_6(CO.NHMe)_2$. [115°] (Henry, *Bl.* [2] 43, 619).

Mono-anilide $CO_2H.CH_2.CHMe.CONHPh$. [147°]. Formed from aniline and pyrotartaric anhydride in chloroform (Arppe, *A.* 90, 141; Anschütz, *A.* 246, 122). Got also by reducing the anilide of mesaconic acid with sodium-amalgam. Is identical with Reissert's 'pyranil-pyroic lactone dihydride.' Bulky needles, m. sol. water.—PbA'_2: white pp.—AgA'.

Phenyl-imide  $CH_3.CH<\begin{matrix}CO.NPh\\CH_2.CO\end{matrix}$. [98°] (Arppe, *A.* 90, 139); [104°] (Biffi, *A.* 91, 105). Formed by heating the acid with aniline at 100° for ten minutes. Minute needles.

p-Nitro-anilide $C_3H_6(CO_2H)(CO.NH.C_6H_4NO_2)$. [above 150°]. Formed by boiling the *p*-nitro-phenyl-imide with Na_2CO_3Aq. Minute tables, v. sl. sol. hot water.—AgA': white pp.

p-Nitro-phenyl-imide $C_3H_6:C_2O_2:NC_6H_4NO_2$. [155°]. Formed by nitrating the phenyl-imide. Needles (from alcohol), almost insol. water.

p-Bromo-anilide $C_3H_6(CO_2H).CO.NHC_6H_4Br$. [158°]. Formed from the anhydride and *p*-bromo-aniline (Anschütz a. Hensel, *A.* 248, 269).

Di-bromo-anilide $C_3H_6(CO_2H).CO.NHC_6H_3Br_2$[1:2:4]. [139°].

Nitrile $CH_3.CH(CN).CH_2CN$. [c. 12°]. (254°). Formed, amongst other products, by the action of KCN on allyl chloride (Pinner, *B.* 12, 2053). Prisms. Prepared from propylene bromide and alcoholic KCy at 100° (Maxwell Simpson, *A.* 121, 160). Liquid, sol. water, alcohol, and ether.

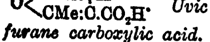
Ethyl ether of the seminitrile $CO_2Et.CH_2.CHMe.CN$. (198). S.G. $\underline{^{24\cdot5}}$ 1·0275. V.D. 4·6. Formed from α-bromo-propionic ether and alcoholic KCy (Zelinsky, *B.* 21, 3162). Oil. —NaA': very hygroscopic.

References.—BROMO-, CHLORO-, IODO-, OXY-AMIDO-, and OXY- PYROTARTARIC ACID.

***n*-Pyrotartaric acid** *v.* GLUTARIC ACID.

Isopyrotartaric acid *v.* DI-METHYL-MALONIC ACID.

PYROTEREBIC ACID *v.* HEXENOIC ACID.

PYROTRITARIC ACID $C_7H_8O_3$ *i.e.*  $O<\begin{matrix}CMe:CH\\CMe:C.CO_2H\end{matrix}$. *Uvic acid. Di-methyl-fur-furane carboxylic acid.* Mol. w. 140. [135°]. S. ·25 at 100°. A product of the distillation of tartaric acid (Wislicenus a. Stadnicki, *A.* 146, 306). Prepared by heating pyruvic acid with NaOAc and Ac_2O at 140°, the yield being 20 p.c. (Böttinger, *B.* 13, 1969; *A.* 172, 241; 208, 122; 247, 255), by heating pyruvic acid (30 g.) with dry sodium succinate (55 g.) at 110° (Fittig a. Parker, *A.* 267, 212), and by heating pyruvic acid (17·5 g.) with dry potassium propionate (20 g.) at 140° (Bischoff, *B.* 24, 2021). Formed also by heating methronic acid as long as CO_2 is given off (Fittig, *A.* 250, 190; *cf.* Harrow, *C. J.* 33, 425). Needles (from hot water), nearly insol. cold water, v. sol. alcohol and ether. Not affected by potash-fusion. PCl_5 gives a chloride, reconverted by water into the acid. Does not react with hydroxylamine or phenyl-hydrazine. Water at 160° forms acetonyl-acetone. By bromine it is converted into a tetra-bromo-derivative and its tetra-bromide, which are both reduced back to pyrotritaric acid by sodium-amalgam. An excess of bromine at 100° forms penta-bromo-pyrotritaric acid. By dry distillation it gives di-methyl-furfurane, a substance which is also obtained by distilling acetonyl-acetone with $ZnCl_2$ (Paal, *B.* 20, 1074; Dietrich a. Paal, *B.* 20, 1077).

Salts.—NaA' 2aq.—CaA'_2 2aq: prisms.—CaA'_2 4aq.—CaA'_2 6aq.—BaA'_2 4aq: plates.—BaA'_2 2aq.—BaA'_2 5aq.—ZnA'_2 8aq.—AgA'.

Methyl ether MeA'. (192°). Got by distilling the Ag salt of carbopyrotritaric monomethyl ether (Knorr a. Cavallo, *B.* 22, 156).

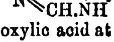
Ethyl ether EtA'. (208°).

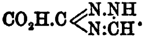
Pyrotritaric carboxylic acid *v.* METHRONIC ACID.

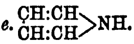
Carbopyrotritaric acid *v.* DI-METHYL-FURFURANE CARBOXYLIC ACID.

PYROXANTHIN $C_{15}H_{12}O_3$. [162°]. Extracted by NaOHAq from the product of the dry distillation of wood (Scanlan, *J. pr.* 7, 94; Gregory, *A.* 21, 143; Hill, *Am.* 3, 332; *B.* 11, 456). Orange needles (from alcohol), sol. benzene and HOAc. Forms a purple solution in H_2SO_4. Reduced by zinc-dust and HOAc to a colourless body. Bromine forms $C_{15}H_{10}Br_6O_3$ crystallising in small colourless triclinic needles, converted by alcohol and powdered Sb into $C_{15}H_{10}Br_2O_3$, crystallising in yellow monoclinic needles, v. sol. hot alcohol.

PYROXYLIN *v.* CELLULOSE.

PYRRODIAZOLE $C_2H_3N_3$ *i.e.*  $N\ll\begin{matrix}CH:N\\CH.NH\end{matrix}$. [121°]. Formed by heating its carboxylic acid at 120° (Andreocci, *B.* 25, 229). Needles, v. e. sol. water and alcohol.

Pyrrodiazole carboxylic acid  $CO_2H.C\ll\begin{matrix}N.NH\\N:CH\end{matrix}$. Formed by oxidising methyl-pyrrodiazole with alkaline $KMnO_4$. White crystalline powder, v. sl. sol. water, alcohol, and ether.

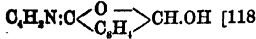
PYRROLE C_4H_5N *i.e.*  $\begin{matrix}CH:CH\\CH:CH\end{matrix}>NH$. *Pyrrhol. Pyrroline.* Mol. w. 67. (130° i.V.). S.G. $\underline{^{12\cdot5}}$ ·9752. S.V. 92·1 (Ramsay). H.F.p. 4,056 (Ramsay). Occurs among the products of distillation of coal (Runge, *P.* 31, 67) and of bones (Anderson, *Tr. E.* 20 [2] 247; 21 [4] 571; *A.* 80, 63; 105, 349).

Formation.—1. By distilling ammonium mucate alone or with glycerin at 190° (Schwanert, *A.* 116, 279; Goldschmidt, *Z.* [2] 3, 280).—2. By heating its carboxylic acid.—3. By distilling succinimide with zinc-dust (Chichester Bell, *B.* 13, 877).—4. By distilling ammonium saccharate (Bell a. Lapper, *B.* 10, 1962).—5. By heating di-chloro-maleic imide with PCl_5 at 200°, and reducing the resulting perchloride C_4Cl_7N with zinc-dust and HOAc (Ciamician a. Silber, *B.* 17, 554; 19, 3027). The dichloro-maleïc imide may be got from succinimide and PCl_5.—6. By reducing tetra-iodo-pyrrole with zinc-dust and KOHAq (C. a. S.).—7. By heating albumen with $Ba(OH)_2$ at 150° (Schützenberger, *Bl.* [2] 25, 289).—8. By distilling pyromucic acid with ammonia-zinc chloride and CaO (Canzoneri a. Oliveri, *G.* 16, 487).—9. By passing di-ethyl-amine through a red-hot tube (Bell, *B.* 10, 1868). 10. By passing ethyl-allyl-amine over PbO at 450° (Koenigs, *B.* 12, 2344).—11. By distilling glutamic acid (Haitinger, *M.* 3, 228).

Preparation.—Bone oil is shaken with acids and distilled. The fraction 98°–150° is heated with KOHAq and distilled, and the portion 125°–140° heated with solid KOH with inverted condenser. The solid C_4H_4NK thus obtained is washed with ether and decomposed by water, and the pyrrole distilled with steam (Ciamician, *B.* 13, 70; 19, 173; *G.* 16, 336).

Properties.—Oil with fragrant odour, resembling chloroform. Tastes hot and pungent. V. sol. alcohol and ether, insol. dilute alkalis. Turns brown in air. Turns pine-wood soaked in HClAq red. Dissolves in cold dilute acids, but on warming the solution pyrrole-red is formed as a bulky amorphous pp. $FeCl_3$ added to its solution in HClAq gives a green colour changing to black. Alcoholic $HgCl_2$ gives a white pp. Isatin and HOAc or dilute H_2SO_4 give a deep-blue pp. which forms a deep-blue solution in HOAc and H_2SO_4 (V. Meyer, *B.* 16, 2974; Ciamician, *B.* 17, 142).

Reactions.—1. HNO_3 forms oxalic acid.—2. *Potassium* acts very strongly, forming a colourless liquid, which solidifies on cooling to C_4H_4NK. Boiling with solid KOH gives the same body (Anderson, *A.* 105, 352). *Sodium* acts but slightly, forming C_4H_4NNa only at a very high temperature. NaOHAq has no action on pyrrole.—3. HCl passed into an ethereal solution ppts. crystalline $(C_4H_5N)_3HCl$, whence ammonia liberates an unstable base (Dennstedt a. Zimmermann, *B.* 21, 1478).—4. *Hydroxylamine* forms NH_3 and crystalline $C_4H_8N_2O_2$ [175°]. Converted by adding Na to its boiling alcoholic solution into tetramethylene-diamine (Ciamician, *G.* 14, 156; *B.* 22, 1968). The compound $C_4H_8N_2O_2$, when heated with phenyl-hydrazine, yields $C_{16}H_{18}N_4$, which crystallises from alcohol in plates [125°].—5. By a dilute solution of sodium hypochlorite (15 pts. of active chlorine in 1,000 pts. of water to 10 pts. of pyrrol) it is converted into di-chloro-maleic acid and chlorinated pyrroles. On the other hand, a concentrated solution of sodium hypochlorite (45 pts. of active chlorine in 500 pts. of water to 10 pts. of pyrrole) yields dichloro-acetic acid. An alkaline solution of bromine yields dibromomaleimide. Iodine in presence of alkalis yields tetra-iodo-pyrrol (Ciamician a. Silber, *B.* 17, 1743; 18, 1763).—6. Potassium pyrrole heated with ethyl iodide yields *ν*-ethyl-pyrrole, di-ethyl-pyrrole $C_4H_3Et{:}NEt$, and probably also $C_4H_3Et{:}NH$. Potassium pyrrole and benzyl-chloride yield *ν*-benzyl-pyrrole (247°) (Ciamician, *B.* 22, 659; *G.* 17, 135).—7. Pyrrole (50 g.), boiled with *paraldehyde* (50 g.) and $ZnCl_2$ (12 g.), forms oily ethyl-pyrrole C_6H_9N (164°) (Dennstedt a. Zimmermann, *B.* 19, 2189).—8. Pyrrole (1 pt.), *acetone* (10 pts.) and a drop of HCl give $C_{14}H_{18}N_2$ [291°], whence alcoholic $AgNO_3$ forms $(C_{14}H_{18}N_2)_2AgNO_3$, crystallising in needles (Baeyer, *B.* 19, 2184). The compound $C_{14}H_{18}N_2$ yields, on distillation, $C_{10}H_{13}N$ (275°–285°), which is probably mesityl-pyrrole, and whence Ac_2O and NaOAc form *ν*-acetyl-pyrrole. The compound $C_{14}H_{18}N_2$, examined by Raoult's method, appears to have the formula $C_{28}H_{36}N_4$. On heating pyrrole with acetone and $ZnCl_2$ isopropyl-pyrrole (174°) is formed. Among the products of the action of acetone on pyrrole there is also a yellow oil $C_{13}H_{17}N$ (?) (300°–305°), which soon blackens in air. This oil forms an acetyl derivative [above 360°], and is reduced by tin and alcoholic HCl to $C_{13}H_{19}N$ (274°), which yields B'HCl [228°] and $B'HSnCl_3$ [170°] (Dennstedt a. Zimmermann, *B.* 20, 850, 2449; 23, 1870).—9. *Di-ethyl ketone*, MeOH, and HCl give $C_{18}H_{26}N_2$ [210°], which yields B'_2AgNO_3, crystallising in needles (Dennstedt a. Zimmermann, *B.* 20, 2455).—10. *Chloroform* converts potassium pyrrole into (*β*)-chloro-pyridine. *Bromoform* acts in like manner, giving bromo-pyridine. CH_2Cl_2 has no action, but CCl_4 forms chloro-pyridine, while benzylidene chloride yields (*β*)-phenyl-pyridine (Ciamician, *B.* 14, 1160; 15, 1172; 20, 191; *G.* 16, 140).—11. Readily combines with diazo- compounds, forming azo- and disazo-bodies, but no compounds analogous to the diazoamides. Their constitution is probably $\mathrm{NH}\!\!<\!\!\begin{array}{l}\mathrm{C(N_2X){:}\underset{|}{C}H}\\ \mathrm{CH{=\!=}CH}\end{array}$ and $\mathrm{NH}\!\!<\!\!\begin{array}{l}\mathrm{C(N_2X){:}\underset{|}{C}H}\\ \mathrm{C(N_2X){:}CH}\end{array}$ (O. Fischer a. Hepp, *B.* 19, 2251).—12. Pyrrole (5 g.) added to a lukewarm solution of *alloxan* (11 g.) in water (300 c.c.) forms colourless crystals of $C_8H_7N_3O_4$ or $NH_2.CO.NH.CO.CO.CO.C_4H_3NH$, sl. sol. hot alcohol, nearly insol. water and ether, and yielding Ag_2A''. Pyrrole-alloxan is converted by caustic potash solution into $C_7H_6N_2O_3$ or $NH_2.CO.CO.CO.C_4H_3NH$, which crystallises in white plates, v. sol. warm alcohol, and yields AgA' and crystalline MeA' (Ciamician, *B.* 17, 106, 1711; 19, 1708; *G.* 16, 198, 357).—13. Pyrrole and MeOH distilled over zinc-dust yield (*α*)- and (*β*)- methyl-pyrrole, di-methyl-pyrrole, and di-methyl-dipyrrole (Dennstedt, *B.* 24, 2559).—14. *Acetyl chloride*, acting on potassium-pyrrole, forms *ν*-acetyl-pyrrole and pyrryl methyl ketone (pseudo-acetyl-pyrrole), which may be separated by steam-distillation. Ac_2O at 300° forms pyrrylene di-methyl diketone (Ciamician a. Silber, *G.* 15, 193).—15. *Propionic anhydride* and *sodium propionate* form, on boiling, *ν*-propionyl-pyrrole, pyrryl ethyl ketone, and pyrrylene di-ethyl diketone (Dennstedt a. Zimmermann, *B.* 20, 1760).—16. Bz_2O and NaOBz at 220° form pyrryl phenyl ketone (pseudo-benzoyl-pyrrole). 17. $COCl_2$ in benzene, added to C_4H_4NK in ether, forms $CO(NC_4H_4)_2$, separating from ligroïn in monoclinic crystals [63°] (238°) (Ciamician a. Magnaghi, *B.* 18, 415).—18. *Phthalic anhydride* and HOAc at 185° form $C_{12}H_7NO_2$ [241°], converted by Br into $C_{12}H_5Br_2NO_2$ [199°], and by boiling KOHAq into $C_{12}H_9NO_3$ [174°–184°], which yields MeA' [105°] (Ciamician, *B.* 17, 2957;

Anderlini, *B.* 21, 2869). The compound $C_{12}H_7NO_2$ is reduced by water and Na to  $C_4H_4N{:}C\left\langle{O\,- \atop C_6H_4}\right\rangle CH.OH$ [118°] (Ciamician, *B.* 19, 2206; 21, 1554).

Salts.—C_4H_4NK. Solid, absorbing CO_2 at 200°, forming pyrrole (β)-carboxylic acid.—$B'2HgCl_2$: crystalline powder, insol. water, sl. sol. cold alcohol.—$B'_4 3CdCl_2$.—B'ICl: black pp. (Dittmar, *B.* 18, 1612).—Picrate: [c. 71°]; unstable (Hooker, *B.* 21, 3299).

Acetyl derivative C_4H_4NAc. (182° i.V.). Formed by the action of AcCl on potassium-pyrrole suspended in ether, and also as a by-product in the preparation of pyrryl methyl ketone by heating pyrrole with Ac_2N and NaOAc (Ciamician, *B.* 16, 2348; 18, 881). Oil, volatile with steam, saponified by hot KOHAq. Reddens acidified pine-wood. Gives a pp. with aqueous $HgCl_2$.

Propionyl derivative $C_4H_4N.COEt$. (193°) (Dennstedt a. Zimmermann, *B.* 20, 1760).

Dihydride C_4H_7N. *Pyrroline.* (90° i.V.). Formed by reducing pyrrole with zinc-dust and HOAc (Ciamician a. Dennstedt, *B.* 16, 1536; 22, 2512; *G.* 15, 481). Hygroscopic liquid, v. sol. water. Yields a nitrosamine $C_4H_6N(NO)$ [38°]. Absorbs CO_2 from the air.—B'HCl. [174°]. Flat prisms, v. sol. hot alcohol.—$B'_2H_2PtCl_6$: triclinic crystals.—$B'HAuCl_4$ [152°].—$B'C_6H_3N_3O_7$. [156°]. Yellow crystals (from water). *Benzoyl derivative* C_4H_6NBz. (160° at 2 mm.). Syrup, formed from the hydrochloride and BzCl at 110°. V. sol. alcohol.

Tetrahydride C_4H_9N. *Pyrrolidine.* (88·5°). S.G. $^{22.5}$ ·8520. Formed by reducing the dihydride by HIAq at P at 250° (Ciamician a. Magnaghi, *G.* 15, 483; *B.* 18, 2079). Formed also, together with tetra-methylene-diamine, by the action of Na on ethylene cyanide or succinimide in alcohol, and by distilling tetramethylene-diamine hydrochloride (Ladenburg, *B.* 19, 782; 20, 442, 2215; Petersen, *B.* 21, 290). Formed from chlorobutylamine hydrochloride and KOHAq (Gabriel, *B.* 24, 3234). Liquid, with pungent ammoniacal odour. Yields a liquid nitrosamine (214°), v. sol. water.—$B'_2H_2PtCl_6$. [200°]. Prisms.—$B'HAuCl_4$. [206°].—$B'C_6H_3N_3O_7$. [112°].—$B'_3H_3Bi_2I_9$.—$B'H_2CdI_4$. [219°]. Needles.

Pyrrole red $C_{12}H_{14}N_2O$? Formed by boiling pyrrole or its carboxylic acid with dilute H_2SO_4 or HCl (Anderson, *A.* 105, 357; Schwanert, *A.* 116, 280). Reddish-brown flakes, insol. water, ether, acids, and alkalis, sl. sol. alcohol. Yields pyrrole on distillation.

Homopyrrole *v.* Methyl-pyrrole.

References.—Bromo-, Chloro-, Iodo, Nitro-, and Oxy-amido- Pyrrole.

PYRROLE - AZO- *v.* Azo- compounds and Disazo- compounds.

PYRROL-CARBO-KETONIC ACID *v.* Pyrryl-glyoxylic acid.

PYRROLE (α)-CARBOXYLIC ACID $C_5H_5NO_2$ *i.e.* $C_4H_3(CO_2H)NH$. *Carbopyrrolic acid.* [191°].

Formation.—1. By the action of boiling baryta on its amide, which is got by distilling ammonium mucate (Malaguti, *A.* 15, 179; Schwanert, *A.* 116, 270; Ciamician, *B.* 17, 1[illegible]1).—2. By boiling pyrocoll with KOHAq (Weidel a. Ciamician, *M.* 1, 285).—3. By fusing potassium (α)-methyl-pyrrole with potash (Ciamician, *B.* 14, 1054; *G.* 11, 228).—4. By heating pyrrole with ammonium carbonate and water at 140° (Ciamician a. Silber, *B.* 17, 1150; *G.* 14, 162).—5. By heating pyrrole with alcoholic potash and CCl_4 (Ciamician a. Silber, *B.* 17, 1437).—6. By the action of CO_2 on potassium pyrrole at a high temperature (C. a S.).

Properties.—Prisms (from water), sol. water and alcohol. Decomposed by heat into CO_2 and pyrrole. HClAq forms, on warming, CO_2, pyrrole red, and NH_3Aq.

Salts.—NH_4A': m. sol. water.—CaA'_2: scales.—BaA'_2 (dried at 100°): plates, sol. water and alcohol.—PbA'_2: nacreous scales, v. sol. water.—AgA': small needles, sl. sol. water.

Methyl ether MeA'. [173°]. Prisms.

Ethyl ether EtA'. [39°] (231°).

Amide $C_4H_4(CONH_2)N$. [173°]. Laminæ, v. sol. alcohol and ether, m. sol. water.

Acetyl derivative $C_4H_3N.CO.OAc$. [75°]. Formed from the Ag salt and AcCl. Scales, readily decomposed by water into acetic acid and pyrrole carboxylic acid. At 75° it decomposes into HOAc and pyrocoll.

Pyrrole (β)-carboxylic acid $C_4H_3(CO_2H){:}NH$. [162°]. Formed by fusing potassium (β)-methyl-pyrrole with potash (Ciamician, *B.* 14, 1054). Needles, partially decomposed by boiling water into CO_2 and pyrrole. The lead salt is sl. sol. water.—BaA'_2: needles. A pyrrole carboxylic acid [166°], got by potash-fusion from isopropyl-pyrrole, and yielding a methyl ether [129°] (Dennstedt a. Zimmermann, *B.* 20, 855), is probably identical with the (β)- acid.

Pyrrole ν-carboxylic acid

Ethyl ether $C_4H_4N.CO_2Et$. *Tetrol-urethane.* (180°). Formed from potassium-pyrrole and $ClCO_2Et$ in ether (Ciamician a. Dennstedt, *G.* 12, 84). Oil.

Amide $C_4H_4N.CONH_2$. [167°]. Formed from the ether and NH_3.

Nitrile $C_4H_4N.CN$. *Tetrol cyanuramide.* [210°]. Got by passing CyCl into potassium-pyrrole in ether (Ciamician a. Dennstedt, *G.* 13, 102). Needles, insol. water, sol. hot alcohol. Boiling alcoholic potash forms pyrrole, CO_2, and NH_3.

Pyrrole dicarboxylic acid $C_6H_5NO_4$ *i.e.* $C_4H_2(CO_2H)_2NH$. Formed by oxidising pyrrylene dimethyl diketone, and fusing the product with potash (Ciamician a. Silber, *G.* 16, 377; *B.* 19, 1958; 20, 2601). Needles (from dilute alcohol), sol. ether and hot water. Blackens at 260°, giving pyrrole and CO_2. $FeCl_3$ gives a brown pp. The Ba salt crystallises in needles. The Ag salt is a curdy pp.

Mono-methyl ether MeHA''. [243°].

Di-methyl ether Me_2A''. [132°].

Di-ethyl ether Et_2A''. [82°].

References.—Bromo-, Chloro, and Nitro-pyrrole carboxylic acids.

PYRROLINE. A name used both for Pyrrole and Pyrrole dihydride.

PYRROLYLENE *v.* Butinene.

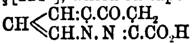
PYRROLYLENE TETRABROMIDE *v.* Tetra-bromo-butane.

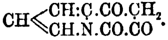
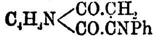
PYRRONE *v.* Di-pyrryl-ketone.

PYRROYL-FORMIC ACID *v.* Pyrryl-glyoxylic acid.

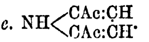
PYRROYL - PYRROL $C_4H_4N.CO.C_4H_3NH$ [63°]. Formed, together with di-pyrryl-ketone

$CO(C_4H_3NH)_2$ by intramolecular transformation of carbonyl-pyrrole by heating it to 250° for a few hours (Ciamician a. Magnaghi, *B.* 18, 1829). White silky plates. Not volatile with steam. By heating with aqueous KOH it is split up into pyrrole and pyrrole-(α)-carboxylic acid.

PYRROYL-PYRUVIC ACID. *Ethyl ether* $C_4H_3NH.CO.CH_2.CO.CO_2Et$. [123°]. Formed by the action of NaOEt and oxalic ether on pyrryl methyl ketone (Angeli, *B.* 23, 1794, 2155). Yellowish plates, v. sol. alcohol, sl. sol. water. Decomposed by alkalis, even in the cold, into oxalic acid and pyrryl methyl ketone. Hydroxylamine forms $C_{10}H_{10}N_2O_3$ [124°], which on saponification yields the acid  $CH<\begin{matrix}CH:C.CO.CH_2\\CH.N.N:C.CO_2H\end{matrix}$ [179°], crystallising in white needles. Aniline (2 pts.) in HOAc forms $C_4H_3NH.CO.CH_2.C(NPh).CO_2Et$ [115°]. Phenyl-hydrazine forms $C_{16}H_{15}N_3O_2$ [168°] which is the ether of an acid [215°].

Anhydride  $CH<\begin{matrix}CH:C.CO.CH_2\\CH.N.CO.CO\end{matrix}$. [250°]. Formed by adding HCl to the mother-liquor from which the ether has separated (Angeli, *B.* 23, 1795). Yellow needles (from benzene), v. sol. alcohol. *o*-Phenylene-diamine forms $C_{14}H_9N_3O$, a reddish-yellow crystalline powder forming a bluish-green solution in H_2SO_4 and yielding a benzoyl derivative [c. 166°]. Aniline forms  $C_4H_4N<\begin{matrix}CO.CH_2\\CO.CNPh\end{matrix}$ [218°], whence cold KOHAq forms an acid $C_{14}H_{12}N_2O_3$ [179°].

PYRRYLENE DIETHYL DIKETONE $C_4H_2NH(COEt)_2$. [117°]. Formed by heating pyrrole with propionic anhydride at 260° (Dennstedt a. Zimmermann, *B.* 20, 1761). Plates.

PYRRYLENE DI-METHYL DIKETONE $C_8H_9NO_2$ *i.e.*  $NH<\begin{matrix}CAc:CH\\CAc:CH\end{matrix}$ [162°]. Formed by heating pyrrole, pyrryl methyl ketone, or acetyl-pyrrole with Ac_2O at 250° (Ciamician, *B.* 17, 432, 2953; 18, 881, 1466; 19, 1957; 20, 2595). Needles, sol. hot water and hot KOHAq. May be sublimed. Yields a nitro- derivative [149°] and a di-bromo- derivative [172°].—AgA'.

PYRRYLENE DISTYRYL DIKETONE $(C_6H_5.CH:CH.CO)_2C_4H_2NH$. [240°]. Formed by heating pyrrylene dimethyl diketone with benzoic aldehyde and KOHAq (Ciamician a. Dennstedt, *B.* 17, 2953). Crystals (from HOAc), sl. sol. alcohol. Forms a violet solution in H_2SO_4.

PYRRYL ETHYL KETONE C_7H_9NO *i.e.* $C_2H_5.CO.C_4H_3NH$. [52°]. (224°). Formed by boiling pyrrole with propionic anhydride and sodium propionate (Dennstedt a. Zimmermann, *B.* 20, 1761). Colourless needles.—AgA': pp.

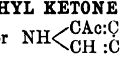
PYRRYL-GLYOXYLIC ACID $C_6H_5NO_3aq$ *i.e.* $C_4H_3NH.CO.CO_2H$ aq or $C_4H_3NH.C(OH)_2.CO_2H$. Formed by oxidation of pyrryl methyl ketone by $KMnO_4$ (Ciamician a. Dennstedt, *B.* 16, 2350; 17, 2949). Crystallises from benzene in yellow needles (of $C_6H_7NO_4$) melting at 76°, v. sol. hot water. After drying over sulphuric acid the acid ($C_6H_5NO_3$) decomposes at 114°. The aqueous solution gives a red colour with $FeCl_3$. On heating with HClAq it gives a crimson colour turned yellowish-green by alkalis.—AgA': colourless needles, sol. hot water.

Methyl ether **MeA'. [72°]. (285°). Monoclinic crystals, sl. sol. water.**

Carboxy-pyrryl-glyoxylic acid $CO_2H.C_4H_2NH.CO.CO_2H$. Formed by oxidation of pyrrylene dimethyl diketone (Ciamician a. Silber, *B.* 19, 1412, 1961). Crystalline, v. sol. hot water.—Ag_2A'': canary-yellow pp.

Methyl ether Me_2A''. [145°].

DI-PYRRYL KETONE $CO(C_4H_3NH)_2$. [160°]. Formed, together with $(C_4H_4N)_2CO$, by the action of $COCl_2$ on C_4H_4NK. Formed also, together with pyrroyl-pyrrole, by heating $(C_4H_4N)_2CO$ at 250° for a few hours (Ciamician a. Magnaghi, *B.* 18, 414, 1829). Trimetric crystals; *a*:*b*:*c* = 2·531:1:2·901. V. sol. alcohol, ether, and benzene, nearly insol. water. Ag_2A'': yellow pp.

PYRRYL METHYL KETONE C_6H_7NO *i.e.* $CH_3.CO.C_4H_3NH$ or  $NH<\begin{matrix}CAc:CH\\CH:CH\end{matrix}$. *Pseudo-acetyl-pyrrole.* [90°]. (220° uncor.). V.D. 3·8 (calc. 3·8). Formed by boiling pyrrole with Ac_2O and NaOAc (R. Schiff, *B.* 10, 1501; Ciamician a. Dennstedt, *B.* 16, 2348; 17, 432, 2944; 18, 1456; 20, 2605; *G.* 15, 175). Formed also by heating pyrrole with Ac_2O and $ZnCl_2$ (Dennstedt a. Zimmermann, *B.* 19, 2204), and by heating $CH_3.CO.C_4H_3N.CO_2K$ with K_2CO_3 at 290° (Ciamician a. Silber, *B.* 19, 1963). Long monoclinic needles, sol. hot water, v. sol. aqueous alkalis, sparingly volatile with steam. Not converted into pyrrole and KOAc by potash.

Reactions.—1. Yields pyrryl-glyoxylic acid when oxidised by $KMnO_4$.—2. *Benzoic aldehyde* and dilute KOH form pyrryl styryl ketone.—3. Water and *sodium-amalgam* reduce it to crystalline pyrryl methyl pinacone $C_{12}H_{16}N_2O_2$ [120°] and pyrryl-methyl-carbinol $CH_3.CH(OH).C_4H_3NH$ an oil (290°-300°). Pyrryl-methyl-pinacone $C_4H_4N.CMe(OH).CMe(OH).C_4H_4N$ crystallises in prisms (containing 2aq) melting at 98° when hydrated.—4. *Oxalic ether* and NaOEt form pyrroyl-pyruvic ether (Angel, *B.* 23, 1357, 1794). 5. Cold fuming H_2SO_4 yields an unstable sulphonic acid, which forms a crystalline K salt.

Salt.—C_4H_3AcNAg. Crystalline pp.

Oxim $CH_3.C(NOH).C_4H_3NH$. [146°]. Needles.

Phenyl-hydrazide $CH_3.C(N_2HPh).C_4H_3NH$. [147°]. White powder.

References.—AMIDO-, BROMO-, BROMO-NITRO-, and NITRO- PYRRYL METHYL KETONE.

PYRRYL METHYL KETONE CARBOXYLIC ACID $C_7H_7NO_3$ *i.e.* $CH_3.CO.C_4H_3N.CO_2H$. [186°]. Formed by saponification of its methyl ether, obtained by heating methyl pyrrole (α)-carboxylate with Ac_2O at 260° (Ciamician a. Silber, *G.* 14, 169; *B.* 17, 1155). Leaflets, sol. water, alcohol, and ether. $FeCl_3$ gives a brown pp.—CaA'_2 7aq: triclinic prisms.—*PbA'_2: needles.—AgA': powder, sl. sol. water.

Methyl ether MeA'. [113°]. Gives with ammoniacal $AgNO_3$ a pp. $C_8H_8AgNO_3$.

PYRRYL PHENYL KETONE $C_{11}H_9NO$ *i.e.* $C_6H_5.CO.C_4H_3NH$. [78°]. Formed by heating pyrrole with benzoic anhydride and dry NaOBz at 200°-240° (Ciamician a. Dennstedt, *B.* 17, 432, 2955). Needles, v. sol. alcohol, sl. sol. hot water.—$C_{11}H_8AgNO$.

PYRRYL STYRYL KETONE $C_{13}H_{11}NO$ *i.e.* $C_6H_5.CH:CH.CO.C_4H_3NH$. [142°]. Formed by boiling pyrryl methyl ketone with C_6H_5CHO and KOHAq (Ciamician a. Dennstedt, *B.* 17, 2947). Yellow needles, sl. sol. alcohol, insol. water.—$C_{13}H_{10}ONAg$: yellow needles, insol. NH_3Aq.

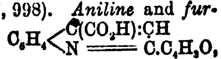
PYRUVIC ACID $C_3H_4O_3$ *i.e.* $CH_3.CO.CO_2H$. *Pyroracemic acid. Di-oxy-propionic acid.* Mol. w. 88. [9°]. (c. 165°). S.G. $\frac{15}{15}$ 1·2752; $\frac{25}{25}$ 1·2700. M.M. 3·557 (Perkin, *C. J.* 61, 836).

Formation.—1. By distilling racemic or tartaric acid (Berzelius, *A.* 13, 61; Völckel, *A.* 89, 65; Wislicenus, *A.* 126, 225).—2. By gradually heating tartaric acid with HClAq in sealed tubes to 180° (Geuther a. Riemann, *Z.* [2] 5, 318).—3. By heating tartaric acid with conc. H_2SO_4 at 40°–50° (Bouchardat, *C. R.* 89, 99).—4. By heating silver di-*a*-chloro-propionate with water (Beckurts a. Otto, *B.* 10, 265; 18, 227).—5. By distilling glyceric acid (Moldenhauer, *A.* 131, 338; Böttinger, *A.* 196, 92).—6. By boiling acetyl cyanide with dilute HCl (Claisen a. Shadwell, *B.* 11, 1563).—7. By oxidation of a cold aqueous solution of calcium lactate by $KMnO_4$ (Beilstein a. Wiegand, *B.* 17, 840).

Preparation.—1. Tartaric acid (3 lbs.) is distilled from a glass retort (30 lbs. capacity). The distillation takes three hours. A fresh quantity of tartaric acid is then added and the operation repeated. The distillate is fractionally distilled (Clewing, *J. pr.* [2] 17, 243).—2. Dried, and finely powdered, tartaric acid is mixed with an equal weight of sand and distilled (Seissl, *A.* 249, 297). 3. Tartaric acid is distilled with $KHSO_4$, the yield being 50 to 60 p.c. (Erlenmeyer, *B.* 14, 321).

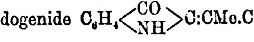
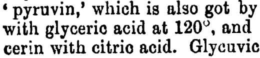
Properties.—Liquid, smelling like acetic acid, v. e. sol. water, alcohol, and ether. Colourless crystals below 9° (Simon, *Bl.* [3] 9, 111). Partially decomposed on distillation. Reduces ammoniacal $AgNO_3$, forming a mirror, and yielding CO_2 and acetic acid. Coloured cherry-red by alkaline sodium-nitroprusside, the colour being discharged by HOAc (Von Bitto, *A.* 267, 377). Readily ppd. by phenyl-hydrazine. Forms an oxim.

Reactions.—1. Dilute H_2SO_4 at 150° splits it up into aldehyde and CO_2 (B. a. W.).—2. By long heating at 170° it is converted into CO_2 and acetic, pyrotartaric, uvic, and citraconic acids (Böttinger, *B.* 9, 670, 837, 1823).—3. HClAq at 100° forms CO_2 and pyrotartaric acids (De Clermont, *B.* 6, 72).—4. Boiling with Ag_2O yields CO_2 and acetic acid.—5. Reduced to lactic acid by *sodium-amalgam*, and by Zn and H_2SO_4.—6. HI reduces it to propionic acid.—7. *Zinc* when added to its alcoholic solution forms $CO_2H.CMe(OH).CMe(OH).CO_2H$ (Böttinger, *B.* 9, 1064).—8. PCl_5 forms di-*a*-chloro-propionic acid (Klimenko, *B.* 3, 465; Beckurts a. Otto, *B.* 11, 386).—9. Dry *bromine* at 0° forms crystalline di-bromo-lactic acid (?). Br and water give di-bromo-pyruvic acid (Wislicenus, *A.* 148, 208; Wichelhaus, *A.* 152, 265).—10. Oxidised by *chromic acid mixture* to CO_2 and acetic acid.—11. HNO_3 forms oxalic acid and CO_2.—12. Boiling *baryta-water* forms uvitic, uvic, pyrotartaric, oxalic, and acetic acids and CO_2 (Finckh, *A.* 122, 182; Böttinger, *B.* 8, 957; *A.* 172, 241, 253; 188, 313; 208, 129). Baryta-water added to a cold solution of pyruvic acid ppts. barium hydruvate $BaC_6H_8O_7$ or the basic salt $Ba_3H_2(C_6H_7O_7)_4$. Hydruvic acid is a syrup.—13. On heating with excess of *quicklime* it yields a little aldehyde (Hanriot, *C. R.* 101, 1156; *Bl.* [2] 45, 81).—14. HCN followed by HCl forms lactic acid. KCN followed by HCl yields $CH_3.C(OH)(CN).CO_2H$ *v.* CYANO-OXY-PROPIONIC ACID. On warming pyruvic acid with HCN under pressure the product is $CMe(NH_2)(CO_2H)_2$, crystallising in unstable prisms (Körner a. Menozzi, *G.* 17, 104).—15. Alcoholic *ammonia* forms methyl-pyridine dicarboxylic acid.—16. *Aniline* added to an ethereal solution forms $C_9H_9NO_2$, *i.e.* $CH_3.C(NPh).CO_2H$ [122°] (Böttinger, *B.* 10, 818). Aniline alone forms, on heating, $C_{14}H_{16}N_2O$, crystallising from dilute alcohol in needles [195°], while *p*-toluidine gives $C_{16}H_{20}N_2O$ [238°] (Lazarus, *B.* 17, 998). *Aniline* and *furfuraldehyde* form



$$C_6H_4<\begin{matrix}C(CO_2H):CH\\N=\!=\!=\!=C.C_4H_3O\end{matrix},$$

crystallising in greenish-yellow needles [210°–215°] (Doebner, *A.* 242, 285). *Tetra-amido-anisole* forms the quinoxaline $C_6H(OMe)(N_2C_3H_4O)_2$ as orange-yellow flakes, v. sol. alkalis (Nietzki a. Kurtenacker, *B.* 25, 284).—17. H_2S passed into water containing the Ag salt forms thiolactic acid (Böttinger, *B.* 9, 404; Lovèn, *J. pr.* [2] 29, 376).—18. PH_3 and HCl passed into an ethereal solution form 'phosphortrianhydropyruvic' acid $C_9H_9PO_6$, crystallising in needles, insol. alcohol and ether, and forming with phenyl-hydrazine the compounds $C_9H_9PO_6 3PhN_2H_3$ [132°] and $C_{45}H_{48}N_{12}O_3$ (?) [162°]. The acid $C_9H_9PO_6$ is converted by aniline into $C_{21}H_{23}N_2PO_6$ [158°], whence phenyl-hydrazine forms $C_{21}H_{23}N_5O_2$ [169°]. Tolylene-diamine converts $C_9H_9PO_6$ into $C_9H_9PO_6 2C_7H_{10}N_2$ [178°] (Messinger a. Engels, *B.* 21, 334, 2919).—19. Pyruvic acid (50 g.) heated with dry *sodium succinate* (92 g.) and Ac_2O (58 g.) at 110° forms di-methyl-maleïc anhydride (pyrocinchonic anhydride) (Fittig a. Parker, *A.* 267, 204). Pyruvic acid (30 g.) heated with dry sodium succinate (55 g.) at 110° forms uvic (pyrotritaric) acid.—20. Pyruvic acid (30 g.) heated with *sodium pyrotartrate* (60 g.) and AcO (36 g.) at 140° forms methyl-ethyl-maleïc anhydride (F. a. P.).—21. *Benzonitrile* and cold H_2SO_4 form an acid $C_{17}H_{16}N_2O_4$, crystallising in tables [172°], insol. water, v. sol. acetone (Böttinger, *B.* 14, 1599).—22. *Phenyl-aceto-nitrile* and H_2SO_4 form, in like manner, $C_{19}H_{20}N_2O_4$ [145°] (B.).—23. By heating with *aldehydes* R.CHO and baryta-water it is converted into *s*-alkyl-isophthalic acids of the form $C_6H_3R(CO_2H)_2$ (Doebner, *B.* 23, 2378).—24. *Benzoic aldehyde* and *aniline* in ether form, in the cold, $C_{22}H_{18}N_2O$ or CHPh:CH.C(NPh).CONHPh [225°], insol. water, acids, and alkalis, sl. sol. alcohol and ether. *Cuminic aldehyde* and *aniline* give $C_{25}H_{24}N_2O$ [216°] (Doebner a. Giesoke, *A.* 242, 290; 249, 102). *Benzoic aldehyde* and *p-toluidine* form, in like manner, $C_{24}H_{22}N_2O$ [205°].—25. *Isobutyric aldehyde* and *aniline* in alcoholic solution react forming CHPr.CH.C(NPh).CONHPh (?) [222°] crystallising from HOAc in needles, while *isovaleric aldehyde* and *aniline* in ether give $C_{20}H_{22}N_2O$ [160°] (Doebner, *A.* 242, 275). Isovaleric aldehyde in warm alcoholic solution forms the acid $C_{14}H_{15}NO_2$.—26. *Thioglycollic acid* gives rise to $CO_2H.CMe(OH).S.CH_2.CO_2H$ [110°] with evolution of heat; while HCl passed through a mixture of pyruvic and thioglycollic acids produces $CO_2H.CMe(S.CH_2.CO_2H)_2$ [162°] crystallising from ether (Bongartz, *B.* 19, 1933; 21, 484).—27. *Phenyl mercaptan* forms the compound $CH_3.C(SPh)(OH).CO_2H$, while *p-bromo-phenyl mercaptan* forms $CH_3.C(SC_6H_4Br)(OH).CO_2H$

[114·5°] (Baumann, *B.* 18, 263).—28. *Ethylene mercaptan* forms a substance [96°] which crystallises from benzene as a fine powder, and may be condensed to $\begin{matrix}CH_2.S\\CH_2.S\end{matrix}\!>\!CMe.CO_2H$ [102°], which on oxidation gives ethylene ethylidene disulphone [198°] (Fasbender, *B.* 21, 1473).—29. *Benzene* and H_2SO_4 form $CH_3.CPh_2.CO_2H$, while phenol and H_2SO_4 yield $C_{15}H_{14}O_4$ (Böttinger, *B.* 14, 1595; 16, 2071).—30. Distillation of the K salt with KOAc forms acetone and pyrotartaric acid (Wichelhaus, *Z.* [2] 5, 254).—31. Pyruvic acid (1 pt.) heated with *urea* (2 pts.) at 100° forms pyvuril or 'pyruvic diureide' $C_5H_8N_4O_3$, which crystallises in tables, S. 10 at 100°, insol. alcohol and ether (Grimaux, *C. R.* 79, 526, 1304, 1478; 80, 53; *A. Ch.* [5] 11, 373). Pyvuril is decomposed by long heating at 160°, forming amorphous 'tetrapyruvic tetraureide' $C_{16}H_{16}N_8O_8$, insol. water. Boiling dilute HClAq converts pyvuril into urea and 'dipyruvic triureide' $C_9H_{12}N_6O_5$, which crystallises from hot water in needles, S. ·4 at 100°, decomposed by boiling alkalis into urea, pyruvic acid, and pyvuril. Boiling conc. HClAq converts pyvuril into urea and 'pyruvic ureide' $C_4H_4N_2O_2$ or $CO\!<\!\begin{matrix}N{=}CMe\\NH.CO\end{matrix}$, a crystalline powder, m. sol. hot water, insol. alcohol. Nitric acid converts pyvuril into nitro-pyruvic ureide $C_4H_3(NO_2)N_2O_2$ [above 200°], which is decomposed by boiling bromine-water into parabanic acid and $CBr_3.NO_2$. Pyruvic acid heated with an equal weight of urea at 100° forms amorphous insoluble 'tripyruvic tetraureide' $C_{13}H_{16}N_8O_7$ and dipyruvic triureide.—32. *Sodium hippurate* and Ac_2O at 100° form the dibasic acid $C_{12}H_9NO_4$ [157°] (A. Hoffmann, *B.* 19, 2555).—33. A solution of *indoxyl* forms on adding conc. HCl the indogenide  $C_6H_4\!<\!\begin{matrix}CO\\NH\end{matrix}\!>\!C{:}CMe.CO_2H$ [197°], crystallising in red needles forming a blue solution in H_2SO_4 (Baeyer, *B.* 16, 2199).—34. *Glycerin* and $KHSO_4$ form 'glycuvic acid,' or 'pyruvin,' which is also got by heating glycerin with glyceric acid at 120°, and by distilling glycerin with citric acid. Glycuvic acid is probably  $CH_3.CO.CO.O.CH_2.CH\!<\!\begin{matrix}CH_2\\O\end{matrix}$. It is crystalline [82°] (241°), and yields pyruvic acid when boiled with baryta (Böttinger, *B.* 10, 286; 14, 316; *A.* 263, 246; Jowanovitch, *M.* 6, 467; Erhardt, *M.* 6, 511; Schlagdenhauffen, *C. R.* 74, 672; De Clermont, *C. R.* 105, 520).

Salts.—The salts crystallise well, provided heat is avoided in their preparation; otherwise they become amorphous. The acid also is changed by evaporation of its aqueous solution into a non-volatile syrupy mass.—NaA': large prisms.—BaA'_2 aq: scales.—BaA'_2 2aq: amorphous.—PbA'_2 aq: crystalline pp.—ZnA'_2 3aq: white microcrystalline powder, sl. sol. water (Beckurts a. Otto, *B.* 18, 227).—CuA'_2 aq.—AgA': scales, sl. sol. water.

Combinations with bisulphites (Clewing, *J. pr.* [2] 17, 241).—$HA'NaHSO_3$ aq: crystals.—$NaA'NaHSO_3$ aq. — $NaA'NaHSO_3$ 1½aq. — $HA'KHSO_3$: octahedra. — $KA'KHSO_3$ aq. — $CaA'_2Ca(HSO_3)_2$ 3aq.—$(CaA'_2)_3(Ca(HSO_3)_2)_2$ 24aq.—$(CaA'_2)_2(Ca(HSO_3)_2)_2$ 3aq.—$SrA'_2Sr(HSO_3)_2$ 5aq.—$BaA'_2Ba(HSO_3)_2$.

Methyl ether MeA'. (c. 136°). S.G. ^{9} 1·154. Got from AgA' and MeI.

Ethyl ether EtA'. Oil. Converted by aniline into two crystalline bodies [144°] and [c. 250°]. The compound $O(CMe(OH).CO_2Et)_2$, formed by the action of nitrous acid on amido-propionic ether, is an oil (80°–86° at 120 mm.) (Curtius, *J. pr.* [2] 38, 472).

Isoamyl ether $C_5H_{11}A'$. Got by distilling the acid with isoamyl alcohol (Simon, *Bl.* [3] 9, 136).

Amide $CH_3.CO.CO.NH_2$. [125°]. Got from acetyl cyanide and HCl (Claisen a. Shadwell, *B.* 11, 1566). Prisms or tables (from alcohol).

Nitrile v. ACETYL CYANIDE.

Phenyl hydrazide $CH_3.C(N_2HPh).CO_2H$. [192°] (F.); [185°] (Japp a. Klingemann, *B.* 20, 3284; *A.* 247, 208; *C. J.* 53, 519). Ppd. when a solution of phenyl-hydrazine hydrochloride is added to a dilute (even 1 in 1000) solution of pyruvic acid (Fischer, *B.* 16, 2241; 17, 578). Prisms, sol. hot water and hot alcohol. Reduced by sodium-amalgam to phenyl-hydrazido-propionic acid [172°]. At 190° it gives off CO_2 and H_2, and forms the phenyl-hydrazide of di-methyl diketone [242°] and the oily phenyl-hydrazide of aldehyde. The ether $CH_3.C(N_2HPh).CO_2Et$ [117°], crystallises in yellow needles (from ligroïn).

o-Chloro-phenyl-hydrazide $C_6H_4Cl.NH.N{:}CMe.CO_2H$. [178°]. Lemon-yellow needles, forming a crystalline ethyl ether [168°] (Hewett, *C. J.* 59, 211).

p-Nitro-phenyl-hydrazide $C_6H_4(NO_2).NH.N{:}CMe.CO_2H$. Yellow plates (Fischer a. Ach, *A.* 253, 64). V. sol. hot alcohol.

p-Sulpho-phenyl-hydrazide $SO_3H.C_6H_4.NH.N{:}CMe.CO_2H$. Solid, insol. ether, v. sol. water and alcohol (Pfülf, *A.* 239, 217).—NaA' aq: nodules.

Phenyl-methyl-hydrazide $C_{10}H_{12}N_2O_2$ *i.e.* $NPhMe.N{:}CMe.CO_2H$. [78°]. Yellowish needles (Fischer, *B.* 16, 2245; 17, 559). Converted by heating with HClAq into methyl-indole carboxylic acid and NH_3. The phenyl-ethyl-hydrazide is converted in like manner into ethyl-indole carboxylic acid.

Di-phenyl-hydrazide $NPh_2.N{:}CMe.CO_2H$. [145°]. White needles (Fischer a. Hess, *B.* 17, 567). Sol. hot benzene and $CHCl_3$, forming deep-yellow solutions. Converted into phenyl-indole carboxylic acid by heating with HClAq.

o-Tolyl-hydrazide $C_6H_4MeN_2H{:}CMe.CO_2H$. [156°] (J.); [159°] (R.) Formed by saponifying the product of the action of *o*-diazotoluene chloride on sodium methyl-acetoacetic ether (Japp, *A.* 247, 213), and from *o*-tolyl-hydrazine hydrochloride and pyruvic acid (Raschen, *A.* 239, 228). Small yellow plates (from benzene). Yields *o*-tolyl-hydrazido-propionic acid [143°] on reduction. At about 160° it forms the di-*o*-tolyl-di-hydrazine of di-methyl-di-ketone, a yellow crystalline powder [198°].

p-Tolyl-hydrazide $C_7H_7N_2H{:}CMe.CO_2H$. [162°]. Formed in the same way as the *o*-isomeride. Yellow plates (from benzene). At 165° it is converted into the di-*p*-tolyl-hydrazide of di-methyl-di-ketone [230°]. Gives an ethyl ether $C_{12}H_{16}N_2O_2$ [106°], crystallising from ligroïn in yellowish plates.

Methyl-p-tolyl-hydrazide $C_{11}H_{14}N_2O_2$. [88°]. Yellow prisms (Hegel, *A.* 232, 215).

Ethyl-p-tolyl-hydrazide $C_{12}H_{16}N_2O_2$. Needles, v. sol. alcohol and ether (H.).

ψ-Cumyl-hydrazide $C_6H_2Me_3NH.N{:}CMe.CO_2H$. [148°]. Yellow needles (Ruhemann, *C. J.* 57, 55).

p-Benzoylphenyl-hydrazide $C_6H_4Bz.N_2H{:}CMe.CO_2H$. [200°]. Lemon-coloured crystals (Ruhemann a. Blackman, *C. J.* 55, 616).

(α)-*Naphthyl-hydrazide* $C_{10}H_7.N_2H{:}CMe.CO_2H$. [159°] (Fischer, *A.* 232, 236). Yields EtA′ [100°] (Schlieper, *A.* 239, 229).

(β)-*Naphthyl-hydrazide* [166°]. Yields EtA′ [131°] (Schlieper, *A.* 236, 176).

(*B.* 4)-*Quinolyl-hydrazide* $C_9H_6N.NH.N{:}CMe.CO_2H$. [174°]. Formed from pyruvic acid and (*B.* 4)-hydrazido-quinoline acetate (Dufton, *C. J.* 59, 758). Light-yellow pp., insol. water, sol. acids and alkalis.

Oxim $CH_3.C(NOH).CO_2H$. *α-Nitroso-propionic acid.* Formed by the action of cold KOHAq on its ether, which is got by adding a dilute solution of KNO_2 (10 pts.) to methyl-acetoacetic ether dissolved in water (3 pts.), KOH (2 pts.), and some alcohol, the yield being 16 p.c. of the methyl-acetoacetic ether used (V. Meyer a. Züblin, *B.* 11, 692; Gutknecht, *B.* 13, 1116). Got also from pyruvic acid and hydroxylamine (V. Meyer a. Janny, *B.* 15, 1527; Schäfer, *A.* 264, 153; Hantzsch, *B.* 24, 50). Crystalline powder, sl. sol. ether, v. sol. water and alcohol. Decomposes suddenly at about 177°. Oxidised by potassium permanganate to ethyl-nitrolic acid $CH_3.CH(NO)(NO_2)$. Yields acetonitrile on heating with hydroxylamine hydrochloride. Reduced by tin and HClAq to alanine. **Salts.**—KA′ aq: pearly plates, sol. water.—BaA'_2: soluble prisms.—$Cu_2OA'_2$ aq.—AgA′: white insoluble powder. *Ethyl ether* EtA′. [94°]. (233° cor.). Formed as above, and also by the action of HNO_2 on methyl-malonic ether and on propionyl-propionic ether (Bergreen, *B.* 20, 533). Needles or prisms, with weak acid properties.

References.—Bromo-, Chloro-, and Oxy-Pyruvic acid.

PYRUVIC ALDEHYDE $CH_3.CO.CHO$. *Methyl-glyoxal.* Got by the action of dilute acids upon $CH_3.C(OH)(SO_3Na).CH(SO_3Na).NHSO_3Na$, which is got from nitroso-acetone and $NaHSO_3$ (Pechmann, *B.* 20, 2543).

Mono-oxim v. Nitroso-acetone.

Di-oxim $CH_3.C(NOH).CH{:}NOH$. *Methyl-glyoxim.* [153°]. Formed by the action of hydroxylamine on $CH_3.CO.CH.NOH$ or upon $CH_3.CO.CHCl_2$ (V. Meyer a. Janny, *B.* 15, 1165; Treadwell, *B.* 15, 2787). Small prisms (from alcohol) or needles (by sublimation). **Salt.**—$AgC_3H_5N_2O_2$ pp.—**Diacetyl derivative** $C_3H_4(NOAc)_2$. [51°]. Prisms (from ligroïn) (Schramm, *B.* 16, 2187).

Phenyl-hydrazide of the oxim $CH_3.C(N_2HPh).CH{:}NOH$. [134°]. Formed from nitroso-acetone and phenyl-hydrazine (Pechmann a. Wehsarg, *B.* 21, 2994; *A.* 262, 278). Prisms or needles (from alcohol). H_2SO_4 forms a reddish-yellow solution, coloured deep blue by $FeCl_3$. Ac_2O yields $CH_3.C(N_2HPh).CH{:}NOAc$ [163°], crystallising in colourless needles.

Phenyl-methyl-hydrazide of the oxim $CH_3.C(N_2PhMe).CH{:}NOH$. [116°]. Orange yellow prisms (from alcohol).

Phenyl-hydrazide $CH_3.CO.CH{:}N_2HPh$. [150°]. Formed from sodium acetoacetic ether and diazobenzene chloride (Japp, *A.* 247, 198, 218; *C. J.* 53, 519). Plates (from benzene or MeOH). Yields $CH_3.CO.CH{:}N_2AcPh$ [93°], crystallising from ligroïn in needles. NaOEt and chloro-acetic ether yield, on saponification of the product, $CH_3.CO.CH{:}N.NPh.CO_2H$ [162°], which crystallises from hot water in needles, and is reduced by tin and HClAq to phenyl-amido-acetic acid [127°].

Di-phenyl-di-hydrazide $CH_3.C(N_2HPh).CH{:}N_2HPh$. [145°]. Formed by heating the phenyl-hydrazide of acetyl-carbinol with phenyl-hydrazine hydrochloride and NaOAc in alcohol at 100° (Laubmann, *A.* 243, 248). Formed also by warming pyruvic aldehyde or its mono-oxim, phenyl-hydrazide, or phenyl-hydrazide of the oxim with phenyl-hydrazine acetate (Pechmann, *B.* 20, 2543; 21, 2755; Japp, *A.* 247, 207). Yellow plates or needles (from dilute alcohol), sl. sol. alcohol. Conc. H_2SO_4 forms an olive-green solution, changing through slaty-blue to violet. Yields a crystalline hydrochloride [197°]. Oxidised by $K_2Cr_2O_7$ and HOAC to $\begin{array}{l}CH{:}N.NPh\\ CMe{:}N.NPh\end{array}$ crystallising in needles [107°], whence boiling HClAq produces $\begin{array}{l}CH{:}N\\ CMe{:}N\end{array}\!\!>\!NPh$ a colourless oil (160° at 60 mm.), oxidised by alkaline $KMnO_4$ to the acid $C_9H_7N_3O_2$ [192°].

Acetyl derivative of the di-phenyl-di-hydrazide $CH_3.C(N_2HPh).CH{:}N.NPhAc$. [229°]. Formed from the acetyl derivative of the phenyl-hydrazide and phenyl-hydrazine (Japp, *C. J.* 53, 519). Yellowish needles.

Phenyl-methyl-hydrazide $CH_3.CO.CH{:}N.NPhMe$. [64°]. Formed from the phenyl-hydrazide, NaOMe, MeOH, and MeI (Japp). Flat needles (from MeOH), v. e. sol. alcohol. Converted by phenyl-hydrazine into $CH_3.C(N_2HPh).CH{:}N.NPhMe$ [152°], crystallising in pale-yellow needles.

Phenyl-ethyl-hydrazide $CH_3.CO.CH{:}N.NPhEt$. [55°]. Prepared in like manner. Prisms (from ligroïn).

PYRUVYL ALCOHOL *v.* Acetyl carbinol.

Q

QUARTENYLIC ACID *v.* Isocrotonic acid.

QUASSIN $C_{32}H_{44}O_{10}$ or $C_{32}H_{42}O_{10}$ or $C_{32}H_{40}O_{10}$ (Oliveri) or $C_{31}H_{42}O_9$ (Christensen). *Quassiin.* [211°]. S. ·253 at 22° (O. a. D.); ·07 at 15° (C.). S. (chloroform) 48 at 15° (C.). $[\alpha]_D = 37{\cdot}5$ in $CHCl_3$. Occurs in quassia-wood (Winckler, *Rep. Pharm.* 54, 85; Wiggers, *A.* 21, 40; Christensen, *Ar. Ph.* [3] 20, 481; Goldschmidt a. Weidel, *Sitz. W.* 74, 389; Adrian a. Moreaux, *Ph.* [3] 14, 507). Prepared by extracting quassia wood

(10 pts.) with boiling water (45 pts.), evaporating (to 10 pts.) at a gentle heat, ppg. by tannin, mixing the pp. with lead carbonate, and extracting with boiling alcohol. The product is recrystallised from water and alcohol (yield ·01 pt.) (Oliveri a. Denaro, *G.* 15, 6).

Properties.—Slender monoclinic needles, v. sol. alcohol and chloroform, sl. sol. ether. Sol. conc. HClAq and KOHAq, insol. Na_2CO_3Aq. Reduces Fehling's solution (Oliveri), or, according to Allen (*An.* 12, 107), has no reducing power. Not coloured by $FeCl_3$. Ppd. by tannin. Quassin appears to be the dimethyl ether of quassic acid, and probably contains two hydroxyls, two CO_2Me, and two CO groups, and is perhaps a derivative of anthraquinone (Oliveri). Phenyl-hydrazine forms $C_{32}H_{40}O_8(N_2HPh)_2$ (?), a yellow amorphous powder, decomposing at about 230° without fusion (Oliveri, *G.* 18, 169).

Reactions.—1. Boiling dilute (4 p.c.) H_2SO_4 forms 'quasside' $C_{32}H_{42}O_9$, a white amorphous very bitter substance [194°], which reduces Fehling's solution, and is reconverted by boiling dilute alcohol into quassin.—2. Ac_2O and NaOAc form, on boiling, the amorphous anhydride $C_{32}H_{40}O_8$ [150°–158°], sol. alcohol and ether.—3. *Bromine* forms $C_{32}H_{41}Br_3O_9$, a very bitter yellow powder [155°].—4. Fuming HClAq in a sealed tube at 100° forms MeCl and quassic acid.—5. PCl_5 gives $C_{32}H_{39}Cl_5O_8$, a yellow powder [120°] decomposed on fusion.—6. HIAq and P at 150°–280° form durene (188°–195°) $C_{11}H_{16}$ (220°–240°) and anthracene (Oliveri, *G.* 17, 575).

Quassic acid $C_{30}H_{38}O_{10}$ or $C_{30}H_{40}O_{10}$. [245°]. S. ·0043 at 23°. Formed, together with MeCl (2 mols.), by heating quassin with HClAq. Monoclinic prisms (containing aq), sol. hot alcohol, sl. sol. ether. Alkalis give a reddish-yellow colour. $FeCl_3$ gives a greenish-yellow colour. Reduces Fehling's solution and ammoniacal $AgNO_3$. Hydroxylamine forms $C_{30}H_{36}(NOH)_2O_8$ (?), crystallising in rectangular prisms [230°].—BaA'' 7aq: reddish-yellow crystals. — PbA'' 6aq: white amorphous pp.—$Fe_2A''_3$: brownish-green pp.

QUEBRACHAMINE. [142°]. Occurs in white quebracho bark (Hesse, *A.* 211, 269). Plates, v. sol. alcohol, benzene, $CHCl_3$, and ether. Its alcoholic solution is alkaline and tastes bitter. H_2SO_4 and $K_2Cr_2O_7$ give a dark-violet colour.

QUEBRACHINE $C_{21}H_{26}N_2O_3$. [216°]. $[\alpha]_D = 62·5$ in a 2 p.c. alcoholic solution at 15°; $= 18·6$ in chloroform. Occurs in white quebracho bark (Hesse, *B.* 13, 2308; *A.* 211, 254). Colourless needles, sol. alcohol, ether, benzene, and $CHCl_3$, v. sl. sol. cold water, NaOHAq, and NH_3Aq. Dextrorotatory. Its solutions are alkaline, bitter, and poisonous. Its solution in H_2SO_4 is turned blue by PbO_2 or $K_2Cr_2O_7$, and finally brown. $FeCl_3$ gives no colour.

Salts.—$B'HCl$.—$B'_2H_2PtCl_6$ 5aq: crystals.—$B'_2H_2SO_4$ 8aq: cubes or short prisms, v. sol. hot water.—$B'_2H_2C_2O_4$.—Tartrate $B'_2H_6C_4O_6$ 6aq.—Citrate $B'_2C_6H_8O_7$: nodular groups of needles.

Hypoquebrachine $C_{12}H_{26}N_2O_2$. [80°]. Strong base with bitter taste, v. sol. alcohol and ether, forming yellow amorphous salts. Platinochloride.—$B'_2H_2PtCl_6$ 4aq (Hesse, *A.* 211, 264).

QUEBRACHITE $C_6H_{11}MeO_6$. [187°]. S.G. 1·54. (c. 210° *in vacuo*). $[\alpha]_D = -80°$. Occurs in the seeds of *Aspidosperma quebracho*, from which it can be extracted with alcohol (Tanret, *C. R.* 109, 908). Trimetric prisms with sweet taste, v. sol. water and alcohol, insol. ether. Does not ferment with yeast or reduce Fehling's solution. Reduces ammoniacal $AgNO_3$. Not affected by dilute acids or alkalis at 100°. Ppd. by ammoniacal lead acetate, but not by lead subacetate. Heated with HI it gives off MeI and a little benzene. Ac_2O and $ZnCl_2$ form an acetyl derivative [89°]. Gives on heating with HNO_3 the same reactions as inosite.

QUEBRACHO BARK. Quebracho blanco, or white quebracho bark, used as a febrifuge, contains about ·8 p.c. of alkaloids, consisting of Aspidospermine, Aspidospermatine, Aspidosamine, Quebrachine, Hypoquebrachine, Quebrachamine, and Quebrachol (Hesse, *A.* 211, 251).

QUEBRACHO GUM. Occurs in quebracho colorado, the bark of *Loxopterygium Lorentii* (Jean, *Bl.* 28, 6; Arata, *Anales de la Sociedad cientifica Argentina*, July 1878; Feb. 1879; *C. J.* 34, 986). Brittle red concretions, with astringent taste, sol. boiling water and alcohol, insol. ether. Quebracho gum contains quebrachitannic acid, a pale-red amorphous mass, m. sol. hot water, giving a green colour with $FeCl_3$, turned dark red by NaOAc. Quebrachitannic acid ppts. $Pb(OAc)_2$, gelatin, albumen, and alkaloids. It yields pyrocatechin and a liquid (100°–120°) on distillation. Potash-fusion gives protocatechuic acid and phloroglucin; nitric acid yields oxalic and picric acids.

QUEBRACHOL $C_{20}H_{34}O$. [125°]. $[\alpha]_D = -29·3°$. Occurs in white quebracho bark (Hesse, *A.* 211, 272; 228, 288). Plates, v. e. sol. alcohol and ether, insol. water and alkalis. When the solution in chloroform is shaken with H_2SO_4 the chloroform is coloured red (*cf.* Cholesterin).

Acetyl derivative $C_{20}H_{33}.OAc$. [115°].

QUERCETAGETIN $C_{27}H_{22}O_{13}$ 4aq. Yellow crystals, extracted by alcohol from the blossoms of the common marigold, *Tagetes patula* (Latour a. Magnier, *Bl.* [2] 28, 337).

QUERCETIN $C_{24}H_{16}O_{11}$ 3aq (Liebermann a. Hamburger, *B.* 12, 1178) or $C_{15}H_{10}O_7$ (Herzig, *M.* 12, 172). (β)-*Rhamnetin* (Herzig, *M.* 10, 561). [above 250°]. S. (alcohol) 5·5 at 78°; ·4 in the cold (Stein, *J.* 1862, 499). Mol. w. (by Raoult's method) 258 (calc. 302). Formed, together with isodulcite, by the action of dilute H_2SO_4 on quercitron, a yellow dye-stuff consisting of the shavings of the bark of *Quercus tinctoria*, growing in the United States (Rigaud, *A.* 90, 289). Rutin and robinin also yield quercetin when treated with dilute H_2SO_4 (Zwenger a. Dronke, *A.* 123, 153; *Suppl.* 1, 261; Schunck, *C. J.* 53, 262; Hlasiwetz, *A.* 112, 96; *J. pr.* 94, 65). Occurs in Persian berries (Kane, *A. Ch.* [3] 8, 380; Bolley, *C. J.* 13, 327), in the ripe fruit, flowers, and leaves of the horse-chestnut (Rochleder, *A.* 112, 112), in the berries of the sea-buckthorn (*Hippophaë rhamnoides*), in apple-tree bark, in tea-leaves, and in catechu (Loewy, *Fr.* 12, 127).

Properties. — Lemon-yellow crystalline powder, sl. sol. water, v. sl. sol. ether. Gives off water of crystallisation at 130°. May be sublimed as yellow needles. Dissolves in alkalis, forming yellow solutions. Dyes fabrics mordanted with alumina yellow; with iron, grey or black. Its alcoholic solution is coloured dark green by $FeCl_3$, the colour becoming dark red on warming.

$Pb(OAc)_2$ gives a brick-red pp. Reduces $AgNO_3$ in the cold, and Fehling's solution on heating.

Reactions.—1. On *fusion with potash* it yields phloroglucin and quercetic acid, and by prolonged fusion, paradatiscetin $C_{15}H_{10}O_8$, quercimeric and protocatechuic acid.—2. Boiling dilute *alcoholic potash* gives phloroglucin and protocatechuic acid (Herzig, *M.* 6, 863).—3. $KClO_3$ and HCl yield protocatechuic acid.—4. *Sodium-amalgam* forms phloroglucin, a compound $C_{13}H_{12}O_5$ crystallising in needles, sl. sol. water, and a compound $C_7H_8O_3$, which forms granular crystals [130°], v. sol. water.—5. *Bromine* in HOAc forms $C_{21}H_{13}Br_3O_{11}$, crystallising in lemon-yellow needles [237°] and yielding $C_{21}H_5Ac_8Br_3O_{11}$. Excess of Br in HOAc forms $C_{21}H_{11}Br_5O_{11}$, whence $C_{21}H_3Ac_8Br_5O_{11}$ may be got, crystallising from HOAc in needles [253°]. Liebermann obtained the compounds $C_{21}H_{14}Br_2O_{11}$, $C_{21}H_{12}Ac_2Br_2O_{11}$ [218°], $C_{21}H_{12}Br_4O_{11}$, and $C_{24}H_{10}Ac_2Br_4O_{11}$ [228°], all crystallising in needles.—6. *Phenyl cyanate* at 160° forms $C_{21}H_{11}O_6(O.CO.NHPh)_5$, a white amorphous powder [200°–205°] (Tesmer, *B.* 18, 2609).—7. Ammonia at 150° forms amorphous 'quercetamide' (Schützenberger a. Paraf, *Z.* 1862, 41).

Salts.—$C_{27}H_{20}K_2O_{13}$ (?).—$C_{27}H_{20}Na_2O_{13}$ (?).—$C_{27}H_{20}ZnO_{14}$ (H. a. F.).

Acetyl derivative $C_{21}H_8Ac_8O_{11}$ or $C_{15}H_5Ac_5O_7$ (Herzig, *M.* 5, 72; 6, 890; 9, 537; 10, 561; 12, 174; *cf.* Liebermann, *B.* 12, 1178; *A.* 196, 319). [191°]. Formed by boiling quercetin or rhamnetin with Ac_2O, and NaOAc. Needles (from alcohol). Liebermann obtained $C_{24}H_{14}Ac_2O_{11}$ [198°], crystallising in needles.

Methyl ether $C_{15}H_9O_6(OMe)$. *Rhamnetin.* Formed, together with isodulcite, by heating xanthorhamnin with dilute H_2SO_4 (Gellatly, *N. E. P. J.* 7, 256; Liebermann a. Hörmann, *B.* 11, 1618; Herzig, *M.* 6, 889; 9, 560; 12, 175. Lemon-yellow powder, nearly insol. water, alcohol, and ether, v. sol. hot phenol. Forms a yellow solution in KOHAq. Reduces ammoniacal $AgNO_3$ and hot Fehling's solution. Yields protocatechuic acid and phloroglucin on fusion with potash or on treatment with sodium-amalgam (Smorawski, *B.* 12, 1595). Converted by HI into quercetin and MeI. Dyes iron mordants black and alumina yellow. Yields $C_{15}H_5Ac_4O_6(OMe)$ [185°]. KOH and EtI give ethyl-rhamnetin [108°], whence Ac_2O and NaOAc form an acetyl-ethyl-rhamnetin [157°]. Rhamnetin yields also (tetra-?) propionyl [158°–162°] and (tetra-?) benzoyl [212°] derivatives, and an acetyl-di-bromo- derivative [212°].

Methyl derivative $C_{21}H_{10}Me_6O_{11}$ or $C_{15}H_6Me_4O_7$. [157°]. Formed from quercetin, KOMe, and MeI (Herzig, *M.* 5, 83) and got also by heating xanthorhamnin with $KMeSO_4$ and MeOH at 120°, and from rhamnetin, KOH, and MeI (Liebermann a. Hörmann, *A.* 196, 317; Herzig, *M.* 6, 889; 9, 552). Golden needles, sl. sol. alcohol, converted by alcoholic potash at 140° into the di-methyl derivative of protocatechuic acid. Boiling Ac_2O and NaOAc give $C_{24}H_8Ac_2Me_6O_{11}$ or $C_{15}H_5AcMe_4O_7$ crystallising in needles [167°].

Ethyl derivative $C_{24}H_{10}Et_6O_{11}$ or $C_{15}H_6Et_4O_7$. [122°]. Got by boiling quercetin with alcoholic potash and EtI (Herzig, *M.* 9, 537). Yellow needles, m. sol. alcohol. Yields $C_6H_3(OEt)_2CO_2H$ when heated with potash at 140°. Ac_2O and sodium acetate give the colourless acetyl derivative $C_{24}H_8Ac_2Et_6O_{11}$ or $C_{15}H_{15}AcEt_4O_7$ crystallising in needles [153°]. Mol. w. (by Raoult's method) c. 426 (Herzig, *M.* 12, 172).

A compound of quercetin and rhamnetin which sometimes occurs in Persian berries (Herzig, *M.* 10, 561) yields an acetyl derivative [171°], an acetyl-ethyl derivative [142°], and an ethyl derivative [102°].

Paradatiscetin $C_{15}H_{10}O_8$. Formed from quercetin by potash-fusion (Hlasiwetz a. Pfaundler, *J. pr.* 94, 65). Yellowish needles (from dilute alcohol), nearly insol. water, m. sol. ether. Acid in reaction. $FeCl_3$ colours its alcoholic solution violet. Potash forms a yellow solution, turning green in air. Reduces $AgNO_3$ and Fehling's solution on heating. Potash-fusion yields phloroglucin but not protocatechuic acid. Boiled with water and $BaCO_3$ it yields BaA'_2 2aq.—SrA'_2 2aq.

Quercetic acid $C_{15}H_{10}O_7$ 3aq (?). Formed, together with phloroglucin, by heating quercetin (1 pt.) with moist KOH (3 pts.) till a sample no longer gives a flocculent pp. with HCl and the residue quickly turns dark red at the edges (Hlasiwetz, *A.* 112, 96; 119, 213; *J. pr.* 94, 65). Slender silky efflorescent needles, sl. sol. cold water, v. sol. alcohol and ether. Its aqueous solution turns yellow, and finally crimson, in air. H_2SO_4 forms a brown solution, whence water gives a red pp. forming a purple solution in NH_3Aq. $FeCl_3$ gives a blue-black colour. Reduces $AgNO_3$ Potash-fusion gives protocatechuic acid. AcCl forms $C_{15}H_8Ac_2O_7$, crystallising from alcohol in prismatic needles.

Quercimeric acid $C_8H_6O_5$ aq (?). Formed from quercetin by potash-fusion. Colourless prisms, v. sol. water, alcohol, and ether. Tastes bitter. Alkalis colour its solutions purple-red. $FeCl_3$ gives a dark-blue colour. Reduces $AgNO_3$ and Fehling's solution. Potash-fusion gives protocatechuic acid.

QUERCIN $C_6H_6(OH)_6$. [340°]. Occurs in oak bark, being obtained from the mother-liquors in the preparation of quercite (Gerber, *A.* 48, 348; Vincent a. Delachanal, *C. R.* 104, 1855; Friedel, 105, 95; *Bl.* [2] 48, 113). Efflorescent monoclinic prisms (containing $x$aq), sl. sol. water, insol. boiling alcohol. Inactive to light. Does not ferment with yeast, nor reduce Fehling's solution. Does not react with phenyl-hydrazine. Reduces ammoniacal $AgNO_3$ after addition of NaOH. Gives a gelatinous pp. with lead sub-acetate. After evaporation with HNO_3 it gives a rose-red colour with NH_3Aq and $CaCl_2$. Not coloured by boiling NaOHAq.

Acetyl derivative.—$C_6H_6(OAc)_6$. [301°].

QUERCITANNIC ACID $C_{17}H_{16}O_9$ or $C_{19}H_{16}O_{10}$. S. ·6. S. (ether) ·035. Occurs in oak bark, from which it is got by powdering, sifting from bast fibres, extracting with dilute alcohol, and shaking the filtrate with ether and EtOAc. The acetic ether when evaporated deposits ellagic acid. The filtrate is evaporated to dryness, and the residue washed with ether and then extracted with Et_2O and EtOAc (Etti, *Sitz. W.* [2] 81, 495; *M.* 1, 264; 4, 514; *cf.* Stenhouse, *A.* 45, 16; Böttinger, *A.* 202, 270; 240, 331; 263, 112; Löwe, *Fr.* 20, 210). Occurs

also in tea (Rochleder, *A.* 63, 205). Reddish-white powder. $FeCl_3$ colours the alcoholic solution dark blue. $Pb(OAc)_2$ ppts. the alcoholic solution. Quercitannic acid is not a glucoside (Etti). At 130° to 140° it forms an anhydride which gives $C_{34}H_{28}BaO_{17}$ (Etti). On evaporating with NaCl it is converted into a mixture of anhydrides which give with bromine-water an amorphous pp. $C_{19}H_{14}Br_2O_{10}$, m. sol. alcohol and EtOAc, v. e. sol. a mixture of these solvents, reacts with hydroxylamine, and is converted by Br into $C_{19}H_{10}Br_4O_{10}$, whence Ac_2O forms $C_{19}H_5Ac_5Br_4G_{10}$.

QUERCITE $C_6H_{12}O_5$. *Penta-oxy-benzene hexahydride?* Mol w. 164. [234°] Böttinger, *B.* 14, 1598). S.G. $\frac{13}{}$1·585. S. 9 at 12°; 11 at 20°. $[\alpha]_D = 24{\cdot}17$. H.C. v. 710,100 (Berthelot a. Recoura, *A. Ch.* [6] 13, 341). H.F. 268,200. R_∞ 58·95 in a 7·7 p.c. aqueous solution (Kanonnikoff). Occurs in acorns (Braconnot, *A. Ch.* [3] 27, 392; Dessaignes, *A.* 81, 103, 251; Prunier, *A. Ch.* [5] 15, 5; *C. R.* 84, 1318; 85, 808; 86, 338, 1460; Hofmann, *A.* 190, 282).

Preparation. — Acorns are extracted with cold water, the extract concentrated at 40°, ppd. by lead subacetate, filtered, mixed with yeast to remove sugar, and, after fermentation, freed from lead by H_2S, and evaporated to crystallisation.

Properties. — Monoclinic prisms, $a:b:c = {\cdot}800:1:{\cdot}766$, $\beta = 68°57'$, insol. ether, benzene, and chloroform, v. sl. sol. hot alcohol. Does not undergo alcoholic fermentation. Dextrorotatory. Does not render borax solution acid.

Reactions.—1. At 100° it slowly loses water, forming $C_{24}H_{16}O_{19}$ (?). At 240° *in vacuo* it gives $C_{12}H_{22}O_9$ [230°], v. sl. sol. water. Rapidly heated to 290° it swells up and gives off quinhydrone and hydroquinone.—2. *Potash-fusion* gives quinone, hydroquinone, CO_2, formic acid, and oxalic acid.—3. H_2SO_4 and MnO_2 give quinone. 4. Conc. HClAq forms, at 100°, $C_6H_7Cl(OH)_4$ [200°], sol. ether, and viscid $C_6H_9ClO_3$, which is converted by baryta-water into amorphous quercitan $C_6H_{10}O_4$, sol. water and alcohol, insol. ether. HClAq at 120°–140° gives $C_6H_7Cl_3(OH)_2$ [155°], converted by further treatment with HCl into $C_6H_7Cl_5$ [102°].—5. Distillation with HIAq forms benzene, phenol, iodo-phenol, quinone, hydroquinone, and hexane.—6. *Nitric acid* forms mucic and tri-oxy-glutaric acids (Kiliani a. Scheibler, *B.* 22, 517).—7. *Phenyl cyanate* at 165° forms $C_6H_7(O.CO.NHPh)_5$ [120°–140°], a white amorphous powder (Tesmer, *B.* 18, 2606). 8. *Benzoic acid* at 200° forms solid 'benzoquercite' $C_6H_{10}Bz_2O_5$ (?) insol. water, sol. alcohol and ether. *Stearic acid* forms a similar body, while tartaric acid gives 'quercitartaric acid $C_{22}H_{32}O_{27}$ (Berthelot, *C. R.* 44, 452; *A. Ch.* [3] 54, 82).

Salts.—$(C_6H_{11}O_5)_2Ba$ 3aq: amorphous, sol. water and alcohol.—$(C_6H_{12}O_5)_2CaSO_4$ 2aq.

Acetyl derivatives. The compounds $C_6H_{11}AcO_5$, $C_6H_{10}Ac_2O_5$, $C_6H_9Ac_3O_5$, $C_6H_8Ac_4O_5$, and $C_6H_7Ac_5O_5$ have been prepared.

Butyryl derivatives. Heating with butyric acid gives rise to $C_6H_{11}(C_4H_7O)O_5$, $C_6H_9(C_4H_7O)_3O_5$, and $C_6H_7(C_4H_7O)_5O_5$, all being amorphous with bitter taste.

Pentanitrate $C_6H_7(NO_3)_5$. **Formed from quercite (1 pt.), H_2SO_4 (10 pts.) and HNO_3 (4 pts.) (Hofmann, *A.* 190, 288).** Resin, insol. water, sol. alcohol and ether. Explodes when heated. Zinc-dust and alcoholic soda give off the N as NH_3.

QUERCITRIN $C_{36}H_{38}O_{20}$ or, more probably, $C_{21}H_{22}O_{12}$ (Herzig, *M.* 14, 53). [168°]. S. ·04 in the cold; ·7 at 100°. S. (alcohol) 4 in the cold 29 at 78° (Stein). S. (ether) ·8 (Schunck, *C. J* 53, 264). Occurs in quercitron-bark, the bark of *Quercus tinctoria* (Bolley, *A.* 37, 101; 62, 136; Rochleder, *J. pr.* 77, 34; Rigaud, *A.* 90, 283; Zwenger a. Dronke, *A. Suppl.* 1, 266; Stein, *J. pr.* 85, 351; Hlasiwetz, *A.* 112, 109). Occurs also in fully-developed horse-chestnut leaves (Rochleder a. Kawalier, *Sitz. W.* 55 [2] 46), in leaves of the ash (Gintl, *Z.* [2] 4, 732), and in leaves of *Andromeda japonica* (Eykman, *R. T. C.* 2, 200).

Preparation.—Quercitron bark is exhausted with alcohol, and the evaporated extract dissolved in water and shaken with ether. The ethereal solution is evaporated, the residue dissolved in alcohol, and the quercitrin ppd. by water and crystallised from boiling water (Löwe, *Fr.* 14, 233; *cf.* Herzig, *M.* 6, 877).

Properties.—Yellow needles or plates (containing 3aq). Neutral and tasteless. Nearly insol. cold water, sol. alkalis and HOAc. $FeCl_3$ colours its solution dark green. $FeSO_4$ gives no colour. Ppd. by $Pb(OAc)_2$. Reduces aqueous $AgNO_3$ in the cold, and Fehling's solution after long boiling. Boiling dilute acids split it up into quercetin (*q. v.*) and isodulcite (Liebermann a. Hamburger, *B.* 12, 1178). Bromine forms $C_{36}H_{34}Br_4O_{20}$, which is crystalline and is decomposed by acids into isodulcite and tetra-bromoquercetin.

Salt.—$C_{36}H_{36}K_2O_{20}$: yellow pp.

Violaquercitrin $C_{42}H_{42}O_{24}$. Occurs in *Viola tricolor* (Mandelin, *J.* 1883, 1369). Yellow needles (from water). Split up by dilute acids into glucose and quercetin.

QUILLAJIC ACID $C_{19}H_{30}O_{10}$. Extracted by water from the bark of *Quillaja Saponaria* (Kobert, *C. C.* 1888, 972). White flakes, sol. water and alcohol, insol. ether. Coloured dark red by H_2SO_4. Boiling dilute acids split it up into sapoginin and an unfermentable glucose. The Na salt violently attacks the mucous membrane, and is very poisonous when injected into the blood.

QUINACETOPHENONE is DI-OXY-ACETOPHENONE.

QUINALDINE *v.* METHYL-QUINOLINE.

QUINALDINIC ACID *v.* QUINOLINE CARBOXYLIC ACID.

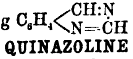
QUINAMINE *v.* vol. ii. p. 179.

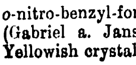
QUINAMICINE *v.* vol. ii. p. 180.

QUINAMIDINE *v.* CINCHONA BASES.

QUINANISOLE *v.* *Methyl derivative* of OXY-QUINOLINE.

QUINAZOLE *v.* METHYL-INDAZINE.

QUINAZOLINE. This name is given to the ring  $C_6H_4<\genfrac{}{}{0pt}{}{CH:N}{N=CH}$; *v.* OXY-QUINAZOLINE.

QUINAZOLINE DIHYDRIDE $C_8H_8N_2$ *i.e.*  $C_6H_4<\genfrac{}{}{0pt}{}{CH_2.NH}{N=CH}$ [127°]. Formed by reducing *o*-nitro-benzyl-formamide by Zn and HClAq (Gabriel a. Jansen, *B.* 23, 2814; 24, 3097). Yellowish crystals, sol. warm water, forming an

alkaline solution.—B′HCl.—B′$C_6H_8N_2O_7$. [215°]. Small crystals, sl. sol. water.—$B'_2H_2PtCl_6$.

QUINENE *v.* vol. ii. p. 181.

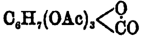
QUINETHONIC ACID $C_{14}H_{18}O_8$ *i.e.* $C_6H_4(OEt).C_6H_9O_7$. [146°]. Occurs in urine after a dose of $C_6H_5.OEt$ (Kossel, *H.* 4, 296; 7, 292; Lehmann, *H.* 13, 181). Crystalline. Lævorotatory. Does not reduce Fehling's solution. Converted by dilute H_2SO_4 into crystalline $C_8H_{10}O_2$. HIAq forms hydroquinone. Oxidising agents yield quinone. — KA′aq: monoclinic crystals.—AgA′aq. Forms with $C_6H_5.O.SO_3H$ the double salt $PhO.SO_3BaA'$aq (dried at 110°) and with cresol and indoxyl the corresponding $C_7H_7O.SO_3BaA'$aq and $C_8H_6NSO_4BaA'$, all three being crystalline (Hoppe-Seyler, *H.* 7, 424).

QUINHYDRONE $C_{12}H_{10}O_4$. Formed by mixing aqueous solutions of quinone and hydroquinone; by oxidising hydroquinone; and by reducing quinone (Wöhler, *A.* 51, 153; Liebermann, *B.* 10, 1614, 2000; Hesse, *A.* 200, 248; Nietzki, *A.* 215, 130; Wichelhaus, *B.* 5, 840; 12, 1500; Stenhouse a. Groves, *B.* 13, 1305). Brownish-red prisms, with green metallic lustre. May be sublimed. Sl. sol. cold water, v. sol. alcohol and ether, forming yellow solutions. Decomposed by boiling water, giving off quinone and leaving a solution of hydroquinone. Its ammoniacal solution is green. Reduces ammoniacal $AgNO_3$.

QUINIC ACID $C_7H_{12}O_6$ *i.e.* $C_6H_7(OH)_4.CO_2H$. Mol. w. 192. [162° cor.]. S.G. $^{8.5}$ 1·637 (Henry a. Plisson, *B. J.* 10, 186). S. 40 at 9°. $[\alpha]_D = -44°$ at 20° in a 20 p.c. solution (Thomsen, *J. pr.* [2] 35, 156). H.C. 833,700. H.F. 238,300 (Berthelot a. Recoura, *C. R.* 105, 144; *Bl.* [2] 48, 703; *A. Ch.* [6] 13, 342). R_∞ 66·52 in an 18 p.c. aqueous solution (Kanonnikoff, *J. pr.* [2] 31, 348). Occurs as calcium salt in cinchona bark (Hoffmann, *Crell's Ann.* 2, 314; Vauquelin, *A. Ch.* 59, 162; Pelletier a. Caventou, *A. Ch.* [2] 15, 340; Liebig, *P.* 21, 1; 29, 70; Baup, *A. Ch.* [2] 51, 5; *A.* 6, 7; Woskresensky, *A.* 27, 260; Hesse, *A.* 110, 194; 112, 52; 114, 292; 176, 124; Clemm a. Will, *A.* 110, 345). Occurs also in the bilberry plant (*Vaccinium Myrtillus*) (Zwenger, *A.* 115, 108; 129, 203; *Suppl.* 1, 77), in the leaves and beans of the coffee-plant (Z.), and in hay (O. Loew, *J. pr.* [2] 19, 310; 20, 476).

Preparation.—Cinchona bark is extracted with dilute H_2SO_4, the extract ppd. by milk of lime, filtered, and evaporated. The residue is boiled with alcohol and the calcium quinate left undissolved is crystallised from water and decomposed by oxalic acid.

Properties.—Monoclinic prisms. V. e. sol. water, m. sol. alcohol, nearly insol. ether. Lævorotatory.

Reactions.—1. *Heated* to 200°–225° it gives off aq, forming quinide $C_7H_{10}O_5$, a crystalline anhydride, v. sol. water, sl. sol. dilute alcohol. Quinide is acid in reaction, and is reconverted by bases into quinic acid. On dry distillation quinic acid gives hydroquinone, phenol, benzoic acid, and pyrocatechin.—2. Ac_2O at 170° forms tri-acetyl-quinide  $C_6H_7(OAc)_3\langle\substack{O\\CO}$ [132°] and tetra-acetyl-quinic acid (Erwig a. Königs, *B.* 22, 1458; *cf.* Hesse, *A.* 200, 233). By further heating with Ac_2O at 240°–250° monoclinic crystals of iso-tri-acetyl-quinide [139°] are obtained.—3. *Bromine* added to an aqueous solution forms protocatechuic acid (Hesse).—4. Hot H_2SO_4 forms CO and hydroquinone disulphonic acid.—5. Hydroquinone is formed by boiling the aqueous solution with PbO_2. Distillation with MnO_2 and dilute H_2SO_4 yields quinone (detection of quinic acid in bark: Stenhouse, *A.* 59, 100).—6. HNO_3 gives oxalic acid. 7. $KClO_3$ and HCl give chlorinated quinones and chlorinated acetones (Städeler, *A.* 69, 300; 111, 293).—8. Conc. HIAq at 120° reduces it to benzoic acid (Lautemann, *A.* 125, 9).—9. Conc. HClAq at 150° gives *p*-oxy-benzoic acid and hydroquinone (Hesse, *A.* 200, 232). Dilute (3 p.c.) HClAq at 100°–120° forms phenol, hydroquinone, and *p*-oxy-benzoic acid (Chadounski, *C. C.* 1888, 1029). — 10. Fuming HBrAq at 130° gives protocatechuic and benzoic acids (Fittig, *A.* 193, 197).—11. PCl_5 forms *m*-chloro-benzoyl chloride (Graebe, *A.* 138, 197). 12. Gives protocatechuic acid on fusion with KOH or NaOH.—13. Boiling with iodine and KOHAq yields iodoform.—14. Calcium quinate fermented by *schizomycetes* in presence of air yields protocatechuic acid, in absence of air it gives propionic, acetic, and formic acids (Löw, *B.* 14, 450).

Salts.—NaA′ 2aq.—NaA′ 5aq. S. 200.—BaA'_2 6aq: dodecahedra, very soluble in water.—CaA'_2 10aq. S. 17 at 16°. Plates, insol. alcohol. —CaA′Ac aq (Gundelach, *B.* 9, 852).—SrA'_2 10aq. —SrA'_2 15aq.—MgA'_2 6aq.—CdA'_2. S. ·4 in the cold.—ZnA'_2.—CoA'_2 5aq.—NiA'_2 5aq: crystals. CuA'_2 5aq: blue needles.—$CuC_7H_{10}O_6$ 2aq. S. ·09 at 18°.—PbA'_2 2aq: needles, sol. alcohol, v. e. sol. water.—$Pb_2C_7H_8O_6$. Amorphous, insol. water.—MnA'_2. S. ·5 in the cold.—$FeC_{14}H_{21}O_{12}$. —AgA′: mammellated groups of crystals.

Ethyl ether EtA′. Viscid mass, with bitter taste, v. sol. water and alcohol. Converted by boiling Ac_2O into $C_6H_7(OAc)_4.CO_2Et$ crystallising from water in plates [135°], sl. sol. boiling water.

Tetra-acetyl derivative $C_6H_7(OAc)_4.CO_2H$. [130°–136°]. Formed by heating quinic acid with Ac_2O and $ZnCl_2$ (Erwig a. Koenigs, *B.* 22, 1461). Crystalline crusts, sl. sol. cold water, insol. ligroïn.—AgA′: needles.

Anilide $C_{13}H_{17}NO_5$. [174°]. Formed by heating quinic acid with aniline at 180°. Small silky needles (containing aq), v. sol. water and alcohol, sl. sol. ether.

QUINICINE *v.* CINCHONA BASES.

QUINIDE *v.* QUINIC ACID.

QUINIDINE *v.* vol. ii. p. 180.

QUINIENE *v.* vol. ii. p. 181.

QUININE $C_{20}H_{24}N_2O_2$. [173° cor.] (Lenz, *Fr.* 27, 559; Hesse, *A.* 258, 133). The trihydrate melts at 57° (H.). S. ·05 at 15° (Regnauld, *J. Pharm. Chim.* [4] 21, 8). S. (of the trihydrate) ·06 at 15° (Hesse, *B.* 10, 2152); ·06 at 20°, ·11 at 100° (Sestini, *Fr.* 6, 359). S. (of the anhydrous base) ·051 at 15° (H.); ·07 at 20°, ·13 at 100° (S.). S. (ether) 100 at 10° (Hesse, *A.* 135, 327); 4·4 at 18° (van der Burg, *J.* 1865, 438). A conc. ethereal solution often gelatinises, the quinine thus separated being less sol. ether (S. about 5 at 15°). S. (chloroform) 57·5 (Pettenkofer, *J.* 1858, 363). S. (benzene) ·5 at 15°; 3·3 at 80° (Oudemans, *J.* 1874, 867). S. (xylene) ·11 at 15°; ·645 at 138° (Swaving, *R. T. C.* 4, 186). $[\alpha]_D = -166°$ at 15°; −162°

at 25° in alcoholic solution (Hesse, *A.* 166, 217) $= -145{\cdot}2 + {\cdot}657p$ in a solution of p grammes in 100 c.c. of 97 p.c. alcohol at 15° (Hesse, *A.* 176, 206; 182, 131). $[\alpha]_D = -158{\cdot}7 + 1{\cdot}911p$ in an ethereal solution containing from 1·5 to 6 p.c. base. In solutions containing not more than 1·6 p.c. quinine, Oudmans, jun. (*Ar. N.* 10, 193), found $[\alpha]_D = -167{\cdot}5°$ (in alcohol); −136° in benzene; −127° in toluene; −117° in chloroform. *Dispersive power*: Grimbert, *J. Ph.* [5] 16, 295, 345.

Occurrence.—In cinchona bark, *v.* vol. ii. p. 175. According to Grimaux (*Bl.* [3] 7, 304), cupreïne heated with NaOMe, MeOH, and MeCl or $MeNO_3$ yields 10 to 15 p.c. of quinine, while MeI gives chiefly quinine di-methylo-di-iodide.

Preparation.—The bark is extracted with dilute H_2SO_4, and the solution ppd. by NaOHAq. The pp. is dissolved in ether, the ether shaken with dilute H_2SO_4, and the boiling solution neutralised by ammonia. Quinine sulphate separates on cooling. The sulphate is decomposed by ammonia.

References. — *Vide* references in articles CINCHONA BARK and CINCHONIDINE, and also Pasteur, *C. R.* 36, 26; 37, 110, 162; Schützenberger, *A.* 108, 347, 350; Robiquet, *A. Ch.* [2] 17, 316; Stratingh, *R. P.* 15, 139; Pelletier, *J. Ph.* 11, 249; Duflos, *B. J.* 27, 1, 110; Strecker, *A.* 91, 155; Thiboumery, *J. Ph.* [3] 16, 369; Alluard, *J. Ph.* [3] 46, 192; Körner, *Z.* [2] 1, 150; Bouchardat, *A. Ch.* [3] 9, 213; De Vrij, *N. J. P.* 14, 268; Laudrin, *C. R.* 108, 750.

Properties.—Ppd. by ammonia from solutions of its salts in an amorphous anhydrous form, which quickly changes, especially in presence of free ammonia, into the crystalline hydrate (containing 3aq), consisting of minute four-sided prisms terminated by pyramids. The hydrate gives off its water of crystallisation over H_2SO_4. Quinine is v. e. sol. ether and alcohol, v. sol. CS_2, m. sol. benzene, v. sl. sol. ligroïn, sol. volatile and fixed oils. It is alkaline in reaction. Its solutions are lævorotatory. A 5 p.c. solution of the sulphate gives $\alpha = -22°$ in a depth of 200 mm. (Rozsnyay, *Fr.* 23, 589). Its solutions in dilute H_2SO_4, HNO_3, H_3PO_4, and HOAc exhibit blue fluorescence, destroyed by HCl, HBr, HI, or H_4FeCy_6. Fluorescence of the sulphate is prevented by a large excess of sulphate of cupreïne (Grimaux a. Arnaud, *Bl.* [3] 7, 304). Chlorine-water and ammonia give a green pp. dissolving in excess of ammonia to an emerald green liquid. On addition of an acid the colour changes through blue (when neutral) to red, the green colour returning on adding ammonia (Brandes, *Ar. Ph.* 13, 65; André, *J. Ph.* 22, 132). Excess of chlorine-water and of ammonia should be avoided. Chlorine does not render a solution of quinine sulphate turbid (Lepage, *J. Ph.* 26, 140). Bromine-water and ammonia give the green colour even in exceedingly dilute solutions (Flückiger, *Fr.* 11, 318). The green colour may be also got by mixing ·01 g. of the salt to be tested with an equal bulk of $KClO_3$ and a drop of conc. H_2SO_4 followed by excess of ammonia (Mylius, *C. C.* 1886, 602). Chlorine-water followed by K_4FeCy_6 gives a red colour in a solution of quinine sulphate (Vogel, *A.* 73, 221; 86, 122). Quinine gives the usual alkaloidal reactions. It is coloured green by potash-fusion (Lenz, *Fr.* 25, 81). Potassium sulphocyanide gives a white pp., sol. excess (Schrage, *Ar. Ph.* [3] 13, 25). Boiled with dilute H_2SO_4 and PbO_2 quinine forms quinetin, a red substance (Marchand). Dilute HNO_3 gives no colour. Sunlight acting on an aqueous solution, even in an atmosphere of H, ppts. brown flocculent quiniretin, insol. water, alcohol, and ether (Flückiger, *Ph.* [3] 8, 885). ICl gives a light-brown crystalline pp., sl. sol. HClAq. Quinine is antiseptic, hindering putrefaction and the alcoholic, lactic, and butyric fermentation. Quinine is a febrifuge. Its salts taste bitter.

Reactions.—1. The sulphate is *oxidised* by $KMnO_4$ to pyridine tricarboxylic acid, oxalic acid, and NH_3 (Hoogewerff a. van Dorp, *B.* 12, 158). At 0° the first product is chitenine $C_{19}H_{22}N_2O_4$, which crystallises in colourless prisms [240°–286°], insol. ether and alcohol, sol. dilute acids and alkalis (Skraup, *B.* 12, 1104; *M.* 10, 39). Quinine (5 g.) is apparently oxidised by $KMnO_4$ (50 g.) to pyridine dicarboxylic acid (Ramsay a. Dobbie, *C. J.* 33, 102). Boiling nitric acid also forms pyridine dicarboxylic (cinchomeronic) acid. Aqueous CrO_3 oxidises quinine to quininic or methoxy-quinoline carboxylic acid.—2. A mixture of HNO_3 and H_2SO_4 reacts, and on diluting an amorphous pp., apparently $C_{20}H_{22}(NO_2)_2N_2O_2H_2O$ is got (Rennie, *C. J.* 39, 469).—3. PCl_5 converts it into colourless quinine-chloride $C_{20}H_{23}N_2OCl$ [151°] which by boiling with alcoholic KOH gives chinen $C_{20}H_{22}N_2O$ (Comstock a. Königs, *B.* 17, 1988).—4. Reduced by *zinc* and dilute H_2SO_4 to hydroquinine $C_{20}H_{26}N_2O_2$, an amorphous bitter resin (containing aq), sol. alcohol and ether, giving a green colour with chlorine-water and ammonia (Schützenberger, *A.* 108, 347).—5. Heated with *water* at 250° it yields quinoline (Reynoso, *C. R.* 24, 795). The same body is formed by heating with conc. KOHAq at 190° (Gerhardt a. Wertheim, *J.* 1840, 370).—6. Fuming H_2SO_4 forms a sulphonic acid. Conc. H_2SO_4 dissolves quinine, forming isocinchonine. Dilute H_2SO_4 at 125° converts quinine into quinicine.—7. *Iodic acid* gives off much gas on warming (Brett, *J. Ph.* [3] 27, 116).—8. Conc. HClAq at 150° forms MeCl and apoquinine (Hesse, *A.* 205, 317). Concentrated HClAq at −17° slowly forms hydrochloroquinine $C_{20}H_{25}ClN_2O_2$ [187°], while hydrogen bromide gives $C_{20}H_{25}BrN_2O_2$, which forms $B'H_2Br_2$ (Comstock a. Königs, *B.* 20, 2510).—9. Heated for a long time with 12 pts. of HIAq. S.G. 1·96 for 3 hours at 100° it gives methyl iodide and a yellow salt $C_{19}H_{22}N_2O_23HI$ [238°] sol. alkalis. Alcoholic NH_3Aq converts it into $C_{19}H_{22}N_2O_22HI$ mixed with a little $C_{19}H_{22}N_2O_2HI$, which yields an oxalate [187°] $(C_{19}H_{22}N_2O_2HI)H_2C_2O_4$ mixed with $(C_{19}H_{22}N_2O_2H_2I_2)_2H_2C_2O_4$ (Schubert a. Skraup, *M.* 12, 684). HBrAq acting on quinine at 100° forms $C_{19}H_{23}BrN_2O_2HBr\,aq$, crystallising in needles, from which sodium carbonate sets free $C_{19}H_{23}BrN_2O_2$, a powder [210°] (Julius, *M.* 6, 751). 10. Quinine dried at 120°, heated with HIAq (S.G. 1·7) at 100°, forms $C_{20}H_{24}N_2O_23HI$ [230°], a yellow crystalline mass, v. sl. sol. water, sl. sol. alcohol, insol. ether and NaOHAq. Alcoholic NH_3 converts this salt into $C_{20}H_{21}N_2O_2HI$? which is white, v. sol. alcohol, sl. sol. ether [155°–

160°]. Its solution in dilute H_2SO_4 shows blue fluorescence, and gives a brownish-yellow pp. with chlorine-water and ammonia. It gives rise to the salts $((C_{20}H_{24}N_2O_2)_2H_3I_3)_23H_2C_2O_4$? and $C_{20}H_{24}N_2O_2H_2I_2HNO_3$? [217°] (Schubert a. Skraup, *M.* 12, 678; *cf.* Lippmann a. Fleissner, *M.* 12, 329).—11. *Bromine* added to a solution of quinine in dilute H_2SO_4 ppts. $B'Br_2$ 2aq, B'_2Br_6, and $B'Br_4$ as bitter yellow curdy pps., melting at 160°–180° (Colson, *C. R.* 108, 678).

Estimation.—*V.* CINCHONA BARK. *V.* also Lenz, *Fr.* 27, 549–631. Quinine may be ppd. as chromate (De Vrij, *C. C.* 1889, 708; *Ar. Ph.* [3] 24, 1073; Vulpius, *Ar. Ph.* [3] 24, 1022; Schlikum, *Ar. Ph.* [3] 25, 128; Hesse, *Ph.* [3] 17, 585). A solution of quinine sulphate requires more ammonia to redissolve the pp. first formed than solutions of the sulphates of the alkaloids usually present with it (Kerner a. Weller, *Ar. Ph.* [3] 25, 712, 749; *Fr.* 1, 159; 27, 115; *cf.* Schäfer, *Ar. Ph.* [3] 25, 1033; Ruddiman, *C. N.* 58, 202, 216, 226; Jungfleisch, *J. Ph.* [5] 15, 5). Use may also be made of the sparing solubility of quinine oxalate in presence of $K_2C_2O_4$ (Schäfer, *Ar. Ph.* [3] 25, 64, 1041).

Constitution.—Chitenine $C_{19}H_{22}N_2O_4$ may be got by oxidation of both quinine and cinchonine. On further oxidation chitenine yields quinic, pyridine tricarboxylic, and cincholeuponic acids. From this it may be surmised that one half of the quinine molecule has the same composition as one half of the cinchonine molecule (Skraup, *M.* 10, 39, 220). Quinine, quinidine, and quinicine are probably stereo-isomeric, since they give the same products of oxidation; they are derivatives of (*B.* 2)-methoxy-quinoline while cinchonine is a derivative of quinoline. Cincholeuponic acid $C_8H_{13}NO_4$ [226°] yields $C_8H_{13}NO_4HCl$ [194°] and $C_8H_{12}AcNO_4$, and is converted by nitrous acid into the dibasic nitroso- derivative $C_8H_{12}(NO)NO_4$. Oxidation of quinine also yields a base, cincholeupone $C_9H_{17}NO_2$ oxidised by CrO_3 to cincholeuponic acid and other products. Cincholeupone when heated with zinc-dust yields (β)-ethyl-pyridine. By nitrous acid cincholeupone is converted into $C_9H_{16}(NO)NO_2$, which is an acid. Ac_2O forms acid $C_9H_{16}AcNO_2$. Oxy-quinoline (cynurine) is also a product of oxidation of quinine. From these experiments Skraup concludes that quinine and cinchonine contain a quinoline nucleus united to an ethyl-pyridine nucleus; quinine being methoxy-cinchonine. Cupreïne heated with NaOMe (1 mol.), MeI (6 mols.), and MeOH forms quinine di-methylo-di-iodide (Hesse, *A.* 266, 244; *cf.* Grimaux a. Arnaud, *C. R.* 112, 774; *A.* 267, 379). The chief product is, however, cupreïne mono-methylo-iodide. When only 1 mol. MeI is used, no quinine is got.

Salts.—$C_{20}H_{23}AgN_2O_2$. Gelatinous pp. got by adding $AgNO_3$ to a solution of quinine in alcoholic NH_3 (Skraup, *M.* 2, 613).—$B'HCl$ 2aq: groups of white needles (Hesse, *A.* 176, 210; 267, 142). Melts (when anhydrous) at 160°, without undergoing any change. S. 2·5 at 10°. V. e. sol. alcohol and ether. $[\alpha]_D = -134^\circ$ in a 2 p.c. solution at 17° (Oudemans). Its solution is not ppd. by silver nitrate (1 mol.) until added in excess (Vulpius, *Ar. Ph.* [3] 20, 361).—$B'HCl$ 1½aq. Large monoclinic octahedra, deposited at 0°.—$B'2HCl$. Groups of white needles, or gelatinous mass. S. 100 in the cold. Melts at 15° (A. Clermont, *J. Ph.* [5] 15, 15).—$B'H_2PtCl_6$ aq: yellowish flocculent pp., soon becoming orange and crystalline (Gerhardt, *B. J.* 23, 354). S. ·07 in the cold; ·8 at 100° (Duflos).—$B'_2H_2PtCl_6$ 3aq: orange amorphous pp. (Hesse, *A.* 207, 308).—$B'H_2HgCl_4$. Ppd. by mixing alcoholic solutions of quinine, HCl, and $HgCl_2$ (Hinterberger, *A.* 77, 201).—$B'_2H_4ZnCl_6$ 2aq: prisms (from alcohol) (Gräfinghoff, *Bl.* [2] 4, 391).—$B'_2H_6ZnCl_8$ 3aq: crystalline.—$B'H_2Br_2$ 3aq: crystals, v. e. sol. water.—$B'HI$: lemon-yellow prisms (Herapath), or heavy white powder. Sl. sol. water, v. e. sol. alcohol (Winckler, *Jahrb. pr. Pharm.* 20, 321). Melts at 150°–155°, but softens at about 100° and then blackens (Lippmann a. Fleissner, *M.* 13, 436).—$B'HIEt_2O$ (from ether). Crystals.—$B'H_2I_2$ 5aq (Regnault). Crystals. *V. Reaction* 9, *supra.*—$B'H_3I_3$. [230°]. Converted by NH_3Aq into $B'HI$.—$B'_2H_2SO_4$ 8aq (Hesse, *A.* 119, 361; 225, 97; Carles, *Bl.* [3] 7, 108; *cf.* Cownley, *Ph.* [3] 7, 189). Commercial specimens are somewhat effloresced. Monoclinic efflorescent prisms. Loses 6aq over H_2SO_4. S. (of $B'_2H_2SO_4$) ·126 at 6°; 3 at 100° (Howard). S. (alcohol of S.G. ·85) 1. S. (glycerin) 2·5. Insol. chloroform and fatty oils. $[\alpha]_D = -163^\circ$ in a 2 p.c. solution in 80 p.c. alcohol.—$B'H_2SO_4$ 7aq. [100°]. Rectangular prisms (from hot solutions) or small needles. S. 9 at 13°; 12·5 at 22°. Loses 6aq over H_2SO_4. $[\alpha]_D = -164\cdot9 + \cdot31p$ in a solution of p g. in 100 c.c. water, where p is between 1 and 6 (Hesse, *A.* 176, 215; 182, 134).—$B'(H_2SO_4)_2$ 7aq: prisms, v. e. sol. water, m. sol. alcohol. Its hot alcoholic solution deposits gelatinous $B'(H_2SO_4)_2$ 5aq. $[\alpha]_D = -170 + \cdot94p$.—$B'_2H_2Cl_2H_2SO_4$ 3aq. Mass of small needles, v. sol. water. S. (of anhydrous salt) 86. [120°] (hydrated); [165°–170°] (anhydrous) (Grimaux, *Bl.* [3] 7, 819).—$B'_2H_2Br_2H_2SO_4$ 3aq. S. 26 at 21°.—$B'_2H_2I_2H_2SO_4$ 2aq: yellow crystals, forming a colourless solution. Crystallises also with 4aq.—$B'_2H_2Cl_2H_3PO_4$ 9aq: small needles, sol. water.—$B'_2H_2Br_2H_3PO_4$ 7aq.—$B'_2H_2I_2H_3PO_4$ 6aq.—$B'_2H_2S_2O_3$ 2aq. S. ·3 (Wetherill, *A.* 66, 150; How, *N. Ed. P. J.* [2] 1, 47).—$B'HNO_3$ aq: prisms (Strecker, *A.* 91, 159).—$B'AgNO_3$ ½aq: crystalline pp. Chlorate.—$B'HClO_3$ 2aq (Tichborne, *Z.* 1866, 665; *cf.* Serullas, *A. Ch.* [2] 45, 279).—$B'(HClO_4)_2$ 7aq: trimetric octahedra.—$B'(HClO_4)$ 2aq. [210°] (Boedeker, *A.* 71, 61).—$B'HIO_4$ 9aq: needles (Langlois, *A. Ch.* [3] 31, 274).—$B'_4(HCl)_3(HI)_5I_4$: small brown crystals.—$B'_3(HCl)_5(HI)_4I_{10}$: blackish-green flat needles (Jörgensen, *J. pr.* [2] 15, 79).—$B'HI_2$ (Bauer, *Ar. Ph.* [3] 5, 214).—$B'HI_5$. Black prisms.—B'_4I_5. Resin.—B'_4I_6.—$B'_4(H_2SO_4)_3(HI)_2I_4$ 6aq. *Herapathite.* Formed by adding an alcoholic solution of iodine to a solution of quinine sulphate in HOAc (Herapath, *P. M.* [4] 3, 161; 4, 186; 6, 171, 346; 7, 352; 9, 366; 14, 224; *C. J.* 11, 130; Haidinger a. Stokes, *Sitz. W.* 10, 106; Jörgensen, *J. pr.* [2] 14, 230). Large colourless plates with metallic green lustre. Polarises light, so that two plates at right angles are opaque. S. (90 p.c. alcohol) ·125 at 16°. Decomposed by cold water. Dried over H_2SO_4 they become $B'_4(H_2SO_4)_3I_6$ 3aq (Hauer, *Z.* [2] 1, 481).—$B'_8(H_2SO_4)_6(HI)_4I_{10}$: thin lustrous plates.—$B'_4(H_2SO_4)_3(HI)_2I_6$ 2aq. Crystals, resembling herapathite, decomposed by hot alcohol into

iodine and herapathite.—$B'_8(H_2SO_4)_6(HI)_4I_{14}$ 4aq: brownish needles.—$B'_2H_2SO_4(HI)_2I_2$: red needles.—$B'_2H_2SO_4(HI)_2I_4$: brown rectangular plates with olive-green reflex.—$B'_2H_2SO_4(HI)_2I_8$: black crystals with green reflex.—$B'_3(H_2SO_4)_2(HI)_2I_3$.—$B'_3(H_2SO_4)_2(HI)_2I_5$ aq. — $B'_3(H_2SO_4)_2(HI)_2I_8$. — $B'H_2SeO_4$ 7aq: trimetric tables, insol. alcohol (Hjortdahl, *J.* 1879, 794).—$B'_4(H_2SeO_4)_3(HI)_2I_4$. Isomorphous with herapathite, which it greatly resembles. Almost insol. cold alcohol (Jörgensen, *J. pr.* [2] 15, 65, 418).—$B'_2H_2CrO_4$. S. ·042 at 15° (André); ·037 at 14°; ·05 at 16° (De Vrij, *Ar. Ph.* [3] 24, 1073; ·625 at 100° (A.). Ppd. by adding K_2CrO_4 to a solution of the neutral or acid sulphate. Tufts of golden needles.—$B'_2H_2CrO_4$ 2aq (Hesse, *Ph.* [3] 17, 585, 665). Becomes anhydrous at 80°, but re-absorbs 2aq on exposure to moist air.—$B'H_2CrO_4$ 7aq. Ppd. by adding $K_2Cr_2O_7$ to a solution of quinine in excess of dilute H_2SO_4 (André, *J. Ph.* [3] 41, 341). Orange pp., decomposed by light, and turned brown when heated to 60°-65° or when boiled with water. More soluble than $B'_2H_2CrO_4$.—$B'H_2CO_3$ aq. Efflorescent needles, with alkaline reaction, deposited from a solution of quinine in aqueous CO_2. Sol. alcohol, insol. ether (Langlois, *A. Ch.* [3] 41, 89).—$B'_2H_3PO_4$ 8aq. S. ·127 at 10° (Hesse). Tufts of long needles.—$B'_3 2H_3PO_4$ 5aq (Anderson, *A.* 66, 59). Crystals.—$B'_3 2H_3PO_4$ 12aq (A.).—$B'_2H_3PO_4$ 2aq (Gerhardt, *Gerh.* iv. 118).—$B'H_3PO_4$. S. 1·33 at 15·5° (L. Smith, *Z.* 1862, 159).—$B'HVO_3$ (Ditte, *A. Ch.* [6] 13, 236).—$B'H_2SiF_6$. Got by passing SiF_4 into a solution of quinine in absolute alcohol (Cavazzi, *G.* 17, 563). Minute crystals, insol. ether and CS_2, sl. sol. hot alcohol. Its aqueous solution is fluorescent.—$B'_2H_3AsO_4$ 8aq. Prisms, v. sol. hot water (Hesse).—$B'_2H_3AsO_4$ 6aq (Sestini).—$B'H_3AsO_4$ 2aq.—$B'H_4FeCy_6$ 3aq (Dollfus, *A.* 65, 227).—$B'H_3FeCy_6$ 1½aq: golden plates.—$B'H_2PtCy_4$aq (Wertheim, *A.* 73, 210). Crystals.—$B'_2H_2PtCy_4$ 2aq. S. ·054 at 18°; 1·8 at 57°. S. (alcohol) 20 at 16° (Schwarzenbach, *Pharm. Viertelj.* 8, 210; Van der Burg, *Fr.* 4, 312).—$B'H_2PtCy_4$ 2aq. ·074 at 18·5°; 5 at 100°.—$B'H_2PtCy_6$.—$B'2HCyS$. Lemon-yellow monoclinic crystals (W.).—$B'HCyS$ aq. S. ·18 at 20° (Hesse, *A.* 181, 48). — $B'_3(HCyS)_2 4HgCl_2$. — $B'_2(HCyS)_2HgCy_2$. — $B'(HCr(CyS)_4(NH_3)_2)_2$ 2aq. Formed by ppg. a solution of the acid sulphate with Reinecke's salt (Christensen, *J. pr.* [2] 45, 366). Red crystals, v. sl. sol. hot water.—Nitro-prusside. S. ·04 (Davy, *Ph.* [3] 11, 756).—**Cyanurates** $B'H_3C_3N_3O_3$ 9aq. [237°]. Sl. sol. hot water (Claus, *J. pr.* [2] 38, 227).—$B'(H_3C_3N_3O_3)_2$ 7aq. [213°]. — Oxalates. — $B'_2H_2C_2O_4$ 6aq. S. ·1 at 10°. Prisms (Hesse, *A.* 176, 218; *cf.* Regnault, *A.* 26, 37).—$B'H_2C_2O_4$ aq. Prisms, m. sol. cold water. — $B'H_2C_2O_4$ 3aq. $[\alpha] = -131°$.—$B'HOAc$. [140°]. Long needles, v. sol. hot water (R.).—$B'Cu(OAc)_2$. Green crystals (Skraup, *M.* 2, 611).—**Chloro-acetate** $B'C_2H_3ClO_2$ 2½aq. S. 1·6 at 21° (Mazzara, *G.* 13, 525).—**Di-chloro-acetate** $B'C_2H_2Cl_2O_2$ 2aq. S. 2·4 at 22°.—**Formate**: colourless needles (Bonaparte, *J. Chim. Méd.* 18, 680).—**Valerate** $B'C_5H_{10}O_2$ 1½aq (Bonaparte, *J. Chim. Méd.* 18, 680; 19, 330; Chatin, *J. Ph.* [4] 1, 268).—$B'C_5H_{10}O_2$ (Stalmann, *A.* 147, 132; Schmidt a. Sachtleben, *A.* 193, 100). S. ·9 in the cold; 2·5 at 100° (Wittstein, *Repert.* 87, 295; Landerer, *N. Br. Arch.* 119, 240). — **Succinate** $B'C_4H_6O_4$ 8aq. S. ·1 at 10°. Prisms, v. sol. hot water.—**Tartrate** $B'_2C_4H_6O_6$ 2aq. Crystalline powder (Hesse, *A.* 243, 134; *cf.* Arppo, *J. pr.* 53, 334).—$B'C_4H_6O_6$ aq (Pasteur, *J.* 1853, 421). The lævo- tartrate is more soluble than the dextro- tartrate, and has a different crystalline form.—$B'C_4H_4(SbOH)O_6$ 2aq. Resin (Clarke, *B.* 15, 1540).—**Citrate** $B'_2C_6H_8O_7$ 7aq. S. ·11 at 12° (Hesse); 44 at 100° (Mandelin, *J.* 1879, 796; Scribani, *G.* 9, 284).—$B'_3 2C_6H_8O_7$: minute prisms. S. ·11 in the cold; 2·4 at 100°.—$B'C_6H_8O_7$. Small prisms. S. ·16 in the cold, 2·6 at 100°.—**Chloro-crotonate** $B'C_4H_5ClO_2$. [201°]. Sl. sol. ether (Daccomo, *J.* 1884, 1385).—**Trichlorocrotonate** $B'C_4H_4Cl_3O_2$. [140°].—**Tri-chloro-lactate** $B'C_3H_3Cl_3O_3$. Sl. sol. ether.—**Di-bromo-pyruvate** $B'C_3H_2Br_2O_3$. [93°] (D.). — **Mucate** $B'_2C_6H_{10}O_8$. Needles (Ruhemann a. Dufton, *C. J.* 59, 754).—**Benzoate** $B'HOBz$. S. ·27 at 10°. Small prisms.—**Salicylate** $B'C_7H_6O_3$. S. ·44 at 16°. S. (ether) ·83 at 16°. Prisms (from alcohol). — **Melitate** $B'_2C_{12}H_6O_{12}$. Crystalline powder, v. sl. sol. cold water (Karmrodt, *A.* 81, 170). — **Tannates** $B'(C_{14}H_{10}O_9)_2$ 4aq and $B'(C_{14}H_{10}O_9)_3$ 8aq (Jobst, *Ar. Ph.* [3] 12, 331; Neumann, *Fr.* 28, 664).—**Meconate** $B'C_7H_4O_7$. Crystals (Austen, *Ph.* [3] 3, 1016).—**Urate** $B'C_5H_4N_4O_3$. Minute prisms. S. ·117 in the cold, 2·7 at 100°. S. (alcohol of S.G. ·823) ·063 in the cold, 2·2 on boiling (Elderhorst, *A.* 74, 77; Andreæ, *Pharm. Viertelj.* 10, 382). **Dextro-tropate.** [187°].—**Lævo-tropate.** [178°] (Ladenburg, *B.* 22, 2590). **Dextro-iso-propyl-phenyl-glycollate** [193°]. S. ·18 at 19°; S. (alcohol) 1·44 at 20°. $[\alpha]_D = -79°$. — **Lævo-iso-propyl-phenyl-glycollate** [205°]. S. ·09 at 15°; S. (alcohol) 54. $[\alpha]_D = -118°$ (Fileti, *J. pr.* [2] 46, 560).

Compound with benzene $B'C_6H_6$. Needles (from benzene) (Oudemans, *J.* 1874, 867).—**Compound with toluene** $B'C_7H_8$. Needles. — **Compounds with phenol** $B'PhOH$. Crystals (from alcohol). S. ·25 at 16° (Romei, *Z.* [2] 5, 383; Jobst, *N. R. P.* 24, 193).—$B'_2H_2Cl_2PhOH$ 2aq: prisms. S. 1 at 15° (Jobst a. Hesse, *A.* 180, 248).—$B'H_2SO_4PhOH$ 2aq (Hesse, *Pharm. Zeit.* 34, 191).—$B'_2H_2SO_4PhOH$ aq. S. ·147 at 15°. Prisms.—$B'_2H_2SO_4PhOH$ 6aq (Cotton, *Bl.* [2] 24, 535).—**Compound with tri-bromo-phenol** $B'C_6H_3Br_3O$. Silky needles (from alcohol) (Purgotti, *G.* 16, 528).—**Compound with anethole** $B'_2C_{10}H_{12}O$ 2aq. Monoclinic crystals (from ether), sl. sol. cold alcohol (Hesse, *A.* 123, 382). **Compound with eugenol** $B'C_{10}H_{12}O_2$. [110°]. S. (ether) 8·5 at 10°. Long silky prisms (Hesse, *A.* 135, 329).—**Compound with pyrocatechin** $B'_2C_6H_6O_2H_2SO_4$aq: colourless needles (Hesse, *C. C.* 1889, 519).—**Compounds with resorcin** $B'C_6H_6O_2H_2SO_4\frac{1}{2}$aq: needles (Malin, *A.* 138, 77).—$B'_2C_6H_6O_2H_2SO_4$ aq (Hesse). — **Compound with phloroglucin** $B'C_6H_6O_2H_2SO_4$ 2aq: stellate groups of needles (Hlasiwetz, *Z.* [2] 1, 613).—**Compound with orcin** $B'C_7H_8O_2H_2SO_4$aq. Needles (Hlasiwetz a. Barth, *A.* 134, 290; 138, 77).—**Compound with chloral** $B'C_2HCl_3O$. [149°]. Amorphous, sl. sol. cold alcohol (Mazzara, *G.* 13, 270).—**Compound with *m*-nitro-benzoic aldehyde** $B'C_6H_4(NO_2).CHO$. [113°-118°]. Yellow powder (Mazzara, *G.* 13, 368).—

Compound with nitro-camphor $B'(C_{10}H_{15}(NO_2)O)_2$ aq. Needles. [c. 131°]. $[\alpha]_D = +46^\circ$ in a 2·7 p.c. alcoholic solution (Cazeneuve, *Bl.* [2] 49, 97).—Compound with urea $B'CON_2H_4H_2Cl_2$ 5aq. S. 6. Small prisms (Drygin, *C. C.* 1878, 622; 1881, 245).—Compounds with quinidine $B'C_{20}H_{24}N_2O_2$ 2½aq.—$B'C_{20}H_{24}N_2O_2$ 3aq.—$B'C_{20}H_{24}N_2O_2C_6H_6$ 2aq (Wood a. Barret, *C. N.* 45, 6; 48, 4; Hesse, *A.* 243, 146).—Compound with hydroquinidine $B'C_{20}H_{26}N_2O_2$ 2½aq: slender white needles, v. sl. sol. water, m. sol. ether.—Compounds with cinchonidine $B'2C_{19}H_{22}N_2O$. Rhombohedra, very slightly sol. ether (Hesse, *A.* 243, 131). — $B'7C_{19}H_{22}N_2O$. Crystals (from alcohol). — $B'_2(C_{19}H_{22}N_2O)_4(H_2SO_4)_3$ 20aq. S. ·597 at 15°. Needles. — $B'_2(C_{19}H_{22}N_2O)_4(C_4H_6O_6)_3$ 6aq. — $B'_2(C_{19}H_{22}N_2O)_4(H_2CrO_4)_3$ 18aq: crystals. — $B'_2C_{19}H_{22}N_2O(H_2C_2O_4)$ 6aq (?). Long colourless needles. — Compounds with cupreïne $B'C_{19}H_{22}N_2O$ 4aq. [177°]. $[\alpha]_D = -236^\circ$. Trimetric prisms (Howard a. Hodgkin, *C. J.* 41, 66; Hesse, *A.* 225, 98; 226, 242; 230, 72). Its solution in dilute H_2SO_4 shows blue fluorescence. —$B'C_{19}H_{22}N_2OH_4PtCl_8$ 2aq: orange-red prisms.—$B'C_{19}H_{22}N_2OH_2SO_4$ 6aq: six-sided prisms. S. 3 at 100°.—$B'C_{19}H_{22}N_2OC_4H_6O_6$ 2aq: needles.

Acetyl derivative $C_{20}H_{23}AcN_2O_2$. [108°]. Formed by heating quinine with Ac_2O (Hesse, *A.* 205, 317). Prisms, sol. alcohol and chloroform, sl. sol. ether. $[\alpha]_D = -54^\circ$ in a 2 p.c. solution in alcohol (of 97 p.c.) at 15°. $[\alpha]_D = -115^\circ$ in presence of 3HCl. Decomposed by alcoholic potash into quinine and HOAc.—$B'H_2PtCl_6$ 2aq. —$B'(HAuCl_4)_2$ aq: yellow flocculent pp.

Propionyl derivative $C_{20}H_{23}(C_3H_5O)N_2O_2$. [129°]. Six-sided prisms, sol. ether and alcohol. $[\alpha]_D = -109^\circ$ in a 2 p.c. solution at 15° (Hesse).—$B'H_2PtCl_6$ 2aq.—$B'(HAuCl_4)_2$ 2aq: yellow amorphous pp.

Benzoyl derivative $C_{20}H_{23}BzN_2O_2$. Amorphous (Schützenberger, *C. R.* 47, 334).—$B'H_2PtCl_6$.

Methylo-iodide B'MeIaq or $C_{10}H_7(OMe)N.C_9H_{14}NMeIO$ (Grimaux, *Bl.* [3] 7, 573). [233°-236°]. Formed by boiling quinine (1 mol.) with MeI (6 mols.) in MeOH (Strecker, *A.* 91, 164; Claus a. Mallmann, *B.* 14, 76). Formed also from cupreïne, NaOEt and MeI (Hesse, *A.* 266, 240). Colourless needles (from water), v. sol. hot water and alcohol. Not attacked by alkalis in the cold. Boiling KOHAq or moist Ag_2O converts it into methyl-quinine $C_{20}H_{23}MeN_2O_2$, an oil which yields an amorphous hydroiodide, crystalline $B'H_2PtCl_6$ aq (Hesse) or $B'H_2PtCl_6$ 2aq (Lippmann, *M.* 12, 512), and $C_{20}H_{23}MeN_2O_2MeI$ aq crystallising in needles, decomposed at 218°.

Methylo-periodides $B'MeI_3$. Black needles (Jörgensen, *J. pr.* [2] 3, 145; 14, 261).—$B'_2Me_2I_6H_2SO_4$. Reddish-brown needles (from alcohol).—$B'_2Me_2I_8H_2SO_4$. Brown plates.—$B'_4Me_4I_{18}2H_2SO_4$. Almost black laminæ.—$B'_4Me_4I_{22}2H_2SO_4$. Almost black needles with green lustre.

Methylo-chloride B'MeCl aq. [182°]. Needles.—$B'_2MeHPtCl_6$: orange prisms.

Methylo-bromide B'MeBr aq. [126°]. Slender needles, sl. sol. cold water.

Di-methylo-di-iodide $B'Me_2I_2$ 3aq. [158°-162°]. Formed by heating B'MeI with MeI and MeOH in sealed tubes at 100°. Got also, together with B'MeI from cupreïne by the action of NaOMe followed by MeI (Hesse, *A.* 266, 240). Yellow tables (from water). Converted by cold NaOHAq, or better NaOH in MeOH, into a resin and a smaller quantity of a yellow crystalline body. S. (boiling MeOH) ·1, melting about 280°, sol. acids and reppd. by alkalis as a jelly. Its solutions are yellow with green fluorescence. A similar body is got by the action of alkalis on the methylo-iodide of methoxy-quinoline (obtained from quinine). — $B'Me_2PtCl_6$ 2aq. — $B'2MeAuCl_4$.

Ethylo-iodide B'EtI aq (Howard, *C. J.* 26, 1180). [211°]. Trimetric needles (from ether), with very bitter taste. Lævorotatory. —$B'EtI_3$: black needles.

Ethylo-chloride B'EtCl 3aq. Slender needles.—$B'EtHPtCl_6$: yellow pp.

Ethylo-bromide B'EtBr 2aq.

Ethylo-sulphates $B'_2Et_2SO_4$ 8aq.—$B'EtHSO_4$ 2aq: needles, v. e. sol. water.

Ethylo-cyanide B'EtCN. [90°]. White needles (Claus a. Merck, *B.* 16, 2746).

Di-ethylo-di-iodide $B'Et_2I_2$ 3aq. [115°]. Prepared by heating quinine with EtI and alcoholic potash (Skraup, *M.* 2, 610). Monoclinic tables, sol. alcohol, insol. ether.

Methylo-ethylo-di-iodide $B'MeEtI_2$ aq. [208°]. Formed by boiling B'MeI with EtI and alcohol (Claus, *B.* 14, 76). An isomeride [157°-160°] is got from B'EtI and MeI.

Benzylo-chloride $B'C_7H_7Cl$. Amorphous. $B'(C_7H_7)HPtCl_6$ 2aq: crystalline (Mazzara, *G.* 13, 530).—$B'(C_7H_7)_2PtCl_6$: yellow powder.

Tolyl-quinine $C_{20}H_{23}(C_7H_7)N_2O_2$. Two modifications are formed by heating quinine with *o*-toluidine, and two from *p*-toluidine. The *o* and *p* (α) modifications form oils soluble in ether; the *o* and *p* (β) modifications form amorphous yellow powders insoluble in ether, soluble in chloroform and alcohol. $B'_2H_2Cl_2PtCl_4$aq: yellow crystalline powders (Claus a. Bottler, *B.* 14, 80)

Quinopropyline $C_{24}H_{28}N_2O_2$. [164°]. Got by heating sodium-cupreïne with $PrNO_3$ and PrOH at 110° (Grimaux a. Arnaud, *Bl.* [3] 7, 310). White powder.—$B'_2H_2SO_4$ 1½aq. Silky needles. [224°]. $[\alpha]_D = 229$ at 22°.

Quinoisopropyline [154°]. Formed in like manner from $PrNO_3$.—$B'_2H_2SO_4$ aq. S. ·3 at 10°. $[\alpha]_D = 229^\circ$.

Quinoamyline $C_{25}H_{32}N_2O_2$. [167°]. Formed from sodium-cupreïne and amyl chloride in amyl alcohol at 105°. Amorphous.—$B'_2H_2SO_4$ 2aq. Needles. S. ·025 at 11°. Its solution in dilute H_2SO_4 fluoresces.

Quinine sulphonic acid $C_{20}H_{23}(SO_3H)N_2O_2$. [209°]. Formed by moistening quinine tetrasulphate with Ac_2O, and treating the product with hot water (Hesse, *A.* 267, 141). Small white prisms (containing aq when air-dried). $[\alpha]_D = -182^\circ$ in a 2 p.c. solution containing HCl (3 mols.).—$H_2A'_2H_2PtCl_6$ 8aq.

Quinine (Iso)-sulphonic acid $C_{20}H_{23}N_2O_2(SO_3H)$. Formed from quinine and fuming H_2SO_4 (Hesse, *A.* 267, 138). V. sol. water, forming a slightly acid lævorotatory solution with blue fluorescence. Gives a dark-green colour with chlorine-water and NH_3Aq.—$HA'HAuCl_4$: yellow flocculent pp.

Apoquinine $C_{19}H_{22}N_2O_2$. [160°]. $[\alpha]_D = -178°$ in a 2 p.c. solution of alcohol (of 97 p.c.) at 15°. $[\alpha]_D = -247°$ in water containing 3HCl. Formed by heating quinine or cupreïne with HClAq at 140° (Hesse, *A.* 205, 323, 341 ; 230, 65). Amorphous powder (containing 2aq), sol. alcohol, ether, $CHCl_3$, and hot water. A solution of its sulphate shows no fluorescence. Chlorine-water and ammonia give a dark-green colour in the cold. The alcoholic solution gives a dark brownish-red colour with $FeCl_3$. Fuming HClAq at 150° forms $C_{19}H_{23}ClN_2O_2$ 2aq [160°], which gives the salts $B'H_2Cl_2$ 3aq, $B'H_2PtCl_6$ 2aq, and $C_{19}H_{21}Ac_2ClN_2O_2$ [184°].

Salts.—$B'H_2PtCl_6$ 3aq. — B'HI. Small crystals (Lippmann a. Fleissner, *M.* 12, 331).

Acetyl derivative $C_{19}H_{20}Ac_2N_2O_2$: amorphous powder, sol. ether and alcohol.

Isoapoquinine $C_{19}H_{22}N_2O_2$. [176°]. Formed by the action of boiling alcoholic potash on $C_{19}H_{22}N_2O_2$3HI [238°] (*v.* QUININE, *Reaction* 8): Crystalline (Lippmann a. Fleissner, *M.* 12, 331). —$B'H_2PtCl_6$ aq : granules, sl. sol. water.

Isoquinine $C_{20}H_{24}N_2O_2$. [186°]. $[\alpha]_D = -181°$ in a 4 p.c. solution. Formed from the compound $C_{20}H_{24}N_2O_2$3HI [230°] (*v.* QUININE, *Reaction* 9) with alcoholic potash (Lippmann a. Fleissner, *M.* 12, 332). Needles (containing aq), v. e. sol. benzene, sl. sol. ether, v. sl. sol. boiling water. Coloured green by chlorine-water and ammonia. —B'HCl 2aq : needles, v. sol. water.—B'2HCl, m. sol. water.—$B'H_2PtCl_6$: yellow crystalline pp.— $B'_2H_2SO_4$ 10aq : needles, v. e. sol. water.— $B'AgNO_3$: needles.

ψ-Quinine $C_{20}H_{24}N_2O_2$. [191°]. Formed, together with nichine $C_{19}H_{24}N_2O_2$ (?), by heating quinine hydroiodide with alcoholic potash (Skraup, *B.* 25, 2911). Lævorotatory. Yields B'HCl, $B'HNO_3$, and B'_2HNO_3, all sl. sol. water and readily crystallised.

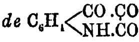
Chinene or **Quinene** *v.* QUINIENE, vol. ii. p. 181.

Homoquinine *v.* CINCHONA BASES.

QUININIC ACID *v.* Methyl derivative of (*B.* 3)-OXY-QUINOLINE CARBOXYLIC ACID.

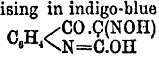
QUINISATIC ACID $C_6H_4(NH_2).CO.CO.CO_2H$. *o-Amido-benzoyl-glyoxylic acid.* Formed by oxidation of (*Py.* 1,2,3)-tri-oxy-quinoline with $FeCl_3$ (Baeyer a. Homolka, *B.* 16, 2219). Yellow prisms, v. sol. water. On reduction with zinc-dust and HOAc and exposure of the filtrate to the air it forms a dark-blue colouring matter.

Anhydride



$C_6H_4\left\langle\begin{array}{l}CO.CO\\NH.CO\end{array}\right.$ [255°-260°].

Formed by heating the acid at 120°. Red crystals, forming a red solution in alcohol. Readily combines with water, with re-formation of the acid. Dilute NaOHAq forms a yellow solution, very quickly becoming colourless. NaOEt gives a body crystallising in indigo-blue needles. Gives an oxim

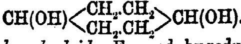


$C_6H_4\left\langle\begin{array}{l}CO.C(NOH)\\N{=}C.OH\end{array}\right.$

crystallising in orange prisms [208°].

QUINITANNIC ACID. An acid occurring in cinchona bark (Schwarz, *J. pr.* 56, 76 ; *cf.* Pelletier a. Caventou, *A. Ch.* [3] 15, 337). Hygroscopic yellow mass. Its alkaline solutions absorb oxygen. Converted by boiling dilute acids into glucose and a brownish-red powder $C_{28}H_{22}O_{14}$, which gives acetic and protocatechuic acid when fused with potash (Rembold, *A.* 143, 270).

QUINITE $C_6H_{12}O_2$ *i.e.*



$CH(OH)\left\langle\begin{array}{l}CH_2.CH_2\\CH_2.CH_2\end{array}\right\rangle CH(OH)$.

Hydroquinone hexahydride. Formed, by reduction with sodium-amalgam in a current of CO_2 from the product of the action of dilute H_2SO_4 on the dihydride of di-oxy-terephthalic ether (succinyl-succinic ether) (Baeyer, *B.* 25, 1037, 1840). V. sol. water and alcohol. Occurs in two modifications, *trans* [144°] and *cis* [90°], which yield acetyl derivatives melting at 106° (*trans*) and 32° (*cis*). Both acetyl derivatives boil at 244°. Quinite is converted by HBr into di-bromo-benzene hexahydride (*trans* [114°], *cis* an oil), which on heating with quinoline give oily benzene dihydride (81°), which forms a tetrabromide [182°].

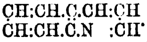
QUINIZARIN *v.* DI-OXY-ANTHRAQUINONE.

QUINIZINE. Substances supposed to be derived from the hypothetical quinizine were subsequently found to be derivatives of phenyl-pyrazole. Thus oxy-methyl-quinizine is oxy-phenyl-methyl-pyrazole (*q. v.*).

QUINOL *v.* HYDROQUINONE.

QUINOLIC ACID $C_9H_6N_2O_4$. Got by oxidation of cinchonine with HNO_3 (Weidel, *A.* 173, 91 ; *B.* 12, 1152). Woolly crystals, almost insol. water, v. sl. sol. alcohol, sol. HClAq. Alkalis give a transient crimson colour. Br and water at 180° give hexa-bromo-quinoline. HNO_3 at 170° forms cinchomeronic acid.—AgA'.— HA'HCl.—$H_2A'_2H_2PtCl_6$: orange needles.

QUINOLINE C_9H_7N *i.e.*



$\begin{array}{l}CH{:}CH.C.CH{:}CH\\CH{:}CH.C.N\ \ {:}CH\end{array}$

Chinoline. Leucoline. Mol. w. 129. (237·5°) (Young, *C. J.* 55, 485) ; (234°) (Schiff, *B.* 19, 566) ; (241° cor.) (Kretschy, *M.* 2, 80). S.G. ⁰ 1·106 (O. de Coninck, *Bl.* [2] 37, 208); ⁰ 1·108 (Skraup). S.V. 139·8 (Schiff). *Vapour-pressure* : Young. *Heat of neutralisation* : Colson, *A. Ch.* [6] 19, 409. *Absorption of ultra-violet spectrum* : Hartley, *C. J.* 41, 47. Occurs in coal-tar (Runge, *P.* 31, 68 ; Hofmann, *A.* 47, 76 ; 53, 427 ; 74, 15 ; Greville Williams, *Tr. E.* 21 [2] ; [3] 377 ; O. Fischer, *B.* 16, 720 ; Jacobsen a. Reimer, *B.* 16, 1084).

Formation.—1. By distilling quinine, cinchonine, or strychnine with potash (Gerhardt, *A.* 42, 310 ; 44, 279 ; O. de Coninck, *C. R.* 94, 87 ; *Bl.* [2] 35, 296). Quinoline free from homologues is got from cinchonine by treatment with potash and CuO (Wyschnegradsky, *B.* 13, 2318).—2. By passing allyl-aniline over heated PbO (Königs, *B.* 12, 453).—3. From hydrocarbostyril (vol. i. p. 180) by treatment with PCl_5 and reduction of the product with HI and HOAc (Baeyer, *B*, 12, 1320).—4. By distillation of acroleïn-aniline (Königs, *B.* 13, 911).— 5. By distilling anil-uvitonic acid with soda-lime (Böttinger, *B.* 13, 2165).—6. By heating a mixture of nitro-benzene, aniline, glycerin, and H_2SO_4 for three hours with inverted condenser (Skraup, *M.* 1, 316; 2, 139, 535).—7. By heating its carboxylic acids with lime.—8. By adding a few drops of NaOHAq to a cold dilute solution of equimolecular quantities of *o*-amido-benzoic aldehyde and acetic aldehyde (Friedländer a. Gohring, *B.* 16, 1833).—9. By heating the hydrochloride of quinoline tetrahydride with water and $Hg(OAc)_2$ at 150° (Tafel, *B.* 25, 1623).—10. By fusing methyl-acetanilide with $ZnCl_2$ at 290° (Pictet, *B.* 23, 1903).

Preparation.—A mixture of aniline (38 pts.), glycerin (120 pts.), nitro-benzene (24 pts.) and H_2SO_4 (100 pts.) is heated with inverted condenser. Potash is then added, and the base distilled over with steam and fractionally distilled. It may be further purified by means of the acid sulphate and freed from aniline by oxidation or by treatment in acid solution with $NaNO_2$. The yield is 60 p.c. (Skraup).

Properties.—Colourless liquid with peculiar odour, slowly becoming yellow. V. sl. sol. water, miscible with alcohol, ether, and CS_2. Quinoline is very hygroscopic, forming the hydrate $(C_9H_7N)_2$3aq, which becomes turbid on warming (Hoogewerff a. Van Dorp, *R. T. C.* 1, 1, 107). It is antiseptic, antipyretic, and antizymotic (Donath, *B.* 14, 178). Quinoline separated from solutions of its salts dissolves in excess of NH_3 or ammonium carbonate, but not in NaOH or Na_2CO_3. Iodine in KI gives a brown pp., insol. HClAq. Phosphomolybdic acid a yellowish-white pp., sol. NH_3Aq. Picric acid a yellow amorphous pp. $HgCl_2$ a white pp., sol. HClAq. K_2HgI_4 a yellow amorphous pp., changed to yellow needles on adding HCl. $K_2Cr_2O_7$ gives crystals, sol. excess. Potassium ferrocyanide an amorphous orange pp. (Donath, *B.* 14, 1769). On shaking with conc. $CuSO_4$Aq a green pp. $(CuSO_4)_2(CuO_2H_2)_3$4aq is got (Borsbach, *B.* 23, 924; *cf.* Lachovitch, *M.* 10, 884). NaOBr gives no reaction (Denigès, *C. R.* 107, 662). Quinoline forms very soluble crystalline compounds with $NaHSO_3$ (Brunck a. Graebe, *B.* 15, 1785). It combines with iodoform (Rhoussopoulos, *B.* 16, 202).

Reactions.—1. On passing through a *red-hot tube* it yields (β)-diquinolyl (Zimmermann a. Müller, *B.* 17, 1965).—2. On boiling with *sodium* or *sodium-amalgam* it is converted into 'diquinoline,' which forms a scarlet hydrochloride which dyes silk a transient orange (Greville Williams, *Pr.* 31, 536; *C. N.* 37, 85).—3. Reduced by *tin* and HClAq to quinoline tetrahydride (244°) (Wyschnegradsky, *Bl.* [2] 34, 339).—4. *Zinc-dust* and NH_3Aq or alcohol and sodium-amalgam give the tetrahydrides of quinoline and of diquinoline (Königs, *B.* 14, 99).—5. Oxidised by bleaching-powder or other *hypochlorites* to oxy-quinoline (carbostyril) and chloro-oxy-quinoline (Erlenmeyer, *B.* 19, 489; Einhorn a. Lauch, *A.* 243, 342). Chlorine passed into its solution in HOAc forms tri-chloro-oxy-carbostyril.—6. On heating with $SbCl_5$ at 170°-400° and passing in *chlorine*, the products are C_2Cl_6 and C_6Cl_6 (Smith a. Davis, *C. J.* 41, 413).—7. *Bromine* (2 pts.) added to a mixture of quinoline (1 pt.) and water (3 pts.) forms the tetrabromide $C_9H_7NBr_4$, which crystallises from chloroform in very unstable red needles, and is converted, by heating with alcohol, into $C_9H_7NBr_2HBr$ [86°] crystallising in red prisms, insol. chloroform, v. sol. alcohol and ether, decomposed at 180° into HBr and bromo-quinoline-hydrobromide (Grimaux, *Bl.* [2] 38, 125; *C. R.* 95, 85). Bromine added to an ethereal solution of quinoline forms the dibromide $C_9H_7NBr_2$, yielding B'HCl [100°-105°] and B'HBr [88° cor.], which form red crystals (Claus a. Collischonn, *B.* 19, 2765).—8. $KMnO_4$ in alkaline solution forms pyridine dicarboxylic acid (Hoogewerff a. Van Dorp, *R. T. C.* 1, 1, 107; *cf.* Dewar, *Pr.* 26, 65). $KMnO_4$ and conc. H_2SO_4 also give quinolinic acid. $KMnO_4$ and dilute H_2SO_4 form quinoline (*B.* 3)-carboxylic acid, diquinolyl being an intermediate product (Georgievitch, *M.* 12, 312).—9. H_2SO_4 at 220° forms the (*B.* 4)-sulphonic acid; at 250° the (*B.* 2)-sulphonic acid is produced (Georgievitch, *M.* 8, 578, 641).—10. *Oxygen* passed through platinised asbestos containing quinoline and quinoline hydrochloride at 190° forms (α)-diquinolyl. Oxygen acting on a mixture of aniline and quinoline hydrochloride forms (*Py.* 3; *B.* 2)-diquinolyl and *p*-amido-(*Py.* 3)-phenyl-quinoline, while quinoline and *o*-toluidine hydrochloride are converted by oxygen into amido-phenyl-methyl-quinoline (Weidel, *M.* 8, 120; 9, 99).—11. *p*-Amido-phenyl-quinoline is also formed by heating quinoline hydrochloride with aniline.—12. BzCl at 240° gives (β)-diquinolyl.—13. *Alloxan* added to a solution of quinoline saturated with SO_2 forms $B'C_4H_2N_2O_4SO_3H_2$ crystallising in yellowish prisms (Pellizzari, *A.* 248, 150).—14. $SiCl_4$ forms $(C_9H_7N)_2SiCl_4$ (Harden, *C. J.* 51, 40). SiF_4 forms $(C_9H_7N)_3 2SiF_4$, crystallising in needles (Comey a. Jackson, *Am.* 10, 176).—15. *Nitroso-di-methyl-aniline* and hydrogen cyanide form $B'(C_6H_4(NO).NMe_2)_2HCy$, crystallising in golden plates (Lippmann a. Fleissner, *M.* 6, 543). — 16. *Glycerin dichlorhydrin* forms $(C_9H_7N)C_3H_5Cl$, which is deliquescent and forms $(B'C_3H_5Cl)_2PtCl_4$ and $B'C_3H_5AuCl_4$.—17. *Ethylene chloride* at 100° forms $B'_2C_2H_4Cl_2$, crystallising in needles, yielding $B'_2C_2H_4PtCl_6$ (Rhoussopoulos, *B.* 16, 879).—18. *Ethylene bromide* (1 mol.) heated with quinoline (1 mol.) at 80° forms the bromo-ethylo-bromide $B'BrC_2H_4Br$, crystallising from alcohol in needles and yielding $B'ClC_2H_4Br$ and $(B'ClC_2H_4Br)_2PtCl_4$ (Berend, *B.* 14, 1349). Ethylene bromide (1 mol.) with quinoline (2 mols.) at 40° forms $B'C_2H_4Br_2$ aq crystallising from alcohol in needles.—19. By heating quinoline (16 g.) with glycolic chlorhydrin (10 g.) and water (10 c.c.) for 3 days at 100° there is formed $B'Cl.C_2H_4OH$, crystallising from alcohol-ether in splendid prisms (Wurtz, *Pr.* 33, 452; *C. R.* 95, 263; 96, 1269). It is hygroscopic, v. sol. water and alcohol, insol. ether. On boiling with moist Ag_2O it forms a caustic liquid that soon turns crimson. It yields $B'(C_2H_4OH)AuCl_4$, crystallising in minute pointed hexagons, and also $B'(C_2H_4OH)Cl6HgCl_2$, and $(B'(C_2H_4OH)Cl)_2PtCl_4$. 20. *Iodoform* (1 mol.) heated with quinoline (2 mols.) for 8 days at 100° forms $B'_2CH_2I_2$, crystallising in long needles [132°] (Rhoussopoulos, *B.* 16, 202, 880, 2004). It is converted by AgCl into $B'_2CH_2Cl_2$ [168°], which gives $B'_2CH_2PtCl_6$. Iodoform (1 mol.) added to quinoline (3 mols.) in ethereal solution forms B'_3CHI_3 crystallising in needles [65°], not affected by AgCl.—21. *Chloro-acetic acid* forms quinoline-betaïne $C_{11}H_9NO_2$ [171°], which separates from alcohol in thick crystals (containing aq) and forms $(C_{11}H_9NO_2)_2H_2PtCl_6$2aq (Gerichten, *B.* 15, 1254; Rhoussopoulos, *B.* 15, 2006).—22. *Chloro-acetic ether* forms $C_9H_7NCl.CH_2.CO_2Et$ crystallising in needles, v. e. sol. water, converted by moist Ag_2O into quinoline. It yields the salt $(C_{13}H_{14}NO_2)_2H_2PtCl_6$. — 23. *Chloral* in ether forms $C_9H_7NC_2HCl_3O$ aq [66°], crystallising from benzene (Rhoussopoulos, *B.* 16, 881). It is insol. water and decomposed by alcohol. It yields $(C_9H_7NC_2HCl_3O\ aq)_2 3PtCl_4$. — 24. *Resorcin* at

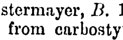
100° forms $(C_9H_7N)_2C_8H_6O_2$, [102°], S. ·25 in the cold (Hock, *B.* 16, 886). It crystallises from dilute alcohol in silvery plates, decomposed by HClAq.—25. *Phthalic anhydride* at 150° forms 'quino-phthalone' $C_{17}H_9NO_2$ [235°] (Traub, *B.* 16, 297).

Salts. — B'HCl. [94°]. Deliquescent nodules, v. e. sol. alcohol, chloroform, and hot ether (O. de Coninck, *Bl.* [2] 37, 208).— $B'_2H_2PtCl_6$ 2aq [225°] (Skraup); [218°] (Lellmann, *A.* 237, 323).—$B'_2H_2PtCl_6$ aq. S. ·07 at 11°.—B'_2PtCl_2: insoluble powder.—$B'_2H_2PtCl_4$.— $B'HAuCl_4$. Canary-yellow needles.—$B'HCdCl_3$aq. —$B'CdCl_2$: white pp.—$B'HgCl_2$. Pearly plates (Bromeis, *A.* 52, 136).—$B'_2H_2HgCl_4$ 2aq. [91°]. Monoclinic crystals.—$B'_2H_2PdCl_4$. **Crystals.**— $B'H_2SnCl_4$ 2aq: needles.—$B'HSnCl_3$. [127°]. Thin needles. — $B'_2H_2SnCl_6$. [above 240°]. — $B'_2H_2UrO_2Cl_4$: yellow prisms. — $B'SbCl_3$. — $B'HSbCl_4$.—$B'_3H_3BiCl_6$.—$B'_2H_2ZnCl_4$.—B'_2ZnCl_2. —B'HClICl. [118°] (Ostermayer). Yellow pp., converted by ammonia into explosive $B'NH_2I$ (Dittmar, *B.* 18, 1613).—B'ICl. [160°]. Small white needles (Pictet a. Krafft, *Bl.* [3] 7, 73).— $B'Br_2HCl$. [100°-105°]. Orange crystals (Claus, *B.* 19, 2766).—$B'HMnCl_3$: rose-red needles (Borsebach, *B.* 23, 433).—$B'HFeCl_4$. [150°]. Formed by adding HCl to a solution containing quinoline and $FeCl_3$ (B.). Small needles, decomposed by boiling water.—B'_2CoCl_2: blue triclinic crystals.—B'_2CuCl_2: nearly black crystals.— $B'Cu(OAc)_2$. [above 240°]. Green crystalline powder.—B'_2ZnI_2: white powder, sl. sol. cold water.—B'_2ZnBr_2.—$B'CdBr_2$.—$B'CdI_2$.—B'_2CdI_2. —$B'HgBr_2$. [204°].—$B'HgI_2$. [168°].—$B'Br_2$. [92°-100°]. Red crystals (Lubavin, *J. R.* 18, 434).—$B'Br_4$. Red needles.—$B'HBr_3$. [86°].— $B'Br_2HCl$. [100°-105°].—$B'I_2$. [90°]. Formed by adding I to a solution of quinoline in CS_2 (Claus a. Istel, *B.* 15, 824). Dark-green lustrous needles.—$B'HI_3$. [67°]. Ppd. by adding I in KI to a solution of quinoline sulphate (Dafert, *M.* 4, 509). Green crystalline pp., sol. alcohol and benzene.—$B'H_2SO_4$. [164°]. S. (alcohol) 2 at 18°; 11 at 78° (Krakau, *J. R.* 17, 364). Deliquescent crystals. — $B'_2H_2Cr_2O_7$. [c. 167°]. Yellow needles (from hot water). S. ·36 at 10°. —$B'HNO_3$. Needles (from alcohol), v. sol. water, insol. ether. — B'_2AgNO_3: needles. — $B'_2Hg(NO_3)_2$: white crystalline precipitate. — $B'_2(HNO_3)_2Ce(NO_3)_4$: orange-red plates (G. Williams, *C. N.* 58, 199).—$B'_2H_2SiF_6$. Long needles (Comey a. Jackson, *Am.* 10, 176).—$B'H_2C_2O_4$. Silky needles (from alcohol). Decomposes at 100° (Williams).—B'_2HgCy_2: long needles (from water) (H. Schiff, *A.* 131, 112).—**Tartrate** $B'_3\,4C_4H_6O_6$. [125°] (Friese, *B.* 14, 2805).— **Cyanurate** $B'_3H_3C_3N_3O_3$. Crystals (Claus, *J. pr.* [2] 38, 226). — $B'HSCy(Cr(SCy)_3NH_3)$. Red lamellæ, sl. sol. hot water (Christensen, *J. pr.* [2] 45, 365). — **Picrate**: [203°]. — ***o*-Oxybenzoate** $B'C_7H_6O_3$. Crystalline powder.

Alkylo-iodides. According to Decker (*B.* 24, 690) the alkylo-iodides B'RI are converted by alkalis into the hydroxides B'ROH which are readily oxidised by the air to crystalline oxy-*ν*-alkyl-quinolines $C_6H_4<\begin{matrix}CH{:}CH\\ NR.CO\end{matrix}$, which melt about 100°. The cyanines may be considered as derived from one molecule of alkylquinoline and one molecule of oxy-*ν*-alkyl-quinoline. The alkylo-hydroxides are converted by warming with alcohols R'OH into compounds B'ROR'.

Methylo-chloride B'MeCl aq. [126°]. On heating with $ZnCl_2$ at 180° it is converted into a base $C_{20}H_{20}N_2O$ [72°-75°] (above 360°), crystallising in large trimetric prisms, and yielding a hydrochloride [112°] and the double salts $C_{20}H_{20}N_2OHAuCl_4$ and $(C_{20}H_{20}N_2O)_2H_2PtCl_6$ [190°] nearly insol. water (Ostermayer, *B.* 18, 593).—$B'_2Me_2PtCl_6$. [230°]. Yellow plates.— $B'MeAuCl_4$. [205°]. — B'MeClICl. [112°]. Formed by adding ICl to the methylo-chloride in aqueous solution. Large yellow plates.

Methylo-tribromide $B'MeBr_3$. [123°]. Orange-red plates. Converted by picric acid solution into $B'MeOC_6H_2(NO_2)_3$ [164°].

Methylo-iodide B'MeI. [73°] (La Coste, *B.* 15, 192; Pictet, *B.* 23, 1903). Large crystals. Converted by moist Ag_2O into a strongly alkaline solution of the hydroxide B'MeOH. Aqueous NaOH in the cold converts B'MeI into the oxide B'_2Me_2O, a white powder, reconverted by HI into B'MeI (possibly oxy-*ν*-methyl-quinoline) (La Coste; Claus, *B.* 15, 475; Bernthsen, *B.* 18, 29; Decker, *B.* 24, 690). Potash, even in cold aqueous solution, forms an oil probably containing methyl-quinoline (lepidine) (Skraup, *Sitz. W.* [2] 81, 593). By the action of KOH on a mixture of B'MeI (2 pts.) and the methylo-iodide of (*Py.* 1)-methyl-quinoline (1 pt.) there is formed **di-methyl-cyanine iodide** $C_{21}H_{19}N_2I$, crystallising in oblong green tablets, [291°], sl. sol. water, forming a reddish-blue solution (Hoogewerff a. Van Dorp, *R. T. C.* 2, 317; 3, 337). The alcoholic solution is violet, with green fluorescence. Its solution in acids is yellow. The aqueous solution is decolourised by CO_2, the colour re-appearing on boiling. The corresponding $C_{21}H_{19}N_2Cl$ 5aq [c. 300] forms $C_{21}H_{19}N_2Cl(HPtCl_5)\frac{1}{2}$aq as yellow crystals. Quinoline methylo-iodide is oxidised by alkaline K_3FeCy_6 to oxy-methyl-quinoline or *ν*-methyl-quinolone  $C_6H_4<\begin{matrix}CH\ {:}CH\\ NMe.CO\end{matrix}$ [72°] (324° at 728 mm.) (Decker, *J. pr.* [2] 46, 31; *cf.* Bernthsen a. Hess, *B.* 18, 37, who took it for di-methyl-di-quinolyl; Ostermayer, *B.* 18, 591). This body is also got from carbostyril and MeI (Friedländer a. Müller, *B.* 20, 2009). It deliquesces with water, forming an oil. **Hydrochloride** [112°].

Ethylo-chloride B'EtCl aq. [93°]. Large trimetric tables (Claus a. Tosse, *B.* 16, 1277).— $B'_2Et_2PtCl_6$. [226°]. Yellow pp.

Ethylo-bromide B'EtBr aq. [80°]. Trimetric tables. By the action of (*Py.* 1)-methyl-quinoline ethylo-bromide it is converted into di-ethyl-cyanine bromide $C_{23}H_{23}N_2Br$ or $C_{23}H_{25}N_2Br$, crystallising in small needles, not melted at 290°, forming a blue solution in alcohol.

Ethylo-iodide B'EtI. [118°] (Spalteholz, *B.* 16, 1851); [160°] (Hoogewerff a. Dorp, *R. T. C.* 2, 321). Monoclinic crystals At 280° it yields (γ)-ethyl-quinoline and di-ethyl-quinoline (Reher, *B.* 19, 2996). Moist Ag_2O forms strongly alkaline B'EtOH, which is sol. water and resinified by atmospheric oxidation. On heating B'EtI (2 pts.) with (*Py.* 3)-methyl-quinoline ethylo-iodide (1 pt.) and alcoholic potash, there is formed **di-ethyl-isocyanine iodide** $C_{23}H_{23}N_2I$

(Hoogewerff a. Van Dorp, *R. T. C.* 3, 344) or $C_{23}H_{25}N_2I$ (Spalteholz, *B.* 16, 1851). This body forms lustrous green prisms (containing $\frac{1}{2}$aq or $\frac{1}{3}$ EtOH or $\frac{1}{5}$ EtOH $1\frac{1}{2}$aq) melting at 152°. It is insol. ether, sl. sol. water, and forms a crimson solution in alcohol. By the action of KOH on a mixture of B'EtI and (*Py.* 1)-methyl-quinoline ethylo-iodide there is formed di-ethyl-cyanine iodide $C_{23}H_{23}N_2I$ [273°], crystallising in green prisms (Hoogewerff a. Van Dorp, *R. T. C.* 2, 317). Quinoline ethylo-iodide is oxidised by alkaline K_3FeCy_6 to $C_6H_4\left<\begin{array}{l}CH:CH\\ NEt.CO\end{array}\right.$ (317°) (Decker, *J. pr.* [2] 47, 36), which body is also got from carbostyril and EtI (Friedländer a. Weinberg, *B.* 18, 1530). Solidifies at −20°. $C_9H_7NEtIHgCy_2$. [138°]. Needles (from water). $C_9H_7NEtBrHgCy_2$. [155°]. Crystals (from alcohol) (Claus, *A.* 269, 271).

Ethylo-nitrate $B'EtNO_3$. [89° uncor.]. Large trimetric crystals (Claus, *B.* 16, 1277).

Propylo-chloride B'PrCl aq. [c. 95°] (hydrated); [135°] (anhydrous). Colourless crystals (Claus a. Collischonn, *B.* 19, 2504). Crystallises from chloroform in prisms (containing $CHCl_3$) [79°]. V. e. sol. water.—$B'PrClBr_2$. [85° uncor.]. Orange-red radiating crystalline mass.—$B'BrClI_2$. [62°]. Brown crystals.

Propyl-bromide B'PrBr 2aq. [66° uncor.] (hydrated); [148° uncor.] (anhydrous). Formed by heating quinoline with PrBr and a little (10 p.c.) alcohol at 100°. Tables, v. e. sol. water and alcohol. The anhydrous crystals (obtained from absolute alcohol) are very deliquescent. Crystals obtained from chloroform (containing $CHCl_3$) melt at 65°-129°.—$B'PrCl_2Br$. [c. 60°]. Formed by passing dry Cl into a solution of B'PrBr in chloroform. Small sulphur-yellow plates. Unstable.—$B'PrBr_3$. [93°]. Formed by adding Br to the aqueous or alcoholic solution of B'PrBr. Triclinic garnet-red crystals. Yields (*Py.* 3)-bromo-quinoline on heating.—$B'PrBrI_2$. [60° uncor.]. Formed by evaporating a mixture of I in ether and B'PrBr in alcohol. Lustrous brown needles.—$B'PrBrI_4$. [49°]. Slender, nearly black, needles with green reflex.

Propylo-iodide B'PrI. [145°]. Small yellow crystals. Not hygroscopic. Crystallises from chloroform with $CHCl_3$, partially melting at 92°. — $B'PrCl_2I$. [87°]. Sulphur-yellow needles.—$B'PrCl_4I$. [145°]. Converted by long boiling with water into B'PrCl.—$B'PrBr_2I$. [77°]. Triclinic orange tables.—$B'PrBr_4I$. [48°-58°]. Very unstable orange powder.—$B'PrI_3$. [62°]. Very stable bronzy brown prisms. — $B'PrI_5$. [50°]. Stable tables.

Iso-amylo-chloride $B'C_5H_{11}Cl$.—
$B'_2(C_5H_{11})_2PtCl_6$. [220°]. Yellow crystalline pp.

Iso-amylo-bromide $B'C_5H_{11}Br$ aq. [87°] (hydrated); [140°] (anhydrous) (Claus a. Tosse, *B.* 16, 1277).

Isoamylo-iodide $B'C_5H_{11}I$. [185°]. Yellow monoclinic needles (Perkin, *C. J.* 14, 246; Nadler a. Merz, *J. pr.* 100, 129; Greville Williams, *C. N.* 1861, 219; Hoogewerff a. Van Dorp, *R. T. C.* 2, 40; 3, 352; Arzruni, *R. T. C.* 4, 62). Does not form cyanine on treatment with potash unless it contains the isoamylo-iodide of (*Py.* 1)-methyl-quinoline, in which case di-isoamyl-cyanine iodide $C_{29}H_{35}N_2I$ [c. 100°] is produced. This body crystallises in lustrous green monoclinic crystals (containing $1\frac{1}{2}$aq); $a:b:c = 2{\cdot}379:1:1{\cdot}669$; $\beta = 88°\,45'$. It also forms brass-yellow crystals. It is very hygroscopic, nearly insol. ether, sl. sol. $CHCl_3$, acetone, and isoamyl alcohol. It is v. sol. alcohol, forming a deep-blue solution. Iodine converts it into $C_{29}H_{35}N_2I_3$ [189°], which is sl. sol. alcohol, v. sol. acetone, forming blue solutions. The solution of di-isoamyl-cyanine iodide in HClAq is colourless, and deposits on evaporation colourless scales of $C_{29}H_{35}N_2I2HCl$, which at 100° gives off HCl, leaving bronzed $C_{29}H_{35}N_2IHCl$. Moist Ag_2O forms uncrystallisable $C_{29}H_{35}N_2(OH)$. Alcohol and AgCl produce $C_{29}H_{35}N_2Cl$ 4aq, crystallising in long blue prisms, and yielding $(C_{29}H_{35}N_2Cl)_2PtCl_4$. Alcohol and $AgNO_3$ give $C_{29}H_{35}N_2(NO_3)$ aq, which forms lustrous needles giving a blue aqueous solution and yielding colourless $C_{29}H_{35}N_2(NO_3)2HCl$ and blue $C_{29}H_{35}N_2(NO_3)HCl$. Alcoholic ammonium sulphide converts the nitrate into reddish-yellow monoclinic crystals of $C_{58}H_{68}N_4S_3O_2$, which yields $C_{58}H_{68}N_4S_3Cl_42PtCl_4$ as an orange pp. (N. a. M.). H_2SO_4 converts di-isoamyl-cyanine iodide into $(C_{29}H_{35}N_2)_2SO_4$ 2aq, crystallising from hot water in blue needles.

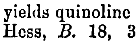
Allylo-iodide $B'C_3H_5I$. [177·5°] (Pictet, *C. R.* 95, 300).

Benzylo-chloride $B'C_7H_7Cl$ 3aq. [65°]. Triclinic tablets. It crystallises also as $B'C_7H_7Cl$ 2aq [130°] in trimetric crystals (Claus, *B.* 13, 2045; 16, 1279; 18, 1305). V. sol. water and alcohol, insol. ether. $KMnO_4$ oxidises it to benzyl-*o*-amido-benzoic acid and its formyl derivative. By treatment with KOH or Ag_2O it is converted into a strong base, v. sol. water. Excess of KOH ppts. an oil which turns red in air. The benzylo-hydroxide yields quinoline on distillation (Bernthsen a. Hess, *B.* 18, 35). Mercuric chloride yields a crystalline pp. [142°].—$(B'C_7H_7)_2PtCl_6$. [246°]. Yellow pp.—$B'C_7H_7ClBr_2$. [92°]. Crystalline.—$B'C_7H_7BrCl_2$. [80°]. Yellow needles.—$B'C_7H_7Br_3$. [100°]. Orange prisms.—$B'C_7H_7BrI_2$. [110°]. Dark-violet needles.

Phenacylo-bromide $B'Br.CH_2Bz$. [115°-165°]. Needles, v. sol. water and alcohol, v. sl. sol. ether (Bamberger, *B.* 20, 3340).—$B'HNO_3$.

References.—AMIDO-, BROMO-, BROMO-AMIDO-, BROMO-NITRO-, CHLORO-, CHLORO-NITRO-, IODO-, NITRO-, OXY-AMIDO-, and OXY- QUINOLINES.

Diquinoline *v.* DIQUINOLYL.

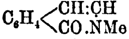
Isoquinoline C_9H_7N *i.e.*  $C_6H_4\left<\begin{array}{l}CH:CH\\ CH:N\end{array}\right.$. [23°]. (241° i.V.). Occurs, as well as quinoline, in coal-tar (Hoogewerff a. Van Dorp, *R. T. C.* 4, 125, 285; 5, 305).

Formation.—1. By the action of HI at 230° or of zinc-dust in a current of H at a low red heat upon the di-chloro- derivative [123°] obtained by the action of $POCl_3$ on the imide of *o*-carboxy-phenyl-acetic acid $C_6H_4\left<\begin{array}{l}CH_2.CO\\ CO\,.NH\end{array}\right.$ (Gabriel, *B.* 18, 3470; 19, 1656, 2361; Le Blanc, *B.* 21, 2299).—2. Together with di-isoquinolyl, which yields $B'_2H_2PtCl_6$ [177°] by distilling benzylidene-ethyl-amine (Pictet a. Popovici, *B.* 25, 733).—3. By heating isocarbostyril or its carboxylic acid with zinc-dust in a current of

hydrogen (Bamberger a. Kitschelt, *B.* 25, 1146; Zincke, *B.* 25, 1497).

Properties.—Hygroscopic tables. Yields phthalic and cinchomeronic acids on oxidation by $KMnO_4$. Tin and HClAq give a tetra-hydride. Forms crystalline compounds with $HgCl_2$ and $AgNO_3$. Bromine in ether gives $C_9H_7NBr_2$, [82°], which forms very unstable $C_9H_7NBr_2HBr$, [c. 133°], converted at 200° into bromo-isoquinoline [40°] (Edinger, *J. pr.* [2] 43, 191).

Salts.—$B'_2H_2PtCl_6 2aq$. [264°]. Reddish-yellow crystals.—$B'HAuCl_4$. [225°]. Yellow needles.—$B'HgCl_2$. [165°]. White needles.—$B'H_2SO_4$. [206°].—$B'H_2Cr_2O_7$: needles.—Picrate $B'C_6H_3N_3O_7$. [223°]. Yellow needles.

Methylo-iodide B'MeI aq. [160°]. Flat yellowish needles. Treatment with AgCl and platinic chloride gives $(B'MeCl)_2PtCl_4$ [240°] (Claus, *J. pr.* [2] 38, 492). KOHAq added to B'MeI forms an oily base which yields $(B'MeCl)_2PtCl_4 6aq$. Oxidised by alkaline K_3FeCy_6 to *ν*-methyl-isoquinoline 
$C_6H_4{<}\begin{array}{l}CH{:}CH\\CO.NMe\end{array}$
[40°] (319°), sol. water, and yielding $B'H_2PtCl_6 2aq$ (Decker, *J. pr.* [2] 47, 37).

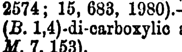
Ethylo-iodide B'EtI. [147°]. Yellowish-red tables. Yields ethyl-phthalimide on oxidation. Gives $(B'EtCl)_2PtCl_4$.

Benzylo-chloride $B'C_7H_7Cl$. V. sol. water and alcohol, sl. sol. ether (Goldschmidt, *M.* 9, 678). Yields benzyl-phthalimide [115°] on oxidation by $KMnO_4$ in a solution kept neutral by HCl.

Phenacylo-bromide $B'BrCH_2Bz$. [205°]. Formed from isoquinoline and *ω*-bromo-acetophenone dissolved in benzene (G.). Prisms (from alcohol), v. sol. water. $AgNO_3$ forms $B'NO_3(CH_2Bz)$ crystallising in needles.

Diquinoline *v.* Diquinolyl.

QUINOLINE (*B.* 1)-CARBOXYLIC ACID


$\begin{array}{l}CH{:}C(CO_2H).C.CH{:}CH\\CH{:}CH — C—N{:}CH\end{array}$
Quinoline ana-carboxylic acid. Quinoline-m-carboxylic acid, [357°].

Formation.—1. Together with a smaller quantity of the (*B.* 3)-acid by heating *m*-amido-benzoic acid with glycerin, H_2SO_4, and *m*-nitro-benzoic acid (Schlosser a. Skraup, *M.* 2, 518; 7, 519).—2. By saponifying its nitrile, which is got by distilling sodium quinoline (*B.* 1)- or (*B.* 4)-sulphonate with KCy (Bedall a. Fischer, *B.* 14, 2574; 15, 683, 1980).—3. By heating quinoline (*B.* 1,4)-di-carboxylic acid (Skraup a. Brunner, *M.* 7, 153).

Properties.—White crystalline powder, sol. dilute acids and alkalis, insol. ether and benzene, v. sl. sol. water and alcohol.

Salts.—HA'HCl $1\frac{1}{2}aq$: white needles.—$(HA')_2H_2PtCl_6$: yellow plates.—$CaA'_2 2aq$.—$CaHA'_3 6aq$: needles.—HO.CuA' 2aq: minute violet plates, insol. water.—AgA': crystalline pp.

Nitrile $C_9H_6N.CN$. [88°]. (above 360°). Formed as above and also from (*B.* 1)-amido-quinoline by diazotisation and treatment with $CuCy_2$ (Freydl, *M.* 8, 581). Crystals, sl. sol. Aq.

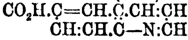
Tetrahydride $C_{10}H_{11}NO_2$. [147°]. Formed by reducing the acid with tin and HCl (Fischer a. Körner, *B.* 17, 765). Yields a crystalline nitrosamine $C_{10}H_{10}N_2O_3$. [186°].

ψ-**Isomeride** $C_{10}H_7NO_2$. [338°]. Perhaps identical with the preceding. Formed by warming quinoline with *m*-amido-benzoic acid, nitrobenzene, glycerin, and H_2SO_4 (Lellmann a. Alt, *A.* 237, 318). Got also by saponifying its nitrile which is formed by fusing sodium quinoline *ψ*-ana-sulphonate with KCy in a current of hot air (Lellmann, *B.* 20, 1449; 21, 397). Snowy powder.—HA'HCl aq.—$H_2A'_2H_2PtCl_6$: needles.—ZnA'_2.—AgA'.

Tetrahydride $C_{10}H_{11}NO_2$. [147°]. Got by reducing the acid or bromo-quinoline carboxylic acid with tin and HClAq.—HA'HCl aq.

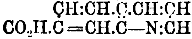
Nitrile $C_9H_6N.Cy$. [89°]. Needles (containing $1\frac{1}{2}aq$), melting at 70°. Effloresces, and then contains $\frac{1}{2}aq$ and melts at 74·5°.—$B'_2H_2PtCl_6$: needles.

Quinoline (*B.* 2)-carboxylic acid


$\begin{array}{l}CO_2H.C{=}CH.C.CH{:}CH\\\quad CH{:}CH.C—N{:}CH\end{array}$
Quinoline-p-carboxylic acid. [291°]. Formed by heating *p*-amido-benzoic acid with glycerin, *p*-nitro-benzoic acid, and H_2SO_4 (Schlosser a. Skraup, *M.* 2, 518). Formed also by heating its nitrile with HClAq at 140° (Fischer a. Wittmack, *B.* 17, 440). Thick prisms, sl. sol. hot water, v. sol. acids and alkalis.—HA'HCl.—$(HA')_2H_2PtCl_6$.—$CaA'_2 2aq$.—AgA'.

Nitrile $C_{10}H_6N_2$. [131°]. Formed by distilling potassium quinoline *p*-sulphonate (from sulphanilic acid) with KCy. Needles, forming a red solution in HClAq.

Quinoline (*B.* 3)-carboxylic acid

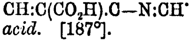

$\begin{array}{l}\quad CH{:}CH.C.CH{:}CH\\CO_2H.C{=}CH.C—N{:}CH\end{array}$
Quinoline-m-carboxylic acid. [248°].

Formation.—1. By oxidation of (*β*)-di-quinolyl with CrO_3 and HOAc (O. Fischer a. Loo, *B.* 17, 1901; 19, 2473).—2. By oxidation of (*B.* 3)-methyl-quinoline (Skraup a. Brunner, *M.* 7, 142).—3. By heating the stannochloride of *c*-amido-phthalic acid with *c*-nitro-phthalic acid, glycerin, and H_2SO_4 (Tortelli, *G.* 16, 367).

Properties.—Needles (from water).

Salts.—Cu(OH)A' aq.—AgA'.—HA'HCl aq: triclinic prisms.—$H_2A'_2H_2PtCl_6$: orange prisms.

Quinoline (*B.* 4)-carboxylic acid


$\begin{array}{l}CH{:}CH — C.CH{:}CH\\CH{:}C(CO_2H).C—N{:}CH\end{array}$
Quinoline-o-carboxylic acid. [187°].

Formation.—1. By heating *o*-amido-benzoic acid with *o*-nitro-benzoic acid, glycerin, and H_2SO_4 (Schlosser a. Skraup, *M.* 2, 518).—2. By heating its nitrile with conc. HClAq at 150° (Lellmann a. Reusch, *B.* 22, 1392).—3. Together with the (*B.* 1)-isomeride, by heating quinoline (*B.* 1,4)-di-carboxylic acid (Skraup a. Brunner, *M.* 7, 153).

Properties.—Needles, m. sol. cold water and alcohol. $FeSO_4$ gives a purple colour in neutral solutions.—HA'HCl: yellowish prisms.—$H_2A'_2HCl$: golden prisms.—$H_2A'_2H_2PtCl_6$: orange needles.—$CaHA'_3$: needles.—AgA': pp.

Methylo-iodide HA'MeI. Slender yellow needles (La Coste, *B.* 15, 196). Moist Ag_2O forms a solution of the hydroxide which reproduces HA' on evaporation.

Nitrile $C_{10}H_6N_2$. [84°]. Needles. Yields $B'_2H_2PtCl_6$, crystallising in orange needles.

Quinoline (*Py.* 1)-carboxylic acid

$C_6H_4{<}\begin{array}{l}C(CO_2H){:}CH\\N{=\!=}CH\end{array}$
Cinchoninic acid. [254°].

Formation.—1. By oxidation of cinchonine,

cinchonidine, cinchotenine, cinchotenidine, cinchonitine, and cincholepidine (Weidel, *A.* 173, 84; *M.* 3, 79; Skraup, *A.* 201, 303; *M.* 2, 601; Forst a. Böhringer, *B.* 14, 436; Schniderschnitsch, *M.* 10, 55).—2. By oxidation of (*Py.* 1)-methyl-quinoline (lepidine) (Hoogewerff a. Van Dorp, *R. T. C.* 2, 11).

Preparation.—By boiling cinchonine with nitric acid of S.G. 1·3 (Königs, *B.* 12, 97; Claus, *B.* 18, 362).

Properties.—Slender needles (containing aq) (Skraup) or triclinic crystals (containing 2aq) $a:b:c = \cdot746:1:\cdot817$; $\alpha = 81° \ 37'$; $\beta = 120° \ 2'$; $\gamma = 86° \ 37'$ (Muthmann a. Nef, *B.* 20, 637). By slow evaporation of an aqueous solution it is obtained in monoclinic forms (containing 2aq), $a:b:c = \cdot276:1:\cdot533$; $\beta = 98° \ 3'$ (Ditscheiner, *A.* 173, 84; Claus, *B.* 20, 1604). V. sl. sol. water and alcohol, insol. ether. Yields quinoline on distillation with lime, and oxy-quinoline carboxylic acid on fusion with potash. On heating with conc. H_2SO_4 it yields quinoline *p*-sulphonic acid (Georgievitch, *M.* 8, 644). Sulphuric acid and P_2O_5 at 175° gives an (α)-sulphonic acid $C_9H_5N(SO_3H)(CO_2H)$, which forms very bitter triclinic crystals (containing aq), nearly insol. cold water, giving the salts $(NH_4)_2A''$ 2aq, CaA'' 2½aq, BaA'' 3aq, PbA'' aq, and CuA'' aq. H_2SO_4 and P_2O_5 at 260° give a (β)-sulphonic acid $C_{10}H_7NSO_5$ crystallising in bitter needles (containing 2aq), m. sol. cold water, forming the salts $(NH_4)HA''$ 2aq, BaA'' aq, and PbA'' 4aq (Weidel, *M.* 1, 845; 2, 565; Georgievitch, *M.* 8, 644).—$KMnO_4$ forms pyridine tricarboxylic acid.

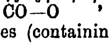
Salts.—HA'HCl.—$(HA')_2H_2PtCl_6$: triclinic prisms.—HA'HClICl 2aq (Dittmar, *B.* 18, 1618).—$HA'HNO_3$.—$(HA')_2H_2SO_4$: long prisms.—KA' ½aq.—CaA'_2 1½aq: prisms (Weidel).—CaA'_2 (Skraup).—CuA'_2: dark-violet plates, sl. sol. hot water.—AgA': crystalline pp.

Dibromide $C_{10}H_7NO_2Br_2$. [188°]. Long red needles, decomposed by boiling water (Claus, *B.* 18, 1307).

Di-iodide $C_{10}H_7NO_2I_2$. [c. 242°]. Steel-blue tables, nearly insol. cold water.

Ethyl ether EtA'. [13°]. Trimetric crystals, v. sl. sol. water, v. sol. ether, sl. sol. alcohol (Van der Kolf a. Van Leent, *R T. C.* 8, 217).—$EtA'HgCl_2$. [153°]. Small needles.—$(EtA')_2H_2PtCl_6$. [204°]. Orange-yellow needles.

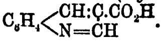
Amide $C_{10}H_8N_2O$. [181°]. Needles, v. e. sol. hot water.—$B'_2H_2PtCl_6$. [250°–255°].

Benzylo-bromide $C_{10}H_7NO_2C_7H_7Br$. [130°]. Silky needles, v. sol. water and alcohol, insol. ether. By heating the aqueous solution or by treatment with alkalis, it is converted, by loss of HBr, into the anhydride  $\begin{matrix}C_9H_6N.C_7H_7\\ CO-O\end{matrix}$, which crystallises in dimetric tables (containing 3aq) [84°] and has a bitter taste. This anhydride is converted by alkalis into $C_9H_5N(C_7H_7)CO_2H$ [218°] (Claus a. Muchall, *B.* 18, 363, 1310).

Tetrahydride $C_{10}H_{11}NO_2$. Formed from cinchonic acid, tin, and HClAq (Weidel, *M.* 2, 29; 3, 61). Yields a nitrosamine [137°].—B'HCl 1½aq: monoclinic crystals; $a:b:c = \cdot932:1:1\cdot942$; $\beta = 90° \ 41'$. Heated with H_2SO_4 it gives disulpho-cinchonic acid and methyl-quinoline (cincholepidine).—$B'_2H_2PtCl_6$.

Acetyl derivative of the Tetrahydride $C_{10}H_{10}AcNO_2$. [164°]. Trimetric crystals; $a:b:c = \cdot848:1:\cdot569$. Sl. sol. cold water and alcohol.—CaA'_2 2aq: minute needles.

Quinoline (*Py.* 2)-carboxylic acid

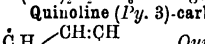
 $C_6H_4<\begin{matrix}CH:C.CO_2H\\ N=CH\end{matrix}$. [273°].

Formation.—1. By heating acridinic acid at 125° (Graebe a. Caro, *B.* 13, 100).—2. By oxidation of (*Py.* 2)-ethyl- (or methyl-) quinoline (Riedel, *B.* 16, 1609; Doebner a. Miller, *B.* 18, 1643).

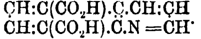
Properties.—Slender needles, sol. alcohol, sl. sol. cold water. Dissolves in acids and alkalis. Oxidised by $KMnO_4$ to pyridine tricarboxylic acid.

Salts.—HA'HCl: needles, v. sol. water.—Picrate: [216°].—CuA'_2.—AgA': small prisms.—$(HA')_2H_2PtCl_6$: orange needles.

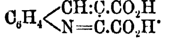
Quinoline (*Py.* 3)-carboxylic acid

 $C_6H_4<\begin{matrix}CH:CH\\ N=C.CO_2H\end{matrix}$. *Quinaldinic acid.* [156°]. Formed from (*Py.* 3)-methyl-quinoline by oxidation with chromic acid mixture (Doebner a. Miller, *B.* 16, 2472). Got also by oxidation of (α)-diquinolyl (Weidel a. Strache, *M.* 7, 300). Needles (containing 2aq), v. sol. hot water, acids, and alkalis.—CuA'_2 2aq.—CaA'_2.—AgA': amorphous precipitate.—$AgHA'_2HNO_3$ aq: silky needles.—HA'HCl aq.—$(HA')_2H_2PtCl_6$ 2aq.—$(HA')_2H_2Cr_2O_7$: sparingly soluble red crystals.

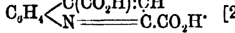
Quinoline (*B.* 1,4)-di-carboxylic acid

 $\begin{matrix}CH:C(CO_2H).C.CH:CH\\ CH:C(CO_2H).C.N=CH\end{matrix}$. [270°]. Formed by heating amido-terephthalic acid with glycerin, H_2SO_4, and *o*-nitro-phenol (Skraup a. Brunner, *M.* 7, 147). Long needles (containing 2aq), v. sl. sol. cold water. Salts.—HA'HCl 1½aq.—$(HA')_2H_2PtCl_6$.—$Cu_3A'_2(HO)_2$ aq: bluish pp.

Quinoline (*Py.* 2,3)-dicarboxylic acid

 $C_6H_4<\begin{matrix}CH:C.CO_2H\\ N=C.CO_2H\end{matrix}$. *Acridinic acid.* Formed by oxidation of acridine with $KMnO_4$ (Graebe a. Caro, *B.* 13, 99). Long needles (containing 2aq), sl. sol. cold water, v. sol. alcohol. Does not combine with acids. Decomposed by heat into CO_2 and a mono-carboxylic acid [275°].

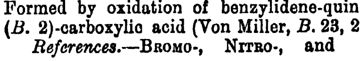
Quinoline (*Py.* 1,3)-dicarboxylic acid

 $C_6H_4<\begin{matrix}C(CO_2H):CH\\ N=\!=\!=\!=C.CO_2H\end{matrix}$. [246°]. Formed from (*Py.* 3)-styryl-cinchoninic acid by oxidation with alkaline $KMnO_4$ (Doebner a. Peters, *B.* 22, 3009). Needles, sl. sol. cold water and alcohol.—CuA'' aq.—Ag_2A'': white pp.

Quinoline (α)-dicarboxylic acid $C_9H_5N(CO_2H)_2$. [270°]. Formed by saponifying its nitrile. Slender needles (containing aq), sl. sol. alcohol and ether.

Nitrile $C_9H_5NCy_2$. [222°]. Formed by heating potassium quinoline (α)-disulphonate with KCy (La Coste a. Valeur, *B.* 20, 99). Needles (from alcohol), insol. Aq, v. sol. alkalis.

Quinoline (*B.* 2, *Py.* 3)-dicarboxylic acid

 $\begin{matrix}CO_2H.C=CH.C.CH:CH\\ \quad CH:CH.C.N=C.CO_2H\end{matrix}$. [275°–280°]. Formed by oxidation of benzylidene-quinoline (*B.* 2)-carboxylic acid (Von Miller, *B.* 23, 2261).

References.—BROMO-, NITRO-, and OXY-QUINOLINE CARBOXYLIC ACIDS.

QUINOLINE (*Py.* 3)-CARBOXYLIC ALDEHYDE $C_9H_6N.CHO$. [71°]. Formed by oxida-

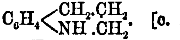
tion of (*Py.* 3)-quinolyl-acrylic acid with $KMnO_4$ (Miller a. Spady, *B.* 18, 3404; 19, 130). Monoclinic plates (from ligroïn), sl. sol. water. Reduces ammoniacal $AgNO_3$. Yields a phenyl-hydrazide $C_{16}H_{13}N_3$ [198°] crystallising in yellow plates.

QUINOLINE HYDRIDES.

Polymeride of quinoline dihydride $C_{18}H_{18}N_2$. [162°]. Formed by reducing quinoline with zinc-dust and HOAc, zinc-dust and NH_3, zinc and HClAq, or alcohol and sodium-amalgam (Königs, *B.* 12, 101, 252; 14, 99; Wyschnegradsky, *B.* 12, 1481; Lellmann, *B.* 22, 1337). Amorphous powder. Its solution in conc. HClAq is ppd. by water and by NaOAc. Yields a nitrosamine.

Quinoline dihydride (?). (220°–226°). Found in small quantity among the products of the action of KOH on quinoline (O. de Coninck, *C. R.* 94, 87).—$B'_2H_2PtCl_6$.

Quinoline tetrahydride $C_9H_{11}N$ *i.e.*


$C_6H_4\!<\!\begin{matrix}CH_2.CH_2\\NH.CH_2\end{matrix}$. [c. 10°]. (240° uncor.).

Formation.—1. By reduction of quinoline with zinc or tin and HClAq (Wyschnegradsky, *Bl.* [2] 34, 339; *B.* 12, 1481; 13, 2400), with zinc-dust and NH_3Aq, with alcohol and sodium-amalgam (Königs, *B.* 14, 99; 16, 727), or with sodium (Weidel a. Glaser, *M.* 7, 328).—2. From carbostyril, alcohol, and Na (Knorr a. Klotz, *B.* 19, 3302).

Properties.—Needles, sol. water, volatile with steam. Secondary base. ICl forms in presence of HCl an amorphous pp. $C_9H_9I_2N$ (Dittmar, *B.* 18, 1619).

Reactions.—1. The vapour passed through a *red-hot tube* yields indole and quinoline.—2. *Chromic acid mixture* yields quinoline.—3. *Nitro-benzene* yields quinoline. *p-Chloro-nitro-benzene* at 200° does the same (Lellmann a. Reusch, *B.* 22, 1389).—4. HI and P reduce it to C_9H_{18}, an oil (147° at 720 mm.) (Bamberger a. Lengfeld, *B.* 23, 1158).—5. Br forms oily $C_9H_{10}BrN$ and $C_9H_9Br_2N$.—6. *Benzene sulphonic chloride* and NaOH form $C_9H_{10}N.SO_2C_6N_5$ [67°], crystallising in plates, sl. sol. alcohol, insol. water (Schotten a. Schlömann, *B.* 24, 3695).—7. *Methyl chloroformate* gives $C_9H_{10}N.CO_2Me$ [c. 35°], which may be oxidised by $KMnO_4$ in the cold to an acid [156°] and at 100° to a compound [175°] crystallising in red needles.—8. *Diazobenzene chloride* and aqueous NaOAc form $C_9H_{10}N.N_2C_6H_5$, which is split up by dilute H_2SO_4 into phenol and quinoline tetrahydride.—9. *Potassium cyanate* acting on the hydrochloride forms $C_9H_{10}N.CO.NH_2$ [150·5°], crystallising in needles, sl. sol. cold water. It is converted by conc. H_2SO_4 and HNO_3 at 0° into $C_9H_8(NO_2)_2N.CO.NH_2$ [191°], sl. sol. alcohol, and $C_9H_9(NO_2)_2N$ [161°], v. sol. alcohol, which forms a nitrosamine [127°] (Thomas, *R. T. C.* 10, 148).—10. *Benzoic aldehyde* and $ZnCl_2$ yield $CHPh(C_9H_{10}N)_2$ [153°], while *p*-nitro-benzoic aldehyde forms a corresponding body [177°] (Einhorn, *B.* 19, 1243).

Salts.—B'HCl. [181°].—$B'_2H_2PtCl_6$.—**$B'H_2SO_4$. [137°]. Prisms (from alcohol) or tables (from water).**

Acetyl derivative $C_9H_{10}NAc$. (295°). **Yields $CO_2H.CO.NH.C_6H_4.CO_2H$ [1:2] on oxidation by $KNnO_4$.**

Benzoyl derivative $C_9H_{10}NBz$. [75°]. **Tables (from alcohol). Oxidised by $KMnO_4$ to benzoyl-isatic acid (Schotten, *B.* 24, 772).**

Nitrosamine $C_9H_{10}N(NO)$. Oil. Converted by alcoholic HCl into the isomeric (*B.* 2)-nitroso-quinoline tetrahydride [134°], which separates from benzene in steel-blue crystals, converted by $NaNO_2$ and HOAc into $C_9H_9N_3O_2$ [98°] (Ziegler, *B.* 21, 864). Phenyl-hydrazine forms $C_9H_{10}N_2O.PhN_2H_3$ [120°]. Zinc-dust and HOAc reduce the nitrosamine to the hydrazine $C_9H_{10}N(NH_2)$ [56°] (c. 255°), which crystallises from ligroïn, and forms $B'_2H_2SO_4$ 2aq, crystallising in yellow plates. The hydrazine is oxidised in ethereal solution by ppd. HgO to the tetrazone $C_{18}H_{20}N_4$, which forms colourless needles [160°], sol. ether, sl. sol. alcohol.

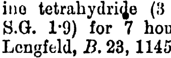
Methylo-chloride v. Hydrochloride of *ν*-METHYL-QUINOLINE TETRAHYDRIDE.

Ethylo-iodide B'EtI. Changed by alkalis into *ν*-ethyl-quinoline tetrahydride, which is a liquid (254°–258°) yielding $(C_9H_{10}NEt)_2H_2CdCl_4$, [105°], and $(C_9H_{10}NEt)_2H_2PtCl_6$ [c. 160°] (Wyschnegradsky, *B.* 13, 2400; Claus a. Stegelitz, *B.* 17, 1329).

Quinoline tetrahydride $C_9H_{11}N$. (213°). Formed by distilling cinchonine (1 pt.) with KOH (3 pts.) (O. de Coninck, *C. R.* 94, 87; *A. Ch.* [5] 21, 478). Got also by distilling brucine with potash (De Coninck, *C. R.* 99, 1077). Slightly hygroscopic oil, v. sol. acids. Reduces $FeCl_3$. May be oxidised to quinoline.—B'HCl: deliquescent needles, v. sol. water.—$B'_2H_2PtCl_6$.—$B'_2H_2PtCl_4$: pale orange plates.

Quinoline hexahydride $C_9H_{13}N$. (227°) at 720 mm. A product of the action of HI and P at 230° on the hydrochloride of quinoline tetrahydride (Bamberger a. Lengfeld, *B.* 23, 1155). Liquid, turning brown in air, m. sol. hot water. $FeCl_3$ gives a brown colour on warming. Diazo benzene sulphonic acid gives a light-red colouring matter. Phosphomolybdic acid gives a white pp. Potassio-mercuric iodide gives no pp. $NaNO_2$ in acid solution gives an oily pp. of the nitrosamine.—B'HCl. [170°]. Silky needles. B'HBr. Long silky needles.

Quinoline decahydride $C_9H_{17}N$ *i.e.*


$\begin{matrix}CH_2.CH_2.CH.CH_2.CH_2\\CH_2.CH_2.CH.NH.CH_2\end{matrix}$. [48·5°]. (204° at 714 mm.).

Formed by heating the hydrochloride of quinoline tetrahydride (3 pts.) with HI (16 pts. of S.G. 1·9) for 7 hours at 230° (Bamberger a. Lengfeld, *B.* 23, 1145). Needles or prisms (from ligroïn). Smells like coniine. Fumes with HCl. Sublimes, in needles, in the cold. M. sol. water, v. sol. alcohol and ether, sl. sol. alkalis. Gives no colour with $FeCl_3$ or diazo salts. Reduces ammoniacal $AgNO_3$ in alcoholic solution. Phosphomolybdic acid gives a white flocculent pp. changing to needles. Potassio-mercuric iodide added to the acid solution gives scarlet crystals changing to black prisms on warming.

Reactions.—1. *Phenyl-cyanate* forms, in ethereal solution, $C_9H_{16}N.CO.NHPh$, crystallising in needles [148°].—2. *Phenyl thiocarbimide* in ether forms $C_9H_{16}N.CS.NHPh$, crystallising from chloroform in tables [134·5°].—3. An ethereal solution of CS_2 gives $C_9H_{16}N.CS.SNH_2C_9H_{16}$, crystallising in needles [120°], not decomposed by boiling alcohol, but converted by iodine into

$(C_9H_{17}N)HI$ and $S_2(CS.NC_9H_{16})_2$, which crystallises in colourless needles [81°], sol. alcohol.

Salts.—B'HCl. [276°]. Small tables.—B'HI. [253°]. Silky needles.—B'HAuCl$_4$. [96°]. Golden needles.—$B'_2H_2PtCl_6$. [207·5°].

Acetyl derivative $C_9H_{16}NAc$. Oil.

Benzoyl derivative $C_9H_{16}NBz$. [44°].

ISOQUINOLINE TETRAHYDRIDE $C_9H_{11}N$. (232°). Formed by the action of tin and HCl upon isoquinoline (Hoogewerff a. Van Dorp, *R. T. C.* 5, 305). Liquid, smelling like isoquinoline, sl. sol. water. Absorbs CO_2 from the air, forming a crystalline carbonate. The aqueous solution reduces $AgNO_3$. Yields an oily nitrosamine.—B'HCl. [196°]. Tables, sol. alcohol. Not hygroscopic.—$B'_2H_2SO_4$: sol. alcohol.—$B'_2H_2PtCl_6$. [232°]. Reddish-yellow tables, decomposed by hot water.

QUINOLINE-HYDROQUINONE *v.* DI-OXY-QUINOLINE.

QUINOLINE-IODOFORM *v.* QUINOLINE, *Reaction* 20.

QUINOLINE-QUINONE $C_9H_5NO_2$ *i.e.* $\begin{array}{l}\text{CH.CO.C.CH:CH}\\ \text{CH.CO.C.N=CH}\end{array}$. Formed by the action of cold chromic acid mixture on (*B.* 4,1)-oxy-amido-quinoline (Fischer a. Renouf, *B.* 17, 1644). Flat needles with green reflex (from alcohol), decomposing at 110°–120°. Its salts are decomposed by water. Reduced by sulphurous acid to di-oxy-quinoline. Aniline in alcoholic solution forms, on boiling, the dianilide $C_{15}H_{10}N_2O_2$ crystallising from dilute alcohol in small copper-red plates with green reflex [c. 190°], forming a violet solution in HClAq.

Mono-oxim $\begin{array}{l}\text{CH.C(NOH).C.CH:CH}\\ \text{CH.CO — C.N=CH}\end{array}$. Formed by the action of $NaNO_2$ and HClAq on (*B.* 4)-oxy-quinoline (Von Kostanecki, *B.* 24, 152). Needles (from alcohol). Gradually blackens below 220°, decomposing completely at 245°.

Di-oxim $\begin{array}{l}\text{CH.C(NOH).C.CH:CH}\\ \text{CH.C(NOH).C.N=CH}\end{array}$. Formed by adding hydroxylamine hydrochloride to an aqueous solution of the mono-oxim (Von Kostanecki a. Reicher, *B.* 24, 156). Minute crystals. Ac_2O yields a crystalline di-acetyl derivative decomposing below 160° with evolution of gas. Dyes cotton mordanted with iron salts greenish-black.

Quinoline-*o*-quinone $C_9H_5NO_2$. Formed by oxidising (*B.* 2)-oxy-(*B.* 1 or 3)-amido-quinoline with $FeCl_3$ in acid solution (Mathëus, *B.* 21, 1887). Unstable.—B'HCl: long reddish-yellow needles. Decomposed by Na_2CO_3, forming a brown solution. The **sulphate** forms yellow plates.

Mono-oxim $C_9H_4N(OH)(NOH)$. Formed from *p*-oxy-quinoline, $NaNO_2$, and HCl (M.). Golden needles (from HOAc), sl. sol. ether.

Di-oxim $C_9H_5N(NOH)_2$. Needles, decomposing at 190° (Von Kostanecki a. Reicher, *B.* 24, 158). Converted by conc. KOHAq into the anhydride $C_9H_5N(N_2O)$, which forms colourless needles, readily volatile with steam.

QUINOLINE (*B.* 1)-SULPHONIC ACID $\begin{array}{l}\text{CH:C(SO}_3\text{H).C.CH:CH}\\ \text{CH:CH — C.N=CH}\end{array}$. A product of the sulphonation of quinoline (O. Fischer, *B.* 15, 693, 1979; 20, 731; La Coste a. Valeur, *B.* 20, 97). Formed also from amido-benzene *m*-sulphonic acid, nitrobenzene, glycerin, and H_2SO at 160° (Lellmann a. Lange, *B.* 20, 1446). Monoclinic needles (containing aq). Yields oxy-quinoline [224°] by potash-fusion.—CaA'_2 5aq: needles v. e. sol. water. According to Lellmann, ther exists an *isomeric* quinoline (*B.* 1)-sulphoni acid, also got by sulphonation of quinoline, with H_2SO_4 (containing 50 p.c. SO_3 extra) at 260° (Lellmann, *B.* 20, 2172). This ψ-acid is converte by conc. H_2SO_4 at 250°–300° into the (*B.* 2)-aci (Lellmann, *B.* 22, 1391). The ψ-acid forms anhydrous crystals.

Tetrahydride $C_9H_{10}N.SO_3H$ aq. [315°] Formed by reducing the above acid (*B.* 4)-bromo-quinoline (*B.* 1)-sulphonic acid and also (*B.* 4)-oxy-quinoline (*B.* 1)-sulphonic acid with tin and HClAq (Lellmann a. Lange, *B.* 20, 3087; Claus, *J. pr.* [2] 42, 344). Trimetric crystals (from dilute solutions) or monoclinic crystals (from conc. solutions). $FeCl_3$ gives a brown colour passing through purple to grass-green on warming.

Quinoline (*B.* 2)-sulphonic acid $\begin{array}{l}\text{SO}_3\text{H.C=CH.C.CH:CH}\\ \quad\text{CH:CH.C.N=CH}\end{array}$. Formed by heating a mixture of amido-benzene-*p*-sulphonic acid, glycerin, nitrobenzene, and H_2SO_4 (Happ, *B.* 17, 191). Formed also (to the extent of 70 p.c.) by heating quinoline with conc. H_2SO_4 at 240°–300° and by heating the (*B.* 1)- or (β 4)- acid with conc. H_2SO_4 at 240°–300° (Georgievitch, *M.* 8, 578, 639). Monoclinic needles (containing 1½aq), sl. sol. alcohol and cold water. Not melted at 260°. Potash-fusion yields (*B.* 2)-oxy-quinoline [193°]. Bromine-water gives a yellow pp. of di-bromo-quinoline [126°] and at 100° Br (3 mols.) forms tri-bromo-quinoline [170°] (Claus a. Küttner, *B.* 19, 2884). Heating with KCy gives $C_9H_6N.Cy$ [131°] which on saponification yields the carboxylic acid [288°].

Salts.—KA' (dried at 120°). Tables.—BaA'_2 (dried at 120°).—AgA': slender needles.—$Ag_2HA'_3$: needles.—$(HA')_{16}K_4I_9$ 6aq: lustrous green crystals.

Ethyl ether EtA'2aq. Crystals, v. sol. water (Claus a. Happ, *B.* 18, 366).—EtA'KI$_3$: unstable brown needles, v. sol. water (Claus a. Stegelitz, *B.* 19, 921).—EtA'KBr$_3$.—EtA'HgCl$_2$.

Benzyl ether C_7H_7A' 2aq. Monoclinic crystals.—$C_7H_7A'KI_3$: needles with blue reflex.

Quinoline (*B.* 3)-sulphonic acid $\begin{array}{l}\quad\text{CH:CH.C.CH:CH}\\ \text{SO}_3\text{H.C=CH.C.N=CH}\end{array}$. [above 300°]. Formed by heating quinoline with H_2SO_4 (containing 15 p.c. SO_3 extra) at 130° (Claus, *J. pr.* [2] 37, 260). Small needles, v. e. sol. water, v. sol. alcohol. Potash-fusion yields oxy-quinoline [165°–200°]. Bromine forms di-bromo-quinoline [255°] and tri-bromo-quinoline [199°].—NaA'3aq. KA' 2aq.—CaA'_2 4aq.—BaA'_2 4aq.—PbA'_2.—CuA'_2 2aq: dark-green crystalline powder.

Ethyl ether EtA'. [275°]. Needles (from alcohol).

Chloride $C_9H_6N.SO_2Cl$. Viscid mass.

Amide $C_9H_6N.SO_2NH_2$. [119°]. Crystalline.

Quinoline (*B.* 4)-sulphonic acid $\begin{array}{l}\text{CH:CH — C.CH:CH}\\ \text{CH:C(SO}_3\text{H).C.N=CH}\end{array}$. ***Quinoline o-sulphonic acid.*** **Formed, together with a smaller quantity of the *p*- acid, by heating quinoline with fuming**

H_2SO_4 **at 170°** (O. Fischer a. Bedall, *B.* 15, 683, 1979; 20, 731; Riemerschmied, *B.* 16, 721; La Coste a. Valeur, *B.* 20, 95; Claus, *B.* 19, 925, 2882; *J. pr.* [2] 37, 260). Formed also by heating quinoline with conc. H_2SO_4 at 220° (Georgievitch, *M.* 8, 641). Monoclinic prisms, v. sl. sol. water. Oxidised by $KMnO_4$ to pyridine dicarboxylic (quinolinic) acid (Fischer, *B.* 17, 755) and a small quantity of (1,2,3)-sulpho-amido-benzoic acid (Zürcher, *B.* 21, 180). Changed by conc. H_2SO_4 at 250° to the (*B.* 2)-isomeride (Georgievitch, *M.* 8, 578). Bromine-water forms a yellow insoluble pp. and, at 100°, tri-bromo-quinoline [198°].

Salts.—NaA′ 5aq (Spies, *J. pr.* [2] 37, 265).—KA′ 2aq.—CaA'_2 9aq. Monoclinic crystals.—PbA'_2.—CuA'_2 2aq: small green needles.

Ethyl ether EtA′. [66°]. Needles (from chloroform). Decomposed by boiling water.

Chloride $C_9H_6NSO_2Cl$. [124°]. Needles.

Amide $C_9H_6N.SO_2NH_2$. [184°]. Needles (from water) (Hoogewerff a. van Dorp, *R. T. C.* 8, 184). Converted by Br and KOHAq into $C_9H_6NSO_2NBrK$ 2aq, crystallising in yellow needles, m. sol. water, and converted by HOAc into $C_9H_6NSO_2NBrH$, crystallising from acetone in needles, yielding $(C_9H_6NSO_2NBr)_2Ba$ 2aq.

Quinoline (α)-disulphonic acid $C_9H_5(SO_3H)_2N$. Formed, together with the (β)-isomeride, by heating quinoline (*B.* 4)-sulphonic acid with fuming H_2SO_4 at 250° (La Coste a. Valeur, *B.* 19, 995; 20, 98). Yellow needles (containing 3aq), v. sol. water, insol. alcohol.—K_2A'' 3½aq: satiny plates, v. e. sol. water.—BaA″ 3aq. S. 4·08 at 15°.

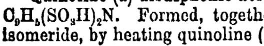
Quinoline (β)-disulphonic acid $C_9H_5N(SO_3H)_2$. Formed as above (La Coste a. Valeur, *B.* 19, 998; 20, 3199). Needles (containing 1½aq), v. sol. water, insol. alcohol.—K_2A'' aq: crusts, sl. sol. cold water.—BaA″ 2aq: white powder, sl. sol. cold water (difference from (α)-isomeride).

References. — BROMO- and OXY-QUINOLINE SULPHONIC ACIDS.

ISOQUINOLINE SULPHONIC ACID $C_9H_6N(SO_3H)$. Formed by heating isoquinoline (1 pt.) with fuming H_2SO_4 (2 pts.) at 100° (Hoogewerff a. van Dorp, *R. T. C.* 5, 305).—BaA'_2 9aq. Needles, v. sol. water.

QUINOLINIC ACID *v.* PYRIDINE DICARBOXYLIC ACID. The name is also given by Dewar (*Pr.* 30, 164) to an acid $C_9H_9NO_3$ [143°] formed in small quantity in the oxidation of quinoline (derived from cinchonine) by boiling aqueous $KMnO_4$.

(α)-DIQUINOLYL $C_{18}H_{12}N_2$ *i.e.*



$$C_6H_4\left\langle\begin{matrix}CH{:}CH\;CH{:}CH\\ N{=}C{-}C{=}N\end{matrix}\right\rangle C_6H_4$$

Diquinoline. [176°]. (above 400°). V.D. 8·73 (calc. 8·86).

Formation.—1. By heating quinoline with sodium at 192° (Weidel, *M.* 2, 491; 7, 327).—2. In small quantity (8 p.c.) by passing dry oxygen into a mixture of quinoline and quinoline hydrochloride in presence of platinum-black (Weidel, *M.* 8, 120).

Properties. — Monoclinic plates, $a{:}b{:}c = 1·37{:}1{:}1·32$; $\beta = 109° 58'$. Insol. water, sol. alcohol, ether, and benzene. Oxidised by $KMnO_4$ and HOAc to cyclothraustic ($C_{17}H_{12}N_2O_8$), quinoline (*Py.* 3)-carboxylic, oxyisocinchomeronic (oxy-pyridine dicarboxylic), and *o*-amido-benzoic acids (Weidel a. Strache, *M.* 7, 280, 306; 8, 197). Alkaline $KMnO_4$ forms isocinchomeronic, *o*-amido-benzoic, and pyridanthrilic ($C_{15}H_{10}N_2O_7$) acid. MeOH and H_2SO_4 form $B''MeSO_4H$ (Ostermayer, *B.* 18, 333, 597).

Salts. — $B''H_2Cl_2$ 4aq: white needles.—$B''H_2PtCl_6$ aq.—$B''HAuCl_4$ 2aq.—$B''H_2SO_4$ aq.

Methylo-chloride $B''Me_2Cl_2$ 6aq: needles.—$B''Me_2Cl_2 2ICl$. [238°]. Lemon-yellow pp.

Methylo-iodide B″MeI. [283°].

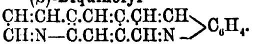
Ethylo-iodide B″EtI. Yellow needles (from water), sl. sol. water (Roser, *B.* 17, 2769).

Sulphonic acid $C_{18}H_{11}N_2(SO_3H)$. Formed by heating diquinolyl with H_2SO_4 (containing 5 p.c. SO_3 extra) (Weidel a. Gläser, *M.* 7, 308). Minute needles, almost insol. hot water, sol. conc. HClAq and H_2SO_4. Converted by potash-fusion into oxy-diquinolyl [208°].—KA′ 2aq: needles, v. e. sol. water.—CuA'_2 2aq.

(α)-*Disulphonic acid* $C_{18}H_{10}(SO_3H)_2N_2$. Formed by heating diquinolyl (10 pts.) with H_2SO_4 (11 pts.) and SO_3 (34 pts.) at 170° (Weidel, *M.* 2, 503). Minute needles, sl. sol. water. Yields, by potash-fusion, di-oxy-diquinolyl [239°].—K_2A'' 5aq: needles.—CuA″ 6aq: bluish-green crystals, nearly insol. water.

(β)-*Disulphonic acid* $C_{18}H_{10}(SO_3H)_2N_2$. Formed, together with the mono-sulphonic acid, by heating (α)-diquinolyl (100 pts.) with H_2SO_4 (332 pts.) and SO_3 (18 pts.) for 20 hours at 190° (Weidel a. Gläser, *M.* 7, 322). Small needles, converted by potash-fusion into di-oxy-diquinolyl [above 305°].—K_2A'' (dried at 120°): crystalline powder.—CuA″ (dried at 120°).

(β)-Diquinolyl



$$\begin{matrix}CH{:}CH.C.CH{:}C.CH{:}CH\\ CH{:}N{-}C.CH{:}C.CH{:}N\end{matrix}\Big\rangle C_6H_4$$

[192°].

Formation.—1. By heating quinoline with BzCl at 250° (Japp a. Graham, *C. J.* 39, 174).—2. In very small quantity by distilling cinchoninic acid with lime (Weidel, *M.* 2, 501).—3. By passing quinoline through a red-hot tube (Zimmermann a. Müller, *B.* 17, 1965).—4. By distilling quinoline (*B.* 4)-sulphonic acid; the yield being 10 p.c. (O. Fischer a. Loo, *B.* 17, 1899; 19, 2472).

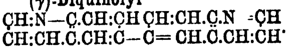
Properties.—Iridescent plates (by sublimation) or colourless prisms (from ether), sol. hot benzene, alcohol, and ether, insol. water. Weak base, the salts being decomposed by water. Oxidised by CrO_3 and HOAc to quinoline (*B.* 3)-carboxylic acid. CrO_3 and H_2SO_4 give pyridyl-quinoline carboxylic acid $C_9H_6N.C_5H_3N.CO_2H$ [273°]. Bromine forms $C_{18}H_{12}N_2Br_4$ [192°].

Salts.—$B''H_2SO_4$: sparingly soluble concentric needles.—$B''H_2PtCl_6$: granular pp.

Ethylo-iodide B″EtI. Very unstable red crystals, decomposed by hot water.

Disulphonic acid $C_{18}H_{10}(SO_3H)_2N_2$. Formed by heating the base (1 pt.) with conc. H_2SO_4 (10 pts.) at 180°. V. e. sol. water.—K_2A'' 3aq: prisms.

(γ)-Diquinolyl



$$\begin{matrix}CH{:}N{-}C.CH{:}CH\;CH{:}CH.C.N{=}CH\\ CH{:}CH.C.CH{:}C{-}C{=}CH.C.CH{:}CH\end{matrix}$$

Di-p-quinolyl. [178°].

Formation.—1. By boiling a mixture of benzidine, nitrobenzene, glycerin, and H_2SO_4 (Roser, *B.* 17, 1817, 2767; O. W. Fischer, *M.* 5, 418; Colson, *C. R.* 108, 677). A better yield is got by using *o*- or *p*- nitrophenol instead of nitro-benzene (Ostermayer a. Henrichsen, *B.* 17, 2444). When crude benzidine is used there is also formed a base $C_{22}H_{18}N_2O_3$, which yields $B'2SnCl_2$ [135°] and $B''H_2PtCl_6$ 2aq (Colson, *C. R.* 107, 1008; 108, 677).—2. By heating azobenzene with glycerin and H_2SO_4 (Claus a. Stegelitz, *B.* 17, 2380).

Properties.—Monoclinic crystals, insol. water, sl. sol. ether, v. sol. hot alcohol and benzene. MeOH and H_2SO_4 at 180° form $B''(MeHSO_4)_2$2aq, crystallising in needles. Bromine in alcohol forms unstable $C_{18}H_{12}N_2Br_2$ and $C_{18}H_{12}N_2Br_4$, converted by HClAq at 190° into $C_{18}H_{11}BrN_2$ [150°–155°].

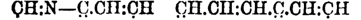
Salts. — $B''H_2Cl_2$ 4aq: white needles. — $B''HAuCl_4$ 2aq: slender needles.—$B''H_2SnCl_4$: colourless needles.—$B''H_2PtCl_6$ (dried at 105°).—$B''H_2Cl_2$2ICl: cheesy pp. (Dittmar, *B.* 18, 1618). — $B''H_2SO_4$ 3aq. — $B''2H_2SO_4$. — $B''2H_2Cr_2O_7$. — $B''C_6H_2(NO_2)_3OH$: minute yellow prisms.

Methylo-iodides B''MeI. Crystals. — $B''Me_2I_2$. [c. 300°]. Yellow needles, sol. water.

Ethylo-iodide B''2EtI. [270°]. Needles.

Disulphonic acid $C_{18}H_{10}(SO_3H)_2N_2$. White powder, insol. water and alcohol.—Na_2A'' 5aq: small needles. The same, or an isomeric, disulphonic acid is got by heating benzidine disulphonic acid with *o*-nitro-phenol, glycerin, and H_2SO_4. It crystallises in plates or needles, and yields K_2A'' aq.

(δ)-**Diquinolyl**



$$\begin{array}{l}CH{:}N-C.CH{:}CH\quad CH.CH{:}CH.C.CH{:}CH\\ CH{:}CH.C.CH{:}C-C-C.N{=}CH\end{array}$$

[148°]. Formed by heating *o*- *p*- di-amido-diphenyl hydrochloride with nitrobenzene, glycerin, and H_2SO_4 (O. W. Fischer, *M.* 6, 546). Leaflets, insol. water, sol. hot alcohol and benzene. Bromine in presence of water forms orange needles of $C_{18}H_{12}N_2Br_4$.—$B''H_2Cl_2$: needles, v. e. sol. water.—$B''H_2PtCl_6$ aq: reddish-yellow crystalline pp.—Picrate. [168°]. Yellow needles.

Methylo-iodide B''MeI. [126°]. Needles.

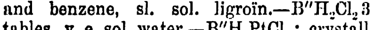
Disulphonic acid $C_{18}H_{10}(SO_3H)_2N_2$. Four-sided tables, not melted at 300°. Sl. sol. hot water.—BaA'' 3aq: needles, m. sol. hot water.

(*Py.* 3, *B.* 1 or 3)-**Diquinolyl** $C_{18}H_{12}N_2$. [159°]. Formed (7 pts.), together with the isomeride [115°], by heating a mixture of *m*-amido-(*Py.* 3)-phenyl-quinoline (20 pts.), glycerin (70 pts.), *o*-nitro-phenol (15 pts.), and H_2SO_4 (60 pts.) (Miller a. Kinkelin, *B.* 18, 1910). Small monoclinic tables, sl. sol. ether, cold alcohol, and chloroform.—$B''H_2Cl_2$2aq: plates.—$B''H_2PtCl_6$.—$B''H_2SO_4$: easily soluble needles.—$B''C_6H_3N_3O_7$. [240°]. Crystalline powder.

Methylo-iodide B''MeI. [263°]. Needles.

(*Py.* 3, *B.* 3 or 1)-**Diquinolyl** $C_{18}H_{12}N_2$. [115°]. Formed as above (M. a. K.). Light-yellow triclinic crystals, v. sol. alcohol, ether, and benzene, sl. sol. ligroïn.—$B''H_2Cl_2$3aq: tables, v. e. sol. water.—$B''H_2PtCl_6$: crystalline.

(*Py.* 3, *B.* 1)-**Diquinolyl**



$$C_6H_4\left\langle\begin{array}{l}CH{:}CH\quad CH.CH{:}CH.C.CH{:}CH\\ N{=}C-C-C.N{=}CH\end{array}\right.$$

[144°]. Formed from *p*-amido-(*Py.* 3)-phenyl-quinoline, glycerin, nitro-benzene, and H_2SO_4 (Weidel, *M.* 8, 140). It is also a product of the action of oxygen on a mixture of quinoline hydrochloride, aniline, and platinised asbestos at 180°. Monoclinic tables (from alcohol).—$B''H_2PtCl_6$: crystalline powder.—B''HCl: yellow.—$B''H_2Cl_2$.

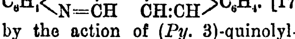
Methylo-iodide B''MeI aq. [232°]. Small needles (from water), sl. sol. boiling water.

Sulphonic acid $C_{18}H_{11}(SO_3H)N_2$. Insoluble powder. Potash-fusion yields an oxy-diquinolyl [187°].

(*B.*, *Py.* 1)-**Diquinolyl** $C_{18}H_{12}N_2$. [122°]. Got by heating (α)-amido-(*Py.* 1)-phenyl-quinoline [150°] with glycerin, nitro-benzene, and H_2SO_4 (Koenigs a. Nef, *B.* 20, 632). Large crystals (from benzene). May be distilled. V. e. sol. alcohol, v. sl. sol. ether. Strong base. — $B''H_2PtCl_6$: granules, sol. conc. HClAq.

(*B.*, *Py.* 1)-**Diquinolyl** $C_{18}H_{12}N_2$. [117°]. Got by heating (β)-amido-(*Py.* 1)-phenyl-quinoline [198°] with glycerin, nitro-benzene, and H_2SO_4 (Koenigs a. Nef, *B.* 20, 634). Tables (from benzene), v. e. sol. alcohol. May be distilled. Strong base. — $B''H_2PtCl_6$: yellow needles.—Picrate. [248°]. Bulky flakes.

(*Py.* 2,3)-**Diquinolyl**



$$C_6H_4\left\langle\begin{array}{l}CH{:}C-C{=}N\\ N{=}CH\quad CH{:}CH\end{array}\right\rangle C_6H_4$$

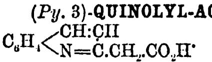
[176°]. Formed by the action of (*Py.* 3)-quinolyl-acetic aldehyde on *o*-amido-benzoic aldehyde in alcoholic solution (Carlier a. Einhorn, *B.* 23, 2895). Plates (from alcohol).—Aurochloride: [248°].—Platinochloride: [278°].—$B''H_2Cl_2$ 4aq.

Methylo-iodide B''MeI.

Diquinolyl tetrahydride $C_{18}H_{16}N_2$. [118°]. Formed by heating (*Py.* 3)-chloro-quinoline with quinoline tetrahydride (Friedländer a. Weinberg, *B.* 18, 1533). Crystals, sl. sol. ligroïn, insol. water. May be distilled. HClAq forms a deep-yellow solution.

Reference.—OXYDIQUINOLYL.

(*Py.* 3)-**QUINOLYL-ACETIC ACID**



$$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ N{=}C.CH_2.CO_2H\end{array}\right.$$

[275°]. Formed from the aldehyde by potash-fusion or by oxidation (Carlier a. Einhorn, *B.* 23, 2896). Formed also by oxidation of α-oxy-quinolyl-propionic acid with $KMnO_4$. Needles (from alcohol).—Hydrochloride: [243°]; needles. — Silver salt: white scales, yielding quinaldine on distilling with lime.

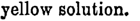
(*Py.* 3)-**QUINOLYL-ACETIC ALDEHYDE** $C_{11}H_9NO$ *i.e.* $C_9H_6N.CH_2.CHO$. [104°]. Formed by careful oxidation of α-oxy-quinolyl-propionic acid (Einhorn, *B.* 18, 3467; 19, 908). Crystals (from alcohol). Yields a phenyl-hydrazide [199°].—$B'_2H_2PtCl_6$ 2aq.—$B'C_6H_3N_3O_7$. [212°].

QUINOLYL-ACETONE *v.* ACETONYL-QUINOLINE.

(*Py.* 3)-**QUINOLYL-ACETYLENE** $C_9H_6N.C{:}CH$. Formed by distilling a solution of di-bromo-quinolyl-propionic acid with Na_2CO_3 (Carlier a. Einhorn, *B.* 23, 2896). Volatile oil. Br forms $C_9H_6N.CBr{:}CHBr$.

(*Py.* 3)-**QUINOLYL-ACRYLIC ACID**

$C_{12}H_9NO_2$ *i.e.*



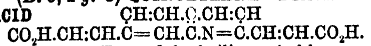
$$C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ N{=}C.CH{:}CH.CO_2H\end{array}\right.$$

[193°]. Formed by the action of boiling potassium carbonate solution upon 'quinolyl-acrylo-trichloride' $C_9H_6N.CH{:}CH.CCl_3$ aq [145°], which is got by heating (*Py.* 3)-methyl-quinoline with chloral at 110° (Miller a. Spady, *B.* 18, 3402, 3465; 19, 130; Einhorn, *B.* 19, 908). Plates. Oxidised by $KMnO_4$ to aldehydo-quinoline. HBr forms β-bromo-quinolyl-propionic acid. — *BaA'_2: needles, sl. sol. cold water.—*HA'HCl: needles.

QUINOLYL-ACRYLO-TRICHLORIDE *v. supra.*

TRI-(*B.* 2)-QUINOLYL-CARBINOL $(C_9H_6N)_3C.OH$. [108°]. Formed by oxidising tri-quinolyl-methane with H_2CrO_4 and HOAc (Noelting a. Schwarz, *B.* 24, 1608). Needles, v. sol. alcohol, sl. sol. ligroïn.

(*B.* 3, *Py.* 3)-**QUINOLYLENE DIACRYLIC ACID**

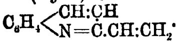


$\begin{array}{l}\qquad\qquad CH:CH.C.CH:CH\\ CO_2H.CH:CH.C=CH.C.N=C.CH:CH.CO_2H.\end{array}$

[over 300°]. Formed by boiling tri-chloro-propenyl-quinolyl-acrylic acid with K_2CO_3Aq (Eckhardt, *B.* 22, 284). Sol. acids and alkalis. Insol. water, sl. sol. hot alcohol.

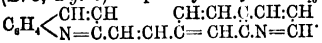
DI-(*B.* 2)-QUINOLYL-ETHANE $C_{20}H_{16}N_2$ *i.e.* $C_9H_6N.CH_2.CH_2.C_9H_6N$. [124°]. Formed by heating di-*p*-amido-di-phenyl-ethane with nitro-phenol, glycerin, and H_2SO_4 (Comey, *B.* 23, 1115). Hexagonal plates, insol. water, sl. sol. ether.—$B''H_2Cl_2$4aq: needles, v. sol. water.—$B''H_2Cl_2$. — $B''H_2PtCl_6$. — $B''2HAuCl_4$. — Sulphate: prisms, m. sol. cold water.

(*Py.* 3)-**QUINOLYL-ETHYLENE** $C_{11}H_9N$ *i.e.*



$C_6H_4<\begin{array}{l}CH:CH\\ N=C.CH:CH_2\end{array}$. Formed by boiling β-bromo-quinolyl-propionic acid with conc. K_2CO_3Aq (Einhorn, *A.* 246, 172). Oil. — $B'_2H_2PtCl_6$4aq. [187°].—$B'HAuCl_4$. [159°].

(*B.* 3, *Py.* 3)-**Di-quinolyl-ethylene** $C_{20}H_{14}N_2$ *i.e.*



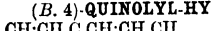
$C_6H_4<\begin{array}{l}CH:CH\qquad\qquad CH:CH.C.CH:CH\\ N=C.CH:CH.C=CH.C.N=CH\end{array}$.

Formed by heating *m*-amido-(*Py.* 3)-styryl-quinoline with *o*-nitro-phenol, glycerin, and H_2SO_4 (Wartmann, *B.* 23, 3650). Oil, v. sol. alcohol, sl. sol. ether.

Methylo-iodide B'MeI 1½aq. [226°]. Golden needles, v. sol. hot water and alcohol. Yields $C_{20}H_{14}N_2Br_2MeI$. [210°].

QUINOLYL-DI-ETHYL-PHENOL $C_{19}H_{19}NO$ *i.e.* $C_9H_6N.C_6H_2Et_2.OH$. This is probably the constitution of apocinchene (Comstock a. Königs, *B.* 20, 2674; *v.* vol. ii. p. 174).

(*B.* 4)-**QUINOLYL-HYDRAZINE** $C_9H_9N_3$ *i.e.*



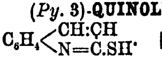
$\begin{array}{l}CH:CH.C.CH:CH.CH\\ CH:N-C \text{———} C.N_2H_3\end{array}$. [64°]. Formed from (*B.* 4)-amido-quinoline by diazotisation and treatment with $SnCl_2$ and HCl (Dufton, *C. J.* 59, 757; Böttinger, *B.* 24, 3277). Needles (from ether) or prisms (from ligroïn). — $B''H_2Cl_2$: prisms. Converted by potassium cyanate and HCl into $C_9H_6N.NH.NH.CO.NH_2$ [235°], and by pyruvic acid into $C_9H_6N.N_2H:CMe.CO_2H$ crystallising in orange needles, converted by boiling HClAq into quinindole (α)-carboxylic acid $C_{12}H_{10}N_2O_2$ [286°].

(*B.* 1)-**Quinolyl-hydrazine** [151°]. Formed in like manner from *ana*-amido-quinoline (Dufton, *C. J.* 61, 785). Yellow needles (from water). Yields B'HCl [248°] and is converted by cyanic acid into $C_9H_6N.NH.NH.CO.NH_2$[255°], by benzoic aldehyde into $C_9H_6N.NH.N:CHPh$ [194°], by acetone into $C_9H_6N.NH.N:CMe_2$ [140°] and by pyruvic acid into the acid $C_9H_6N.NH.N:CMe.CO_2H$ [185°], whence boiling HClAq forms the corresponding quinindole carboxylic acid, which decomposes at about 300°.

DIQUINOLYLINE is Diquinolyl.

DI-(*B.* 2)-QUINOLYL KETONE $(C_9H_6N)_2CO$. [174°]. Formed from di-*p*-amido-benzophenone, glycerin, H_2SO_4, and picric acid (Noelting a. Schwarz, *B.* 24, 1608). Needles, v. sol. alcohol, sl. sol. hot water. — $B''H_2Cl_2$. [over 200°]. Needles, v. e. sol. water and alcohol.

(*Py.* 3)-**QUINOLYL-MERCAPTAN**

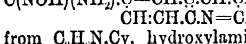


$C_6H_4<\begin{array}{l}CH:CH\\ N=C.SH\end{array}$. [174°]. Formed by heating (*Py.* 3)-oxy-quinoline with P_2S_5 at 145° (Roos, *B.* 21, 620). Yellow plates, sl. sol. hot water, v. sol. hot alcohol. Yellow dye. Combines with acids and bases. Does not react with hydroxylamine or phenyl-hydrazine.

Ethyl derivative $C_9H_6N.SEt$. Formed from quinolyl-mercaptan, NaOEt, and EtI. Oil, decomposed by distillation.—B'HI. [154°].—$B'_2H_2PtCl_6$ aq. [c. 190°]. Octahedra.

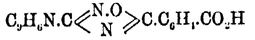
TRI-(*B.* 2)-QUINOLYL-METHANE $CH(C_9H_6N)_3$. [202°]. Formed from *p*-rosaniline, glycerin, H_2SO_4, and picric acid at 150° (Noelting a. Schwarz, *B.* 24, 1606). Needles (containing EtOH), melting at 98°. Melts at 202° when anhydrous. — B'''3HCl: plates, sol. water. — $B''C_6H_3N_3O_7$: yellow needles. — $B'''_4H_{12}Pt_3Cl_{24}$: yellow crystals.—B'''3MeI. [266°].

(*B.* 2)-**QUINOLYL-METHENYL-AMIDOXIM**



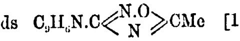
$\begin{array}{l}C(NOH)(NH_2).C=CH.C.CH:CH\\ \qquad\qquad\qquad\quad CH:CH.C.N=CH\end{array}$. [105°]. Formed from $C_9H_6N.Cy$, hydroxylamine hydrochloride, Na_2CO_3, and dilute alcohol (Biedermann, *B.* 22, 2761). Yellowish needles, m. sol. hot water. Fehling's solution gives a greyish-green pp. $FeCl_3$ gives a deep-red colour. $AgNO_3$ gives a white pp. yielding a mirror.

Reactions.—1. *Phthalic anhydride* on warming forms

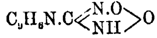


$C_9H_6N.C\begin{array}{c}\diagup N.O \diagdown\\ \diagdown\ N\ \diagup\end{array}C.C_6H_4.CO_2H$ [203°].

2. Ac_2O yields



$C_9H_6N.C\begin{array}{c}\diagup N.O \diagdown\\ \diagdown\ N\ \diagup\end{array}CMe$ [175°], crystallising in needles.—3. The hydrochloride is converted by potassium cyanate into $C_9H_6N.C(NOH).NH.CO.NH_2$ [165°]. 4. *Chloro-formic ether* forms $C_9H_6N.C(NH_2):NO.CO_2Et$ [97°], which is converted by NaOHAq into



$C_9H_6N.C\begin{array}{c}\diagup N.O \diagdown\\ \diagdown NH \diagup\end{array}O$ [155°].

Salts.—B'HCl: needles.—$B'_2H_2PtCl_6$.

Acetyl derivative $C_9H_6N.C(NOAc).NH_2$. [115°]. Formed by means of AcCl in the cold. Needles, insol. cold water, sl. sol. ether.

Ethyl ether $C_9H_6N.C(NOEt).NH_2$. [85°]. Formed from the amidoxim, NaOEt, and EtI. Needles, v. sol. alcohol and hot water.

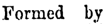
(*Py.* 3)-**QUINOLYL-PROPIONIC ACID** $C_9H_6N.CH_2.CH_2.CO_2H$. [116°]. Formed by reducing quinolyl-acrylic acid with sodium-amalgam (Carrier a. Einhorn, *B.* 23, 2896).

Ethyl ether EtA'. [116°]. Needles.

Reference.—Oxy-quinolyl-propionic acid.

DI-(*Py.* 3)-QUINOLYL DISULPHIDE $(C_9H_6N)_2S_2$. [137°]. Formed by oxidising quinolyl-mercaptan with H_2O_2 in dilute alcohol (Roos, *B.* 21, 622). Plates (from alcohol), insol. water and alkalis.

QUINONE $C_6H_4O_2$ *i.e.*



$\begin{array}{l}CH.CO.CH\\ CH.CO.CH\end{array}$. *Benzoquinone.* Mol. w. 108. [116°]. V.D. (H = 1) 53·4 (calc. 54) (Hofmann, *B.* 3, 583). H.C. 659,020. H.F. 45,200 (from diamond) (Berthelot a. Recoura, *Bl.* [2] 48, 699; *A. Ch.* [6] 13, 312, 335; *C. R.* 104, 1572).

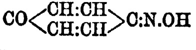
Formation.—1. By oxidation of quinic acid with MnO_2 (4 pts.), H_2SO_4 (1 pt.), and water (½ pt.) (Woskresensky, *A.* 27, 268).—2. By oxidation of hydroquinone (Wöhler, *A.* 51, 148). 3. By oxidation of benzidine, of aniline, and of *p*-phenylene-diamine by MnO_2 and H_2SO_4 (Hofmann, *Pr.* 13, 4).—4. By action of MnO_2 and H_2SO_4 on amido-benzene *p*-sulphonic acid and on phenol *p*-sulphonic acid (Schrader, *B.* 8, 759).

Preparation.—1. By adding conc. $Na_2Cr_2O_7Aq$ to a cold solution of aniline (1 pt.) in H_2SO_4 (8 pts.) and water (25 pts.), and extracting with ether (Nietzki, *B.* 19, 1467).—2. 20 g. of aniline are dissolved in 600 c.c. of water containing 160 g. of H_2SO_4; 20 g. of finely-powdered potassium bichromate are added by degrees, with constant agitation, keeping the temperature at 10°–15°. After standing over night 33 g. more potassium bichromate are added; the quinone is then extracted with ether, dried over $CaCl_2$, and the ether removed by distillation. The yield is about 86 p.c. of the theoretical amount (Schniter, *B.* 20, 2283; *cf.* Seyda, *B.* 16, 687; Nietzki, *B.* 11, 1102; *A.* 215, 127).—3. From *p*-amido-phenol. *p*-Amido-phenol sulphate is dissolved in water, some H_2SO_4 added, and then PbO_2 gradually, with shaking, till the violet colour first formed disappears. The quinone is extracted with ether. Yield theoretical (Schmitt a. Siepermann, *J. pr.* [2] 19, 317).

Properties.—Yellow monoclinic prisms (from water) or plates (from EtI) (Hesse, *A.* 114, 299), or needles (by sublimation). Its odour is characteristic. V. sl. sol. cold water, m. sol. alcohol and ether. The solutions turn the skin brown. Sol. HClAq and conc. HNO_3. Its alkaline solution turns brown in air (Laurent, *C. R.* 26, 35). An alcoholic solution of hydrocœrulignone deposits, even in dilute solutions, crystals of cœrulignone with steel-blue reflex.

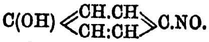
Reactions.—1. *Chlorine* forms tri-chloro-quinone.—2. HCl and $KClO_3$ give tetra-chloro-quinone (Hofmann, *A.* 52, 55).—3. Conc. HClAq forms chloro-hydroquinone (Wöhler; Städeler, *A.* 69, 308).—4. HIAq forms quinhydrone and hydroquinone.—5. HBr passed into a solution in chloroform ppts. quinhydrone, and finally forms bromo-hydroquinone. HBrAq forms, on heating di-bromo-hydroquinone (Sarauw, *A.* 209, 99).—6. *Bromine.* (1 mol.) in $CHCl_3$ is instantly absorbed. Excess of bromine (2 mols.) appears to form $C_6H_4Br_4O_2$, which is split up by heat into HBr and two di-bromo-quinones $C_6H_2Br_2O_2$ [2:5:4:1] and [2:6:4:1] (Nef, *J. pr.* [2] 42, 167).—7. HNO_3 on heating yields oxalic and picric acids and HCy (Nietzki, *A.* 215, 138).—8. *Ammonia* gas forms emerald-green quinonimide C_6H_5NO, sol. water, the solution soon turning black (Woskresensky). NH_3 in presence of chloroform produces hydroquinone, quinhydrone, and brown $C_6H_5NO_2$ (Zincke, *B.* 16, 1556).—9. An alcoholic solution exposed to sunlight yields hydroquinone and aldehyde (Ciamician, *G.* 16, 111).—10. *Hydrazine hydrate* gives hydroquinone and a compound $C_6H_4(OH)_2N_2H_4$ (Curtius a. Thun, *J. pr.* [2] 44, 191).—11. Heated in a sealed tube alone at 160°, or with water at 100°, it yields hydroquinone and quinhydrone (Scheid, *A.* 218, 227).—12. PCl_5 forms a thick oily product, $C_{12}H_7O_4P_3Cl_8$. Water acting upon this forms mono- and di-chloro-hydroquinone.—13. Heated with $POCl_3$, quinone gives mono- and di-chloro-hydroquinone. An amorphous body $C_{21}H_{14}O_{11}$ is also formed.—14. Alcoholic H_2S form $C_{12}H_{12}SO_4$, a yellowish crystalline mass, melting below 100°.—15. AcCl forms in the cold the di-acetyl derivatives of chloro-hydroquinone. On warming it also forms $C_6H_2Cl_2(OAc)_2$ (Schulz, *B.* 15, 652). AcBr, in like manner, gives $C_6H_3Br(OAc)_2$ and $C_6H_2Br_2(OAc)_2$.—16. Ac_2O does not act below 200°, when it forms $C_6H_4(OAc)_2$ and a brown mass. 17. Cold dilute NaOAc converts it into hydroquinone (Hesse, *A.* 220, 365).—18. *Aniline* in boiling alcoholic solution forms di-phenyl-di-amido-quinone and hydroquinone $3C_6H_4O_2 + 2NH_2Ph = C_6H_2(NHPh)_2O_2 + 2C_6H_4(OH)_2$. Other primary and secondary bases act in like manner.—19. *o-* and *p- Nitro-aniline* form red crystals $C_6H_4O_2C_6H_4(NO_2).NH_2$ melting at 97° and 120° respectively (Hebebrand, *B.* 15, 1976). *o*-Nitro-aniline in HOAc forms $C_6H_2O_2(NH.C_6H_4.NO_2)_2$ [1:4:2:5] [305°] crystallising from alcohol in red needles (Leicester, *B.* 23, 2794).—20. *o-Amido-phenol* in hot alcohol forms a base ($C_{24}H_{18}N_4O_4$?) which crystallises in violet needles [250°], sl. sol. alcohol (Zincke a. Hebebrand, *A.* 226, 61). In dilute acids it forms a red solution. Ac_2O yields $C_{24}H_{16}Ac_2N_4O_4$ [285°], while Bz_2O at 150° gives $C_{24}H_{16}Bz_2N_4O_4$ [265°]. Yields a crystalline nitrosoamine $C_{24}H_{16}(NO)_2N_4O_4$. Forms the salts $B''H_2Cl_2$, crystallising in needles with green lustre, $B''H_2SO_4$, $B''H_2PtCl_6$, and a picrate crystallising in steel-blue needles [236°].—21. $C_6H_4(NH_2)(OMe)$ [1:2] forms $C_{20}H_{18}N_2O_4$ or $C_6H_2O_2(NH.C_6H_4.OMe)_2$ crystallising in reddish-violet needles [230°], forming a blue solution in H_2SO_4.—22. *p-Amido-phenol hydrochloride* gives $C_6H_2O_2(NH.C_6H_4.OH)_2$ crystallising in violet-brown needles, not melted at 290°.—23. (1,3,2)-*Amido-o-cresol* forms a compound [285°], which gives a crystalline acetyl-derivative.—24. (2,4,1)-*Nitro-toluidine* forms $C_6H_3O_2.NH.C_7H_6NO_2$, decomposing at 300°, and $C_6H_2O_2(NH.C_7H_6.NO_2)_2$ (L.).—25. *Acetoacetic ether* and $ZnCl_2$ at 100° form $C_{16}H_{16}O_6$ [184°], crystallising in needles, insol. water, sol. hot alcohol. Conc. H_2SO_4 forms a deep-blue solution. Alcoholic potash forms $C_{14}H_{10}K_2O_6$ 2aq, the salt of an insoluble acid $C_{14}H_{12}O_6$ (Von Pechmann, *B.* 21, 3005).—26. $C_6H_4(OH)(OMe)$ [1:4] in hot ligroïn forms di-methyl-quinhydrone $C_{20}H_{20}O_6$, crystallising in lustrous greenish-black prisms, decomposed by warm water (Hesse, *A.* 200, 253).

Mono-oxim



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CH:CH}\\\mathrm{CH:CH}\end{matrix}\Big\rangle\mathrm{C:N.OH}$$

or



$$\mathrm{C(OH)}\Big\langle\!\!\Big\langle\begin{matrix}\mathrm{CH.CH}\\\mathrm{CH:CH}\end{matrix}\Big\rangle\!\!\Big\rangle\mathrm{C.NO.}$$

p-Nitroso-phenol.

Mol. w. 123.

Formation.—1. By boiling nitroso-di-methyl-aniline (or nitroso-di-phenyl-aniline) hydrochloride with dilute NaOHAq (Baeyer a. Caro, *B.* 7, 809, 967; Ter Meer, *B.* 8, 622; Fischer, *B.* 19, 2995).—2. By adding KNO_2 and HOAc to an aqueous solution of phenol (B. a. C.; *cf.* Stenhouse a. Groves, *A.* 188, 360).—3. By adding hydroxylamine hydrochloride to a cold dilute aqueous solution of quinone (Goldschmidt, *B.* 17, 213).—4. Formed also from aqueous phenol, hydroxylamine hydrochloride and H_2O_2 (Wurster, *B.* 20, 2631). Free hydroxylamine merely reduces quinone to hydroquinone.

Properties.—Nearly colourless needles or greenish trimetric plates; $a:b:c = \cdot598:1:2\cdot469$. M. sol. water, forming a light-green solution which turns brown on boiling. V. sol. ether, acetone, and aqueous alkalis, sl. sol. HOAc. Decomposes at 120°–130°. Decomposed by hot conc. HClAq. When dissolved in phenol it gives, on addition of H_2SO_4, a cherry-red solution turned blue on addition of KOHAq. In this reaction the compound $C_{18}H_{15}NO_3$ is formed. Polyhydric phenols, containing two hydroxyls in the *m*-position, give by like treatment fluorescent 'dichroïns'; thus resorcin gives $C_{18}H_{15}NO_6$, $C_{36}H_{28}N_2O_{10}$, and azoresorcin (Brunner a. Chuit, *B.* 21, 249).

Reactions.—1. *Oxidised* by alkaline K_3FeCy_6 to *p*-nitro-phenol.—2. *Reduced* by tin and HClAq to *p*-amido-phenol.—3. *Nitrous acid gas* passed into an ethereal solution forms diazo-phenol nitrate (Jaeger, *B.* 8, 894).—4. Gaseous HCl passed into a cooled ethereal solution forms di-chloro-amido-phenol [175°] and tri-chloro-amido-phenol (J.; Hirsch, *B.* 13, 1908).—5. A solution of HCl in MeOH in presence of ice forms $C_6H_2Cl_2(NH_2)(OMe)$ [72°]; while EtOH and HCl give $C_6H_2Cl_2(NH_2)(OEt)$ [46°] (275°). 6. Conc. KOHAq at 180° forms azophenol $C_{12}H_{10}N_2O_2$ [214°] (Jaeger). — 7. $KClO_3$ and HClAq form $C_6H_4ClNO_2$, crystallising in yellow needles, v. sol. alcohol, insol. water, and exploding at 70° (Möhlau, *B.* 19, 281).—8. $ClCO_2Me$ added to its sodium salt forms $C_6H_4(NO).O.CO_2Me$ [137°], while $ClCO_2Et$ yields $C_6H_4(NO).O.CO_2Et$ [109°] (Walker, *B.* 17, 400). 9. BzCl added to the sodium salt in ether forms $C_6H_4(NO).OBz$, crystallising in yellowish needles [168°–175°], sol. hot alcohol (Walker).—10. *Aniline* forms azophenine $C_6H_2(NPh)_2(NHPh)_2$. *p*-Chloro-aniline forms, in like manner, tetra-chloro-azophenine [265°] (Fischer a. Hepp, *B.* 21, 677).—11. *Bromine* forms $C_6H_2Br_2O(NOH)$, crystallising in small leaflets, decomposed by water (O. Fischer, *B.* 21, 674).—12. *Phenyl cyanate* gives $C_6H_4O.NO.CO.NHPh$, crystallising in short yellow prisms decomposed at 160° without melting. It is converted by alkalis into the oxim, aniline, and CO_2 (Goldschmidt a. Strauss, *B.* 22, 3105).

Salts.—$C_6H_4(NO)(ONa)\,2aq$. Red needles (from alcohol), v. sol. water, insol. ether. Decomposed by boiling water. Ppd. by NaOH from aqueous solution.—$(C_6H_4(NO).O)_2Ba$ (dried at 100°). Red needles (from warm water).—$C_6H_4(NO).OAg\,aq$. Violet crystals with green reflex.

Dioxim $C(NOH)<\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>C(NOH)$. Formed by the action of hydroxylamine hydrochloride on the mono-oxim, on hydroquinone, and on *p*-nitroso-aniline (Nietzki, *B.* 20, 613; 21, 430; Fischer, *B.* 21, 685). Yellowish needles (from hot water). Decomposes at 240°. Reduced by $SnCl_2$ and HCl to *p*-phenylene-diamine. Oxidised by alkaline K_3FeCy_6 into insoluble di-nitroso-benzene. Ac_2O forms a crystalline di-acetyl derivative, sol. hot alcohol.

Quinone-chlorimide $C_6H_4<\genfrac{}{}{0pt}{}{NCl}{O}$. [85°]. Formed by the action of bleaching powder on a solution of the hydrochloride of *p*-amido-phenol (R. Schmitt, *J. pr.* [2] 8, 1; 19, 316; Hirsch, *B.* 11, 1980; 13, 1903; Fogh, *B.* 21, 890; Andresen, *J. pr.* [2] 23, 167) or $C_6H_4(NH_2).OEt$. Purified by steam-distillation. Golden crystals (from HOAc). Sl. sol. cold water, v. sol. alcohol and ether. Explodes above 86°. Smells like quinone. Stains the skin brown. Turned brown by alkalis. Reduced by tin and HCl to *p*-amido-phenol. Water at 100° forms quinone. Aqueous SO_2 forms amido-phenol sulphonic acid. HCl gives chlorinated amido-phenols. Gives Liebermann's colour reaction with phenol and H_2SO_4.

Quinone-di-chlorimide $C_6H_4N_2Cl_2$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{NCl}{NCl}$. Formed from *p*-phenylene-diamine hydrochloride and bleaching-powder solution (Krause, *B.* 12, 47). Needles (from water), decomposing at 124°. Almost insol. cold water. Its solution stains the skin brown. Reduced by $SnCl_2$ to *p*-phenylene-diamine. HCl forms tetra-chloro-*p*-phenylene-diamine. Br gives di-chloro-di-bromo-quinone. (β)-Naphthylamine forms amido-naphthophenazine. (β)-Naphthol forms $C_{16}H_{10}N_2O$, which dyes silk crimson and yields $B'HNO_3$ (Nietzki a. Otto, *B.* 21, 1745).

Quinone-phenylimide $C_{12}H_{11}NO$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{NPh}{O}$ [97°]. Formed by oxidising *p*-oxy-di-phenyl-amine in benzene by HgO (Bandrowski, *M.* 9, 134, 415). Red crystals, v. sol. alcohol, ether, and chloroform. Decomposed by water and alkalis. Acids reproduce quinone. Reacts with aniline, forming *p*-oxy-di-phenyl-amine and di-phenyl-di-amido-quinone-phenyl-imide.

Quinone-*p*-tolylimide $C_{13}H_{11}NO$. [70°]. Formed in like manner from *p*-oxy-phenyl-*p*-tolyl-amine (B.). Dark-red scales (from ligroïn), sol. most solvents.

Di-methyl-amido-phenylimide $C_{14}H_{14}N_2O$ *i.e.* $C_6H_4<\genfrac{}{}{0pt}{}{N.C_6H_4NMe_2}{O}$. *Phenol-blue.* Formed by the action of nitroso-di-methyl-aniline on an alkaline solution of phenol, or by oxidation of a mixture of phenol and phenylene-di-methyl-*p*-diamine (Möhlau, *B.* 16, 2851; 18, 2913). Formed also from quinone-chlorimide and di-methyl-aniline (Fogh, *B.* 21, 889). Steel-blue prisms (from water) (containing $\frac{1}{2}$aq). Its solution in HClAq is blue. Conc. H_2SO_4 forms quinone and $C_6H_4(NH_2)(NMe_2)$. Boiling NaOHAq forms NMe_2H and $C_6H_4<\genfrac{}{}{0pt}{}{N.C_6H_4.OH}{O}$. The sulphonic acid $C_{14}H_{14}N_2SO_4\,\frac{1}{2}aq$, formed from *p*-amido-phenol-sulphonic acid in water by successive treatment with Cl and dimethylaniline, crystallises in bronzed needles, forming a blue solution in NaOHAq.

Quinone tetrahydride $CO<\genfrac{}{}{0pt}{}{CH_2.CH_2}{CH_2.CH_2}>CO$. *Diketohexamethylene.* [78°]. Formed by heating the dihydride of di-oxy-terephthalic acid (succinyl-succinic acid) of 200° and distilling the product under reduced pressure (Hermann, *A.* 211, 322; Baeyer a. Noyes, *B.* 22, 2170). Prisms, v. sol. water. $FeCl_3$ does not colour its solution. Its alkaline solution turns brown in the air. Bromine forms $C_6Br_4O_2$. Reduces Fehling's solution. HCy forms $C_6H_8(OH)_2Cy_2$ [180°]. Yields a di-oxim which when quickly heated melts at 200°; when slowly heated at 192°. The di-phenyl-di-hydrazide $C_6H_8(N_2HPh)_2$ is obtained as a white pp. [125°] crystallising from alcohol in yellow prisms [150°], yielding a crystalline hydrochloride $B''H_2Cl_2$.

An isomeride of the tetrahydride $C_6H_8O_2$, [170°], is got by the action of NaOHAq on succinyl-succinic ether. It crystallises in prisms (containing ½aq). It changes into the preceding isomeride on distillation. It reduces Fehling's solution.

References.—AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, CHLORO-NITRO-, IODO-, NITRO-AMIDO-, OXY-AMIDO-, and OXY-QUINONE.

TRIQUINONE *v.* BENZENE-TRI-QUINONE.

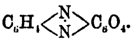
QUINONE DICARBOXYLIC ACID *dihydride* *v.* DI-OXY-TEREPHTHALIC ACID.

Tetrahydride v. Dihydride of DI-OXY-TEREPHTHALIC ACID.

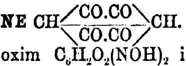
Quinone tetracarboxylic acid. *Methyl ether* $C_6O_2(CO_2Me)_4$. [207°]. Formed by oxidation of $C_6(OH)_2(CO_2Me)_4$ with HNO_3 (Nef, *A.* 258, 318). Colourless prisms (containing 2MeOH) (from MeOH) or yellow needles (by sublimation).

Ethyl ether $C_6O_2(CO_2Et)_4$. [149°]. Formed by oxidising di-amido-pyromellitic ether with conc. HNO_3 (Nef, *C. J.* 53, 428; *A.* 237, 28). Golden needles (from alcohol). May be sublimed. On treatment with KOHAq or with H_2SO_4 in HOAc it yields hydroquinone tetracarboxylic ether. Zinc-dust and HOAc also reduce it to hydroquinone tetracarboxylic ether.

QUINOPHENOL *v.* OXY-QUINOLINE.

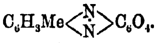
DIQUINO-PHENAZINE 
$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6O_4$.

Formed by the action of dilute HNO_3 on $C_6H_4{:}N_2{:}C_6O_2(OH)_2$, which is got from rhodizonic acid and *o*-phenylene-diamine (Nietzki a. Schmidt, *B.* 21, 1228). Yellowish needles (containing 3aq), sl. sol. water. Converted by *o*-phenylene-diamine sulphate into $C_{21}H_{12}N_6$, crystallising in greenish needles.

DIQUINOQUINONE 
$CH\genfrac{}{}{0pt}{}{\diagup CO.CO \diagdown}{\diagdown CO.CO \diagup}CH$. *Diquinoyl.* The di-oxim $C_6H_2O_2(NOH)_2$ is di-nitrosoresorcin (*q.v.*) (Goldschmidt a. Strauss, *B.* 20, 1611; Kehrmann a. Messinger, *B.* 23, 2816). The dioxim is converted by hydroxylamine into the tetra-oxim, which, on heating with Ac_2O, yields the anhydride $C_6H_2N_4O_2$ crystallising in needles [61°], sol. ether. The tetra-oxim may be reduced by $SnCl_2$ and HCl to tetra-amido-benzene.

Triquinoquinone *v.* BENZENE TRIQUINONE.

Reference.—OXY-DIQUINOYL.

DIQUINO-TOLAZINE 
$C_6H_3Me{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_6O_4$.

Formed from rhodizonic acid and tolylene-*o*-diamine, the product being oxidised by HNO_3 (Nietzki a. Kehrmann, *B.* 20, 324). Yellow needles (containing 2aq). On warming with an aqueous solution of a salt of tolylene-*o*-diamine it is converted into $C_{27}H_{18}O_6$, which crystallises from chloroform in needles (containing $CHCl_3$).

QUINOVATANNIC ACID $C_{14}H_{18}O_8$? Occurs in the bark of *Cinchona nova* (*Quina nova*) (Hlasiwetz, *A.* 79, 129). Translucent yellow mass, sol. water and alcohol, insol. ether. $FeCl_3$ gives a dark-green colour. NH_3Aq colours its solution brown. Its alkaline solution absorbs oxygen from the air. Boiling dilute H_2SO_4 splits it up into sugar and 'quinova red' $C_{28}H_{28}O_{12}$ (Rembold, *A.* 143, 273), which also occurs in the bark. Quinova red is a nearly black resin, nearly insol. water, v. sol alcohol, ether, and alkalis, gives no colour with $FeCl_3$, and yields protocatechuic acid on fusion with potash.

QUINOVIN $C_{30}H_{48}O_8$ (Hlasiwetz) or $C_{38}H_{64}O_{11}$ (Oudemans, jun., *R. T. C.* 2, 160). *Quinova-bitter. Quinovic acid.* $[\alpha]_D = +59°$. Occurs in false cinchona bark from *Cinchona nova* (Pelletier a. Caventou, *J. Ph.* 7, 112; Winckler, *Rep. Pharm.* 51, 193; Buchner, jun., *A.* 17, 161; Peterson, *A.* 17, 165; Schnedermann, *A.* 45, 277; Rochleder a. Hlasiwetz, *A.* 79, 129; 111, 182). Occurs also in true cinchona bark (Schwarz, *A.* 80, 330; De Vrij, *J. Ph.* [3] 37, 255), in all parts of *Cinchona Calisaya* (from Java), and in tormentilla root (Rembold, *A.* 145, 9).

Preparation.—The bark is extracted with boiling milk of lime, the extract ppd. by HCl, and the pp. repeatedly dissolved in alcohol and thrown down by water.

Properties.—Needles (from alcohol), almost insol. hot water, v. sl. sol. ether, v. sol. dilute alcohol. Tastes bitter. Dextrorotatory. Sol. aqueous alkalis. Resolved by acids into quinovic acid and quinovite. Does not reduce Fehling's solution.

Salts.—$PbC_{30}H_{46}O_8aq$.—$(CuO)_3 4C_{30}H_{48}O_8$.

(β)-Quinovin. [c. 235°]. $[\alpha]_D = +28°$ in a 2·7 p.c. alcoholic solution. Occurs in cuprea bark (from *Remijia*) (Liebermann a. Giesel, *B.* 16, 928). Scales (from dilute alcohol). Insol. ether, v. e. sol. alcohol. Dextrorotatory. Forms with alcohol the compound $C_{38}H_{62}O_{11}5EtOH$, crystallising in large prisms. Split up by dilute acids into quinovic acid and quinovite.

Quinovite $C_6H_{12}O_4$ *i.e.* $C_6H_9O(OH)_3$. *Quinova-sugar.* (c. 300°). $[\alpha]_D = 60°$ (O.); $= +78°$ (L. a. G.). Formed by the action of HCl on a hot alcoholic solution of quinovin; quinovic acid crystallises out, and the mother-liquor is neutralised by $BaCO_3$, filtered, and evaporated. Hygroscopic mass, sol. ether. Has a bitter-sweet taste. Does not ferment with yeast. Reduces Fehling's solution.

Tri-acetyl derivative $C_6H_9O(OAc)_3$. [47°]. (c. 303°). White needles (Liebermann, *B.* 17, 872).

Quinovic acid $C_{33}H_{50}O_6$ (Oudemans, *R. T. C.* 2, 160); $C_{24}H_{38}O_4$ (Hlasiwetz a. Gilm, *A.* 111, 182); $C_{32}H_{48}O_6$ (Liebermann). $[\alpha]_D = +86°$. Occurs in tormentilla root (Rembold, *A.* 145, 6). Formed from quinovin as above. White sandy powder composed of minute trimetric six-sided laminæ, insol. water, v. sol. hot alcohol, sl. sol. ether. Tasteless. Ppd. from alkaline solutions by acids in a gelatinous form, gradually becoming pulverulent. Dextrorotatory. H_2SO_4 gives off CO and forms novic acid, quinochromin $C_{30}H_{46}O_2$ (crystallising in needles), quinovene $C_{32}H_{42}$ (?), and apoquinovic acid $C_{16}H_{26}O_4$ (crystallising in needles; whence $C_{16}H_{25}NaO_4 3\frac{1}{2}aq$).

Salts.—$K_2C_{24}H_{36}O_4 1\frac{1}{2}aq$: bulky pp. — $CuA''Cu_3(OH)_6 5aq$: light-blue pp. — Ag_2A'': bulky pp.

Ethyl ether $C_{32}H_{46}Et_2O_6$. [127°–130°]. Crystals, v. sol. alcohol and ether.

Pyroquinovic acid $C_{31}H_{48}O_4$. (above 360°). Formed by heating quinovic acid (Liebermann a. Giesel, *B.* 16, 936). Needles, insol. water, v. sol. alcohol and ether. Its alkaline solution is lævorotatory. On distillation, the distillate solidifies to a clear glassy mass, easily soluble in ether, and resembling gum copal in its proper-

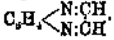
ties. When this substance is heated with HI and P it yields a terpene (quinoterpene) which probably has the formula $C_{30}H_{48}$. This terpene is also formed by direct reduction of pyroquinovic acid with HI and P (Liebermann, *B.* 17, 869).

Salts.—KA' (dried at 110°).—BaA'$_2$.

Quinoterpene $C_{30}H_{48}$. (above 360°). Formed as above. Dextrorotatory.

Oxy-quinoterpene $C_{20}H_{18}O_2$ or $C_{20}H_{34}O$. *Cholestol.* [139°]. (above 360°). Accompanies quinovin in false cinchona bark (Liebermann, *B.* 17, 871; 18, 1803; Hesse, *A.* 234, 377). Needles (from alcohol). Reduced by HI and P to quinoterpene. Yields an acetyl derivative [126°] and a benzoyl derivative [144°].

QUINOXALINE $C_8H_6N_2$ *i.e.*



$C_6H_4\left\langle\begin{matrix}N:CH\\N:CH\end{matrix}\right.$.

[27°]. (222° uncor.). Formed by the action of *o*-phenylene-diamine on glyoxal in aqueous solution (Hinsberg, *B.* 17, 320; *A.* 237, 334). White crystals, smelling like quinoline and piperidine, miscible with cold water, alcohol, ether, and benzene. Partially separated from aqueous solution by warming or by adding KOHAq. Its aqueous solution gives white pps. with $HgCl_2$ and $AgNO_3$. Yields a sparingly soluble oxalate. Little attacked by oxidising agents. Sodium reduces it, in alcoholic solution, to phenylene-ethylene-diamine (Merz a. Ris, *B.* 20, 1190).—B'HCl: needles, v. sol. water. Decomposes at 184°.—$B'H_2SO_4$. [187°]. Silvery plates, v. sol. water.—$B'_2H_2PtCl_6$ (dried at 100°). Needles.

References.—AMIDO- and OXY-QUINOXALINE.

R

RACEMIC ACID *v.* Tartaric acid.

RACEMIC CAMPHOR *v.* Camphor.

RADICLE. Lavoisier and his followers regarded an acid as a substance formed by the combination of much oxygen with another body; the body with which the oxygen was combined was called by de Morveau the radicle of the acid, and the name was used in this sense by Lavoisier. 'Il faut donc distinguer dans tout acide la base acidifiable, à laquelle M. de Morveau a donné le nom de radical, et le principe acidifiant, c'est-à-dire, l'oxigène' (*Traité élémentaire de Chimie* [1789] 1, 69). That the radicle of an acid might be either a simple or a compound substance is evident from de Morveau's use of the term; in speaking of the nomenclature of acids of unknown composition, he says: 'Nous nous sommes contentés de désigner l'être simple qui y modifie l'oxigène par l'expression de *base acidifiable*, ou, pour abréger, de *radicle*, de tel acide' (*Mémoire sur le Développement des Principes de la Nomenclature Méthodique* [1787]). Lavoisier, in 1789, extended the meaning of the term radicle when he said (*Traité*, 1, 209) that most of the oxidisable and acidifiable radicles of mineral compounds were simple bodies, whereas the radicles of compounds of vegetable and animal origin were generally composed of at least two simple bodies. The notion of radicles was here, and elsewhere, extended by Lavoisier to mean the bases or foundations whereon more complicated bodies were built up, generally by the addition of oxygen.

As organic chemistry advanced, and many compounds were obtained from animal and vegetable sources, attempts were naturally made to find some reason for the existence of so vast a number of compounds all composed of but three or four elements. Lavoisier's assertion that the radicles of organic compounds are themselves composed of two or more elements, was revived, adopted, and developed. Berzelius, Liebig, Dumas, and other earlier workers in organic chemistry were struck by the enormous number of compounds produced by the union of the four elements carbon, hydrogen, oxygen, and nitrogen. They said the true elements of organic chemistry are the radicles cyanogen, amidogen, benzoyl, ethyl, &c., &c. Dumas (*C. R.* 5, 300) said: 'In mineral chemistry the radicles are simple, in organic chemistry they are compound; therein consists the whole difference. The laws whereby the compounds are formed and their reactions are regulated are the same in both.' Liebig said: 'Organic chemistry is the chemistry of compound radicles.' In 1832 Liebig and Wöhler made apparent the meaning and wide applicability of the dictum that 'organic chemistry is the chemistry of compound radicles' by their researches into the constitution of the compounds obtained from oil of bitter almonds. By regarding these bodies as compounds of the radicle benzoyl, C_7H_5O, they became comparable with the compounds of the radicles potassium and other metals. From this time the conception of the radicle was firmly established.

The elements are the simple radicles, on which, and by the combinations of which, compounds are built up. The reactions of a series of compounds often show such similarities that we are obliged to conclude that the compositions of these compounds are also similar; in many cases this similarity of composition can be made apparent only by supposing that a certain group, or collocation, of elements enters into the composition of all the compounds. Such a group of elements, playing the part of a simple body throughout a series of reactions, but nevertheless separable into two or more elements, is called a compound radicle.

For an example of the working out of the conception of the radicle *v.* Ammonium compounds, vol. i. pp. 200-201.

M. M. P. M.

RADI OIL. The product of the distillation of the wood of a juniper. Contains a sesquiterpene $C_{15}H_{24}$, whose hydrochloride $C_{15}H_{24}2HCl$ melts at 118° (Wallach, *A.* 238, 82).

RAFFINOSE $C_{18}H_{32}O_{16}5aq$ (Morris a. Brown, *C. J.* 53, 619; De Vries, *R. T. C.* 8, 326; *C. R.*

106, 751; Tollens a. Mayer, *B.* 21, 1569). *Melitose. Gossypose. Melitriose.* Mol. w. 528 to 644 (by Raoult's method) (cal. 594); 596 (by rate of osmosis in leaves of *Tradescantia*). [c. 87°]. S. 17 at 16° (R.); 14 at 20° (Loiseau). S. (80 p.c. alcohol) 1·4 at 70°. $[\alpha]_D = 104{\cdot}6$ (M. a. B.). $[\alpha]_j = 116{\cdot}6$. H.C. 2,019,700 (Stohmann, *J. pr.* [2] 45, 320; *cf.* Berthelot a. Matignon, *C. R.* 111, 13). Discovered by Johnston (*C. S. Mem.* 1, 159) in a manna, which drops from various kinds of eucalyptus in Tasmania. Further examined by Berthelot (*C. R.* 41, 392) and Rischbiet a. Tollens (*B.* 18, 2611). Occurs also in cotton-seed (Ritthausen, *J. pr.* [2] 29, 351; Böhm, *J. pr.* [2] 30, 37), in beet-root molasses (Loiseau, *Bl.* [2] 26, 365; Tollens, *B.* 18, 26; *A.* 232, 201; Lipmann, *B.* 18, 3087; Lindet, *C. R.* 110, 795; *Bl.* [3] 3, 682).

Preparation.—Cotton-seed cake is extracted with spirit (S.G. ·848). The extract is boiled down to a small bulk, and then shaken with ether (to remove colouring matters). After a time lumps of sugar separate; these are dissolved in 80 p.c. alcohol at 70°, boiled with animal charcoal, and allowed to stand. In a week glittering needles, arranged in hemispherical masses, separate (H. Ritthausen, *J. pr.* [2] 29, 351).

Properties.—Groups of needles, v. e. sol. hot water, v. sl. sol. alcohol. Has a slightly sweet taste. Does not reduce Fehling's solution. Not turned brown by boiling KOHAq. At 108° it gives off its water of crystallisation without melting; the anhydrous raffinose is not very hygroscopic. A second hydrate (containing 6aq) may be got as lamellæ by crystallisation from dilute alcohol (Berthelot, *C. R.* 109, 548; *Bl.* [3] 2, 656). Readily ferments, giving with good yeast approximately as much alcohol as cane-sugar, while with feeble yeast only one-third of that quantity is formed. Raffinose can be assimilated by young plants, being converted into starch (Brown a. Morris, *C. J.* 57, 486).

Reactions.—1. Boiling dilute H_2SO_4 splits it up into lævulose and 'melibiose' $C_{12}H_{22}O_{11}$, which yields with phenyl-hydrazine the osazone $C_{24}H_{32}N_4O_9$. The mixture of lævulose and melibiose shows $[\alpha]_D = 50°$. On further boiling with dilute H_2SO_4 the melibiose is hydrolysed, the product consisting of galactose (1 mol.), lævulose (1 mol.), and dextrose (1 mol.) (Scheibler a. Mittelmeier, *B.* 22, 1678, 3118; Tollens, *A.* 238, 308; 249, 227). Melibiose is identical with eucalyn, and may be reduced by sodium-amalgam to melibiotite $C_{12}H_{24}O_{11}$, a syrup which does not reduce Fehling's solution, but yields galactose on boiling with dilute acids. Invertin also splits up raffinose first into lævulose (which may be fermented by yeast) and melibiose, and then this melibiose may be split up at 36° by a conc. solution of invertin into dextrose and galactose. The *Pneumococcus* of Friedländer sets up fermentation in suitable solutions of raffinose (Percy Frankland, *C. J.* 59, 270).—2. NaOEt gives a compound containing 6 to 7 p.c. sodium.—3. Boiling HNO_3 (S.G. 1·15) gives 23 p.c. of mucic acid. Saccharic acid is also formed.

Salts (Beythien a. Tollens, *A.* 255, 195).—$NaC_{18}H_{31}O_{16}$. — $Na_2C_{18}H_{30}O_{16}$ aq. Crystals. — $C_{18}H_{32}O_{16}(SrO)_2$aq. Sl. sol. water.—$C_{18}H_{32}O_{16}SrO$.—$C_{18}H_{32}O_{16}BaO$.—$C_{18}H_{32}O_{16}2BaO$. Crystals.—$C_{18}H_{32}O_{16}(CaO)_3$ 2aq.—$C_{18}H_{32}O_{16}3PbO$.

Estimation.—In a mixture of cane-sugar and raffinose, the amount of raffinose may be determined by observing the change of rotatory power after hydrolysis (Creydt, *B.* 19, 3115; Gunning, *Fr.* 28, 45). The raffinose may also be ppd. by lead acetate from a solution in methyl alcohol, and the effect on the polarising action of the liquid observed (Lotman, *Chem. Zeit.* 12, 391; Gunning).

RANGIFORMIC ACID $C_{11}H_{18}O_3$. [106°]. Occurs, together with atranoric acid, in the lichen *Cladonia rangiformis* (Paterno, *G.* 12, 259). Plates (from benzene), sol. ether. Its ammoniacal solution gives a flocculent pp. of AgA′ on adding $AgNO_3$.

RAPIC ACID $C_{18}H_{34}O_3$. Occurs as glyceride, together with the glycerides of erucic and behenic acids, in rape-seed oil (Reimer a. Will, *B.* 20, 2387). Oil. Yields stearic acid on fusion with potash. The zinc salt melts at 78°. The Na salt is gelatinous, v. sol. water, sl. sol. alcohol.

REDUCINE $C_{12}H_{26}N_6O_9$ or $C_6H_{11}N_3O_4$. An alkaloid occurring, as well as para-reducine $C_6H_9N_3O$, according to Thudichum (*C. R.* 106, 1803) in urine. It reduces ferric, cupric, mercuric, and silver salts, and forms an insoluble barium compound.

REDUCTION. This term is used as synonymous with deoxidation in its widest sense. *v.* Deoxidation, vol. ii. p. 377; and *cf.* Oxidation, vol. iii. p. 657.

REGIANIN *v.* Juglone.

RENNET *v.* Milk and Proteïds.

RESACETIC ACID *v.* vol. i. p. 18.

RESACETOPHENONE *v.* Di-oxy-acetophenone.

RESINS. Amorphous substances, occurring in all parts of plants, but especially in the bark (Wiesner, *Sitz. W.* 52 [2] 118). Frequently associated with essential oils. Resins are also formed from various oils by atmospheric oxidation or by the action of alcoholic potash. Boiling aqueous potash resinifies aldehydes. P_2O_5 converts various aldehydes (*e.g.* benzoic aldehyde) into resins. These resins are solid, translucent, with conchoidal fracture, insol. water, wholly or partially sol. alcohol and aqueous alkalis. The resins, therefore, contain acids. The resins soften when heated, but are decomposed by distillation. By potash-fusion protocatechuic acid is obtained from guaiacum, benzoïn, dragon's blood, asafœtida, esparto resin, myrrh, acaroid resin, and opopanax. By potash-fusion *p*-oxy-benzoic acid is got from benzoïn, dragon's blood, aloes, and acaroid resin; phloroglucin from dragon's blood, esparto resin, and gamboge; and resorcin from galbanum, asafœtida, gum ammoniac, sagapenum, and acaroid resin (Hlasiwetz a. Barth, *A.* 134, 265; 138, 61; 139, 83). Dammar, sandarac, mastic, and incense-resin are not attacked by fused potash. Resins containing gum or mucilage, soluble in water, are called gum-resins. Resins mixed with essential oils are termed balsams. The following resins are completely soluble in alcohol of 95 p.c.: benzoïn, caranna, resins and balsams from conifers (colophony), dragon's blood, guaiacum, mani-resin, mastic from Alexandria and from Bombay, black balsam of Peru, podocarpus resin, sandarac, balsam of Tolu, xanthorrhœa resin. The following resins are only partially dissolved by alcohol of 95 p.c.: ammoniac, asafœtida, bdellium, Canada balsam, ceradia resin, copaiba balsam, copal, dammar, elemi, euphorbium, euryops resin, galbanum, gamboge, liquidambar, common mastic, Mecca balsam, myrrh, olibanum, opopanax, white balsam of Peru, sagapenum, sonora-lac, and liquid storax (Hirschsohn, *Ar. Ph.* [3] 10, 481; 11, 54, 152, 247, 312, 434). Ether dissolves completely: caranna, Canada balsam, conifer resins, copaiba balsam, dragon's blood, elemi, guaiac-resin, mani-resin, mastic, podocarpus resin, and sandarac. Most other resins are partially soluble in ether. $FeCl_3$ gives in alcoholic solution a blue colour with guaiacum and caranna, a dark-green colour with benzoïn and some sorts of asafœtida, and a black colour with gamboge, balsam of Peru, opopanax, storax, sagapenum, shellac, and xanthorrhœa resin. $FeCl_3$ gives in an alcoholic solution of Canada balsam and of some sorts of dammar, a pp. which disappears on heating, and with copal and sonora-lac a pp. which does not disappear on heating. Alcohol containing HCl is coloured brick-red by white balsam of Peru and ceradia-resin; red to violet by common myrrh and euryops-resin; blue to violet by some sorts of elemi; yellowish-brown to green by guaiac-resin; yellow, changing through brown to cherry-red, by benzoïn and balsam of Tolu; crimson by xanthorrhœa resin; greenish, changing to dingy violet, by asafœtida; yellow by gamboge and caranna; light rose-coloured by podocarpus resin; and brown by other resins. Conc. H_2SO_4 forms a cherry-red solution with benzoïn from Siam and with balsam of Tolu; a yellow solution with gamboge; a solution with yellowish-brown fluorescence with asafœtida; and brown with other resins. A drop of H_2SO_4 added to a solution of pine-wood resin in HOAc gives a red or violet colour as the liquids mix (Morawski, *C. C.* 1888, 1630). Fossil resins (*e.g.* amber) are often found in beds of coal and lignite, being clearly derived from plants. Schmidt a. Erban (*M.* 7, 655; *cf.* Kremel, *Fr.* 26, 262) have determined, for a great variety of commercial resins, the quantity of alkali necessary to neutralise an alcoholic solution, and the amount required for saponification, and also the amount of iodine the resins can take up. They also base a method of separation upon the relative solubilities of resins. A classification of red resins according to their solubility in chloroform, benzene, and CS_2 is given by Dobbie a. Henderson (*Tr. E.* 30, 624). Colophony softens under boiling water, while powdered shellac, mastic, elemi, and dammar agglomerate, and sandarac, copal, and amber remain unchanged (Kliebhau, *C. C.* 1888, 87). The products of distillation of colophony have been examined by many chemists (Fremy, *A. Ch.* [2] 59, 13; *A.* 15, 284; Pelletier a. Walter, *A. Ch.* [2] 67, 267; Thénard, Robiquet, a. Dumas, *C. R.* 1838, i. 460; Schiel, *A.* 115, 96; Couerbe, *J. pr.* 18, 165; Curie, *C. N.* 30, 189; Kelbe, *B.* 13, 1157; *B.* 14, 1240; *A.* 210, 1; *B.* 15, 308; Renard, *C. R.* 91, 416; *B.* 13, 2000; *Bl.* [2] 36, 215; Tilden, *B.* 13, 1604; Anderson, *C. N.* 20, 76; Mills, 'Destructive Distillation,' 31; Tichborne, *Ph.* [3] i. 302; Morris, *C. J.* 41, 167) by whom the following substances have been described as constituents: water, retinaphtha C_7H_8 (108°) (P. a. W.), retinyl C_9H_{12} (150°) (P. a. W.), retinol C_8H_8 [150°] (236°–246°) (P. a. W.), retisterene [67°] (325°) (T. R. a. D.), carbonic acid, carbonic oxide, ethylene (S.), propylene (S.), heptane (97°) (T.), octane (S.), a valerylene (50°) (C.), cymenes (170°–178°) (K.), heptinene C_7H_{12} (104°) (R.), colophenone $C_{11}H_{18}O_2$ (S.) (97°), a terpene (160°) (S.), abietic acid (K.), isobutyric and methyl-propyl-acetic acids (K.), hydrocarbons $C_{11}H_{18}$ (190°–200°) (K.), and iso-butyric aldehyde (T.). Renard (*A. Ch.* [6] 1, 223) found among the products of distillation of colophony (rosin oil), pentane, amylene, hexane, hexylene, toluene, toluene tetrahydride, toluene hexahydride, xylene, xylene tetrahydride, xylene hexahydride, *m*-ethyl-propyl-benzene, terpenes, isobutyric aldehyde and acid, and valeric aldehyde and acid. Lwoff (*B.* 20, 1017) found, in resin oil, valeric, heptoic, ennoic, and hendecoic acids. Resin oil is coloured violet by H_2SO_4 of S.G. 1·53 (Holde, *C. C.* 1888, 952).

Resin of *Pinus Laricio* (Poir). [c. 100°]. V. sol. alcohol, ether, and oil of turpentine; insol. ligroïn. Contains much methoxyl (Bamberger, *M.* 12, 441). Turned red by air, and finally brown. It contains a little free caffeïc acid $C_6H_3(OH)_2CH{:}CH.CO_2H$ [195°] and ferulic acid [4:3:1] $C_6H_3(OH)(OMe).CH{:}CH.CO_2H$ [169°]. 4 p.c. of caffeïc and 1 p.c. of ferulic acid may be extracted by boiling with water. The resin also contains some vanillin $C_6H_3(OH)(OMe).CHO$. The resin yields pyrocatechin and protocatechuic acid on fusion with potash.

Resin of *Picea vulgaris* (Link). [c. 100°]. Contains methoxyl (Bamberger, *M.* 12, 456). Contains *p*-coumaric acid and vanillin. Potash-fusion gives protocatechuic and *p*-oxybenzoic acids.

Resin of *Pinus sylvestris* contains an acid $C_{40}H_{58}O_5$ [143°], insol. water, v. sol. alcohol, ether, and HOAc. $[\alpha]_j = -74°$. It yields the salts $C_{20}H_{29}AgO_3$, $(C_{20}H_{29}O_3)_2Ba\,2aq$, $(C_{20}H_{29}O_3)_2Ca$, and $(C_{20}H_{29}O_3)_2Cu$, and oily $C_{20}H_{29}EtO_3$, which on distillation forms oily $C_{20}H_{27}EtO_2$. Alcoholic HCl converts the acid into an isomeride [160°], $[\alpha]_j = -93°$ (Shkateloff, *J. R.* 20, 477).

Resin from *Ficus rubiginosa* contains 'sycoceryl acetate' $C_{34}H_{56}O_2$ [121°] which on saponification gives acetic acid and sycoceryl alcohol $C_{32}H_{54}O$ [114°] (De la Rue a. Müller, *Tr.* 1860, 43; Rennie a. Goyder, *C. J.* 61, 916).

References.—Abietic acid, Aldehyde resin, Amber, Arbol-a-brea resin, Asafœtida, Asphalt, Benzoïn (gum), Canada balsam, Colophony, Copaiba balsam, Copal, Dammara resin, Dragon's blood, Elemi, Euphorbium, Galbanum, Guaiacum, Gum ammoniac, Gutta percha, Jalap, Lac, Larch fungus, Larrea resin, Masopin, Mastic, Maynas resin, Mecca balsam, Myrrh, Olibanum, Opopanax, Palisander resin, Podocarpic acid, Podophyllin, Sagapenum, Sandarac, Scammony, and Storax.

RESORCIN $C_6H_6O_2$ *i.e.* $C_6H_4(OH)_2$ [1:3]. [112°]. (267°) (Kopp). S. 86·4 at 0°; 147·3 at 12·5°; 228·6 at 30° (Calderon, *Bl.* [2] 29, 234). V.D. 3·85 (calc. 3·81) (Troost, *C. R.* 89, 351). H.C.v. 683,100. H.C.p. 683,400. H.F. 87,600 (Stohmann, *J. pr.* [2] 45, 335). S.V. 108 (Lossen, *A.* 254, 59). S.V.S. 93·05.

Formation.—1. By potash-fusion from galbanum (Hlasiwetz a. Barth, *A.* 130, 354), *m*-iodo-phenol (Körner, *Bl.* [2] 7, 261), phenol-*p*-sulphonic acid (Glutz, *Bl.* [2] 8, 361), *p*-chloro-benzene sulphonic acid (Oppenheim a. Vogt, *A. Suppl.* 6, 376), from umbelliferone (Hlasiwetz a. Grabowski, *A.* 139, 99), from asafœtida, from gum ammoniac, from sagapenum, from acaroid resin (Hlasiwetz, *A.* 130, 354; 138, 63; 139, 78), from *o*-, *m*-, and *p*- bromo-phenol (Fittig a. Mager, *B.* 8, 362), from *p*-chloro-phenol (Faust, *B.* 6, 1022), from *p*-iodo-phenol above 165° (Nölting a. Wrzesinsky, *B.* 8, 820), from phenol (Barth a. Schreder, *B.* 12, 420), and from benzene *m*- or *p*- disulphonic acid (Barth a. Senhofer, *B.* 8, 1483; Fahlberg, *Am.* 2, 195).—2. By dry distillation of brazilin (E. Kopp, *B.* 6, 446).—3. By the action of nitrous acid on *m*-amido-phenol (Bantlin, *B.* **11**, 2101).

Preparation.—By fusing benzene *m*-disulphonic acid with NaOH (Mühlhäuser, *D. P. J.* 263, 154).

Properties.—Colourless trimetric tables (from water, alcohol, or ether); $a:b:c = \cdot 912:1:1\cdot 059$ (Calderon, *C. R.* 84, 779) or needles (from benzene). V. sol. water, alcohol, and ether, insol. chloroform and CS_2. Acquires a reddish tint on exposure to air. Neutral to litmus. Has a sweet taste. $FeCl_3$ colours its aqueous solution dark violet. Its ammoniacal solution, exposed to the air, becomes rose-red and finally brown. The ammoniacal solution leaves on evaporation a dark-blue mass, which forms a blue solution, turned red by acids. Bleaching-powder gives a transient violet colour. A drop of a solution of NaOCl gives a violet colour, quickly changing to yellow, and on heating to dark-red or brown (Stark, *Ph.* [3] 21, 848; Boddé, *Ar. Ph.* [3] 27, 656). Resorcin reduces boiling ammoniacal $AgNO_3$ and boiling Fehling's solution. On heating resorcin with a few drops of nitro-benzene and conc. H_2SO_4 a blue mass is got which, when poured into water and made alkaline, gives a solution with vermilion fluorescence. If resorcin is added to conc. H_2SO_4 and a little $NaNO_2$, and the mixture is heated to 100°, a product is got which, when mixed with water and rendered alkaline by NH_3, imparts to fusel oil a crimson colour with vermilion fluorescence (Bindschedler, *M.* 5, 168). Resorcin fused with phthalic anhydride forms fluoresceïn, which dissolves in aqueous alkalis with strong green fluorescence (Baeyer, *A.* 183, 8). Resorcin heated with alcohol, beet-sugar, and HClAq gives a reddish-violet colour (Ihl, *Chem. Zeit.* 13, 264). A solution of resorcin (1 pt.) in absolute alcohol (2 pts.), mixed with an aldehyde and a few drops of conc. HClAq, gives, after standing for some hours and then pouring into water, a resinous or crystalline pp. (Michael a. Ryder, *Am.* 9, 134). A mixture of resorcin and furfuraldehyde touched with a drop of HCl gives an indigo-blue substance, which dissolves with green colour in water, and is ppd. by HCl in blue flakes (Baeyer, *B.* 5, 25). On warming a liquid containing chloral or chloroform with resorcin and NaOH a yellowish-red colour with green fluorescence is got (Schwarz, *Fr.* 27, 668). Cupric sulphate and excess of ammonia form a deep-black liquid, which dyes wool black (Wagner, *D. P. J.* 220, 96).

Titration.—1. Bromine-water is run in until all the resorcin is converted into tribromo-resorcin, which is ppd.: $C_6H_4(OH)_2 + 3Br_2 = C_6HBr_3(OH)_2 + 3HBr$. The excess is determined by adding KI and titrating with hyposulphite (Degener, *J. pr.* [2] 20, 322).—2. Potash and potassium iodide are added to the solution, and then a neutral solution of bleaching-powder is run in. On adding HCl a pp. of tri-iodo-resorcin is formed, and the excess of iodine is titrated by hyposulphite (Degener).

Reactions.—1. *Soda-fusion* gives phloroglucin (65 p.c.), some pyrocatechin (3 p.c.), and tetra-oxy-diphenyl (1½ p.c.) (Barth a. Schreder, *B.* 12, 503).—2. Exhaustive *chlorination* in presence of I forms CCl_4 and CO_2 (Ruoff, *B.* 9, 1483).—3. ICl forms tri-iodo-resorcin (Michael a. Norton, *B.* 9, 1752).—4. An alkaline solution gives with KI a violet-red pp. of $C_6H_2I_3KO_2$ (Messinger a. Vortmann, *B.* 22, 2320).—5. A solution of resorcin (10 g.) in water (100 c.c.) gives a purple colour with ·5 c.c. of very dilute solutions of nitrates, to which a drop of 15 p.c. HClAq and 2 c.c. of H_2SO_4 have been added (Lindo, *C. N.* 58, 176).—6. Resorcin (15 g.) dissolved in water (70 c.c.) and warmed with a mixture of (60 c.c. of) HBrAq (S.G. 1·47) and (20 c.c. of) HNO_3 (S.G. 1·39) gives $C_{48}H_{35}BrN_2O_{13}$ as a lustrous violet mass, which forms a red solution in alcohol, changed by alkalis to a blue liquid (Brunner a. Krämer, *B.* 17, 1873; 21, 2481). It yields $C_{48}H_{29}Ac_6BrN_2O_{13}$ as an orange-red amorphous powder [120°], v. sol. hot alcohol. 7. Resorcin (15 g.) heated with water (60 g.), HNO_3 (20 c.c. of S.G. 1·39), and HCl (60 c.c. of S.G. 1·2) for half an hour on a water-bath forms a violet mass $C_{66}H_{48}ClN_3O_{18}$, insol. chloroform, sol. alcohol and ether. It yields yellowish-brown flocculent $C_{66}H_{40}Ac_8ClN_3O_{18}$ (Brunner, *B.* 21, 2479).—8. A blue colouring matter (lacmoid) is got by heating resorcin (55 pts.) with $NaNO_2$ (18 pts.) at 130°, dissolving in NH_3Aq and reppg. by HCl (Benedikt a. Julius, *M.* 5, 534).—9. *Bromine* in CS_2 forms $C_6H_2Br_2(OH)_2$ [111°] (Zehenter, *M.* 8, 293).—10. With Al_2Cl_6 it gives the compound $(C_6H_4O_2)Al_2Cl_4$, which is v. sol. hot CS_2, less sol. cold CS_2; decomposed at once by water into resorcin, Al_2O_3, and HCl (Claus a. Merklin, *B.* 18, 2934).—11. Dry *ammonia* passed into a solution of resorcin in dry ether forms $(C_6H_6O_2)NH_3$, which separates as a liquid, solidifying as colourless deliquescent crystals, turning green and afterwards blue in the air (Malin, *A.* 138, 80).—12. H_2O_2 and NH_3Aq give, after acidification, a brown pp. ('lacmoid') which forms an indigo blue solution in alkalis (Zulkowsky a. Peters, *M.* 11, 243; *cf.* Wurster, *B.* 20, 2934).—13. *Ammonium carbonate* solution at 125° forms (4,2,1)- and (6,2,1)- di-oxy-benzoic acid (Senhofer a. Brunner, *Sitz. W.* [2] 80, 504).—14. *Ammoniacal* $CaCl_2$ at 300° forms a brownish-red colouring matter [72°], insol. water and alkalis, sol. alcohol (Seyewitz, *C. R.* 109, 946).—15. *Sulphur* and NaOHAq form, on boiling, $C_6H_4O_2S_2$, a yellow powder, sol. alkalis, insol. water, and decomposing before fusion (Lange, *B.* 21, 263).—16. $K_2S_2O_7$ acting on potassium resorcin forms $C_6H_4(OH)(O.SO_3K)$ and $C_6H_4(O.SO_3K)_2$. The latter salt is converted, by heating in the dry state at 160°, into a salt of resorcin disulphonic acid (Baumann, *B.* 11, 1911).—17. $COCl_2$ forms

$C_6H_4{:}CO_2$, a red amorphous substance, insol. water, v. sol. alcohol (Birnbaum, *B.* 14, 1753).—18. An alcoholic solution of *potassium xanthate* forms $C_6H_3(OH)_2.CS_2H$, crystallising in yellow needles [131°], sol. hot water (Lippmann a. Fleissner, *M.* 9, 296).—19. *Acetone dicarboxylic acid* and conc. H_2SO_4 form (β)-umbelliferone-acetic acid $\begin{matrix}C(OH){:}CH.C.O.CO\text{———}\\ CH{=}CH.C.C(CH_2.CO_2H)\end{matrix}{>}CH$ [202], crystallising in needles (containing aq), insol. ether (Michael, *J. pr.* [2] 37, 469).—20. *Benzene sulphonic chloride* added to a solution kept slightly alkaline forms $C_6H_4(O.SO_2C_6H_5)_2$, crystallising from hot alcohol in needles [70°] (Georgesen, *B.* 24, 417).—21. *Hydrogen ammonium o-sulphobenzoic acid* forms $C_{13}H_{13}NSO_6$ 2aq as pale-yellow crystals, v. sol. water and alcohol. Its alkaline solutions are slightly fluorescent. Conc. HClAq at 220° reconverts it into the parent substances (Fahlberg a. Barge, *B.* 22, 754). Resorcin (4 mols.) heated with o-sulphobenzoic acid (1 mol.) forms $C_{31}H_{20}NSO_8$ 4aq.—22. *Chloro-acetic acid* forms $C_6H_4(O.CH_2.CO_2H)_2$ [194°], which yields a di-bromo- derivative (Gabriel, *B.* 12, 1640).—23. $ClCO_2Et$ acting on $C_6H_4(OK)_2$ forms $C_6H_4(O.CO_2Et)_2$, a thick oil (300°) (M. Wallach, *A.* 226, 84).—24. Dry *oxalic acid* (1 mol.) in a sealed tube at 200° forms 'resorcin-oxaleïn' $C_{20}H_{14}O_7$, a hygroscopic red powder, sol. alcohol and ether (Claus, *B.* 10, 1305; 14, 2563). At 100° it becomes $C_{20}H_{12}O_6$, which is less sol. alcohol. Dilute alkaline solutions are yellow, with dark-green fluorescence. Bromine gives $C_{20}H_7Br_5O_6$. HNO_3 forms $C_{20}H_8(NO_2)_4O_6$. H_2SO_4 yields $C_{20}H_9(SO_3H)_3O_6$. Ac_2O forms red $C_{20}H_{10}Ac_2O_6$ and colourless $C_{20}H_9Ac_3O_6$.—25. Crystallised oxalic acid (1 mol.) heated with resorcin (2 mols.) at 120° yields two compounds $C_{14}H_8O_5$ one of which fluoresces green in alkaline solutions (Gukassianz, *B.* 11, 1184). 26. HOAc and $ZnCl_2$ at 145° form di-oxy-acetophenone. Resorcin (100 g.) boiled with HOAc (200 g.) and $ZnCl_2$ (300 g.) for two hours forms 'acetfluoresceïn' $C_{21}H_{18}O_5$ and 'resaceteïn' $C_{16}H_{12}O_4$. Resaceteïn crystallises by spontaneous evaporation of its ammoniacal solution in red needles. Its solution in KOHAq is red, but soon turns brown. It yields the salts B'HCl 2aq and $B'_2H_2SO_4$ (dried at 110°) and a triacetyl derivative $C_{16}H_9Ac_3O_4$ [229°]. Acetfluoresceïn forms minute brownish-red crystals. Its dilute alkaline solutions exhibit green fluorescence (Nencki a. Sieber, *J. pr.* [2] 23, 540; Rasiński, *J. pr.* [2] 26, 58).—27. Resorcin (20 pts.) heated with *formic acid* (10 pts.) and $ZnCl_2$ (20 pts.) for 30 minutes at 140° forms 'resaurin' $C_{19}H_{14}O_6$ or $(C_6H_3(OH)_2)_2C{<}\begin{matrix}O\\ C_6H_3(OH)\end{matrix}$. Resaurin is a brick-red hygroscopic powder, forming a red solution in alkalis, sol. alcohol, insol. ether and acids (Nencki a. Schmid, *J. pr.* [2] 23, 547).—28. On heating with $ZnCl_2$ and *acetoacetic ether* or citric acid 'resocyanin' is formed (Wittenberg, *J. pr.* [2] 24, 125; 26, 74; Schmid, *J. pr.* [2] 25, 81). Resocyanin can be prepared by heating dry *citric acid* (60 g.) with resorcin (60 g.) and H_2SO_4 (150 g.) for an hour at 180°. Resocyanin $C_{21}H_{18}O_6$ [185°] is insol. cold water, sl. sol. ether, v. sol. alcohol. Its alkaline solutions are colourless with blue fluorescence. Its solutions are not coloured by $FeCl_3$. It yields $C_{21}H_{12}Br_6O_6$ [250°] and $C_{21}H_{16}Ac_2O_6$ [150°]. Resocyanin yields resorcin when fused with potash. It may be reduced to a hydride $C_{21}H_{20}O_6$ [259°] which yields $C_{21}H_{18}Ac_2O_6$ [222°]. NaOMe and MeI give $C_{21}H_{16}Me_2O_6$ [159°].—29. A cold alcoholic solution of *sodium malonic ether* forms $C_{11}H_8O_4$ [191°], which is v. sol. hot alcohol, insol. cold water. Its alkaline solutions are fluorescent. It splits up when heated above 191° into CO_2 and methyl-umbelliferone (Michael, *Am.* 5, 434; *J. pr.* [2] 35, 455; 37, 469).—30. Resorcin (7 pts.) heated with *phthalic anhydride* at 200° forms FLUORESCEÏN (vol. ii. p. 557).—31. Resorcin (2 mols.) heated with phthalimide (1 mol.) and H_2SO_4 at 100° forms $C_{20}H_{13}NSO_7$, a light-yellow powder, insol. benzene and ether, v. sol. alcohol. It forms $C_{20}H_{12}NaNSO_7$ 7aq and $C_{20}H_{11}Ac_2NSO_7$, a yellowish-green crystalline powder (Ostersetzer, *M.* 11, 425).—32. *o-Benzoyl-benzoic acid* forms, on heating, di-oxy-tri-phenyl-carbinol carboxylic anhydride (*v.* vol. iii. p. 738).—33. *Maleic anhydride* forms, on heating, maleïc-fluorescein $\begin{matrix}CH{:}CH\\ CO-O\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}{>}O$, which exhibits deep green fluorescence in alkaline solution and gives crystalline $C_{16}H_8Et_2O_5$ and $C_{16}H_8Ac_2O_5$ [157°] (Burckhardt, *B.* 18, 2864).—34. *Succinic acid* (13 g.) heated with resorcin (20 g.) and H_2SO_4 (40 g.) at 195° forms 'succinyl-fluoresceïn' $C_{16}H_{12}O_5$ or $\begin{matrix}CH_2.CH_2\\ CO\text{——}O\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}{>}O$, which is crystalline (containing 3aq) and fluoresces in alkaline solution. It yields $C_{16}H_8Br_4O_5$ (Nencki a. Sieber, *J. pr.* [2] 23, 153).—35. *Tartaric acid* (1 mol.) heated with resorcin (2 mols.) and H_2SO_4 (1 p.c.) at 165° forms resorcin-tartreïn, a dark olive-green powder, which fluoresces in alkaline solution (Fraude, *B.* 14, 2558).—36. Na_2CO_3 added to a solution of resorcin and *quinone* forms a deep-green solution changing through yellow to brownish-red on shaking with air (Wurster, *B.* 20, 2934).—37. Heated with *aniline* and $CaCl_2$ it yields *m*-oxy-di-phenylamine. With aniline and $ZnCl_2$ it yields di-phenyl-*m*-phenylene-di-amine (Calm, *B.* 16, 2786; *cf.* Merz a. Weith, *B.* 14, 2345).—38. *Aldehyde* in presence of weak acids forms $C_{14}H_{14}O_4$ or $CH_3.CH(O.C_6H_4.OH)_2$, yellow crystals, insol. water and ether, sol. alcohol. At 120° this body is converted into brown crystalline $C_{28}H_{26}O_7$. By heating the compound $C_{14}H_{11}O_4$ with zinc-dust in a current of hydrogen at 300°, resorcin is produced. Ac_2O at 140° gives $C_{14}H_{12}Ac_2O_4$ [282°] (Causse, *Bl.* [2] 47, 89; *J. Ph.* [5] 13, 354).—39. *Chloral hydrate* in aqueous solution containing $NaHSO_4$ forms silky needles of $C_{14}H_{12}O_6$, insol. water and benzene, sol. ether and alcohol. Its alkaline solutions are fluorescent. It yields a diacetyl derivative [252°] (Causse, *Bl.* [3] 3, 861). Resorcin and *glyoxylic acid* yield the same $C_{14}H_{12}O_6$. By boiling chloral hydrate (5 pts.) with resorcin (10 pts.) and water (40 pts.) there is formed $C_8H_6O_3$ crystallising from dilute alcohol in yellowish needles, and yielding $C_8H_4Ac_2O_3$ [159°] and $C_8H_4Bz_2O_3$ [165°] (Michael a. Comey, *Am.* 5, 350).—40. *Benzoic aldehyde*, alcohol, and a little HCl give $C_{26}H_{20}O_4$ *x*aq [above 330°], a colourless resin, insol. water, v. e. sol. alcohol. Its alkaline solution absorbs oxygen from the air. Ac_2O and NaOAc form $C_{26}H_{16}Ac_4O_4$. HCl

**converts it into the isomeric $C_{26}H_{20}O_4$ 4aq crystallising from alcohol in dimetric tables, reduced by sodium-amalgam to $C_{26}H_{22}O_4$ crystallising from alcohol in prisms, and converted by Ac_2O and NaOAc into $C_{26}H_{16}Ac_4O_4$ crystallising from xylene in prisms (Michael, *Am.* 5, 340).—41. $CH_3.CCl_3$ and caustic soda form $CH_3.C(O.C_6H_4.OH)_3$ [159°], v. sol. alcohol, sl. sol. hot water (Heiber, *B.* 24, 3684).—42. *Camphor* forms the compounds $C_6H_6O_2(C_{10}H_{16}O)$ [29°], $[\alpha]_D = 22·5°$, crystallising in hygroscopic rectangular plates, and $C_6H_6O_2(C_{10}H_{16}O)_2$, a syrupy liquid, S.G. $\frac{15}{15}$ 1·037; $[\alpha]_D = 25·9°$ (Léger, *C. R.* 111, 110). 43. *Phenyl-hydrazine* (2 mols.) rubbed with powdered resorcin (1 mol.) forms $C_6H_6O_2 2N_2H_3Ph$, crystallising in unstable satiny needles [76°], v. sol. benzene alcohol, and ether. It is decomposed by water and alkalis (Baeyer a. Kochendörfer, *B.* 22, 2195).—44. *Quinone* (1 mol.) added to a solution of resorcin (1 mol.) in hot benzene forms $C_{12}H_{10}O_4$ [c. 90°] crystallising in dark-red needles with green reflex, m. sol. water (Nietzki, *A.* 215, 136).—45. *Cyanic acid* passed into an ethereal solution of resorcin forms $C_8H_8N_2O_4$ [120°], sl. sol. ether, m. sol. hot water (Traube, *B.* 22, 1579).—46. *Phenyl cyanate* forms at 100° $C_6H_4(O.CO.NHPh)_2$ [164°] (Snape, *C. J.* 47, 772).—47. *Urea* (2 pts.) in a current of CO_2 at 250° forms $C_{30}H_{20}N_6O_8$ 6aq, an olive-brown amorphous powder, melting above 360°, v. sl. sol. hot HOAc, sol. alkalis (Birnbaum, *B.* 13, 1619).—48. Heated with aqueous $KHCO_3$ or ammonium carbonate it yields di-oxy-benzoic acid.—49. Resorcin (1 pt.) mixed with acetone (2 pts.) and fuming HClAq (1 pt.) forms $C_{15}H_{16}O_4$ or $CMe_2(O.C_6H_4.OH)_2$, which crystallises in small prisms [213°], insol. water and ether, sol. KOHAq and Na_2CO_3Aq. It is decomposed by heat into acetone and resorcin. It forms a crystalline hydrate $C_{15}H_{16}O_4$ aq. Ac_2O yields $C_{15}H_{14}Ac_2O_4$ [126°] while BzCl gives $C_{15}H_{14}Bz_2O_4$ [115°] (Causse, *Bl.* [3] 7, 563).—50. Resorcin (20 g.) heated with K_2CS_3 under pressure at 100° forms $C_7H_6S_2O_2$ [150°-155°], sl. sol. CS_2, converted by potash-fusion into resorcin and (4,2,1)-di-oxy-benzoic acid [205°] (Pribram a. Glücksman, *M.* 13, 626).

Mono-methyl ether $C_6H_4(OH)(OMe)$. (244°). V.D. (H = 1) 62·2 (obs.). Formed by heating resorcin (1 mol.) with KOH (1 mol.) and $KMeSO_4$ at 160° (Habermann, *B.* 10, 868). Formed also from resorcin, NaOMe, and MeI (Tiemann, *B.* 13, 2362; 14, 2019). Prepared by heating resorcin with MeOH and $KHSO_4$ for 10 hours at 180° (Wallach, *B.* 16, 151). Liquid, sol. hot water, alcohol, ether, benzene, and NaOHAq. Slightly volatile with steam. $FeCl_3$ colours its solution violet. Acetic anhydride forms $C_6H_4(OAc)(OMe)$ (255°). KOH and $K_2S_2O_7$ form $C_6H_4(OMe)(SO_4K)$, crystallising in plates, sol. water and hot alcohol.

Di-methyl ether $C_6H_4(OMe)_2$. (215°) (R. Schiff, *B.* 19, 562); (224°) (Stohmann). V.D. 68·8 (obs.). S.V. 157·13. S.G. $\frac{0}{0}$ 1·075. H.F.p. 74,034 [$C,O_2 = 94,000$; $H_2,O = 69,000$] (Stohmann, *J. pr.* [2] 35, 27). S.V. 157·1. Prepared by heating resorcin (1 pt.) with MeOH, KOH (1·5 pts.), and MeI (3 pts.) for 6 hours at 250° (Oechsner de Coninck, *Bl.* [2] 34, 149). Oil, v. sol. alcohol and ether. Volatile with steam. Not coloured by $FeCl_3$.

Methyl ethyl ether $C_6H_4(OMe)(OEt)$. (216°). Formed from $C_6H_4(OH)(OMe)$, KOH, and $KEtSO_4$ at 165°; the product being distilled with steam (Spitz, *M.* 5, 488). Liquid.

Methyl propyl ether $C_6H_4(OMe)(OPr)$. (226°). Colourless liquid.

Methyl isobutyl ether $C_6H_4(OMe)(OCH_2Pr)$. (234°). Liquid.

Methyl isoamyl ether $C_6H_4(OMe)(OC_5H_{11})$. (236°). Liquid.

Mono-ethyl ether $C_6H_4(OH)(OEt)$. Liquid. HNO_3 saturated with nitrous acid added to its ethereal solution at 0° forms $C_6H_3(NO_2)(OH)(OEt)$ and two colouring matters: $C_{24}H_{20}N_2O_8$ [230°] crystallising in red needles, insol. water, sl. sol. boiling alcohol, forming a purple solution in H_2SO_4; and $C_{11}H_{11}NO_3$ [228°] crystallising in orange-red needles, forming a bluish-violet solution in H_2SO_4 (Weselsky a. Benedikt, *M.* 1, 891).

Di-ethyl ether $C_6H_4(OEt)_2$. [12·4°]. (229°) (Pukall, *B.* 20, 1140); (235°) (Herzig a. Zeisel, *M.* 11, 300). Formed from resorcin, KOH, and EtI. Colourless prisms, volatile with steam. On adding one drop of KNO_2 solution followed by HClAq to its solution in HOAc, an intense emerald green colour is produced. Yields two di-bromo- derivatives [101°] and [77°]. Converted by dissolving in HOAc, adding $NaNO_2$, and passing in HCl into $C_6H_3(NO)(OEt)_2$ [123°] and $C_6H_3(NO)(OH)(OEt)$, whence BzCl forms yellow crystals of $C_6H_3(NO)(OEt)(OBz)$ [155°] (Kraus, *M.* 12, 374).

Hexa-chloro-di-vinyl ether $C_6H_4(OC_2Cl_3)_2$. [54°]. Formed by heating $C_6H_4(OAc)_2$ with PCl_5 at 100° (Michael, *Am.* 9, 210). Long prisms, insol. hot water.

Di-propyl ether $C_6H_4(OPr)_2$. (251°). V.D. 7·02 (obs.). Liquid, m. sol. hot water, sol. alcohol, ether, and ligroïn (Kariof, *M.* 1, 258; *B.* 13, 1677). Br forms $C_6H_3Br(OPr)_2$ [70°].

Mono-benzyl ether $C_6H_4(OH)(OC_7H_7)$. Formed from resorcin, KOH, alcohol, and benzyl bromide (Schiff a. Pollizzari, *A.* 221, 376; *G.* 13, 504).

Di-benzyl ether $C_6H_4(OC_7H_7)_2$. [76°]. Glittering tables (from alcohol).

Tetra-nitro-di-phenyl ether $C_6H_4(O.C_6H_3(NO_2)_2)_2$. [184°]. Formed from resorcin, NaOEt, and (1,2,4)-chloro-di-nitro-benzene in alcohol (Nietzki a. Schündelen, *B.* 24, 3586). Colourless plates. Converted by HNO_3 into a penta-nitro- derivative [68°], and by H_2SO_4 and HNO_3 into the hexa-nitro-di-phenyl ether [220°].

Di-acetyl derivative $C_6H_4(OAc)_2$. (273°) (Nencki, *J. pr.* [2] 23, 147); (278° i.V.) (Typke, *B.* 16, 552). Formed from resorcin and AcCl (Malin, *A.* 138, 78). Oil.

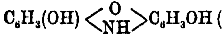
Di-benzoyl derivative $C_6H_4(OBz)_2$. [117°]. H.F. 124,598 (Stohmann, *J. pr.* [2] 36, 10). From resorcin (5 g.), benzoic acid (11 g.) and $POCl_3$ (13 g.), the latter being added slowly (Rasiński, *J. pr.* [2] 26, 64). Formed also by shaking resorcin with BzCl and NaOHAq (Hinsberg, *A.* 254, 254). Plates (from ether).

Anhydride $C_{12}H_{10}O_3$ *i.e.* $O(C_6H_4.OH)_2$. *Resorcinyl oxide. Resorcin ether.* Formed by heating resorcin with NaOH and CO_2 (Böttinger, *B.* 9, 182), with Na and CO_2 (Barth, *B.* 9, 308), with HClAq under pressure (Barth a. Weider, *B.* 10, 1464), or with H_2SO_4 (Barth, *A.* 164, 122; Kopp, *B.* 6, 447; Annaheim, *B.* 10, 976). Formed also by heating resorcin at 195° with the disulphonic acid of resorcin or of phenanthrene (Hazura a. Julius, *M.* 5, 191). Brownish-red amorphous powder, acquiring by pressure a green metallic lustre. Nearly insol. water, v. sl. sol. cold alcohol and ether. KOHAq forms a dark red solution with green fluorescence. Potash-fusion reconverts it into resorcin. Oxidised by nitric acid to isophthalic acid. Yields $C_{12}H_8Ac_2O_3$, which forms a reddish-violet solution in alkalis, and $C_{12}H_6Br_4O_3$.

Anhydride $C_{24}H_{18}O_5$. Formed, together with $C_{12}H_{10}O_3$, by heating resorcin with HClAq at 180°. Brick-red powder, v. sol. alcohol and ether. Its alkaline solution is brownish-yellow with violet-blue fluorescence. Yields $C_{24}H_{16}Ac_2O_5$ and $C_{24}H_{12}Br_6O_5$. Oxidised by nitric acid to isophthalic acid.

Resazurin $C_{12}H_9NO_4$ (B. a. K.), or $C_{12}H_7NO_4$ (Nietzki, *B.* 22, 3021; 24, 3366). *Diazoresorcin. Azoresorcin. Resazoïn.* Formed by the action of nitrous acid on an ethereal solution of resorcin (Weselsky, *B.* 4, 613; *M.* 1, 889; 5, 607). Formed also by the action of MnO_2 and H_2SO_4 on an alcoholic solution of resorcin and nitroso-resorcin. Prepared by adding fuming HNO_3 (6 c.c.) to resorcin (10 g.) dissolved in ether (500 c.c.) at −7°. Dark-red prisms with green reflex. Insol. water and ether, v. sl. sol. cold alcohol and HOAc. Its alkaline solutions are bluish-violet. Conc. H_2SO_4 forms a red solution. HCl forms a crystalline hydrochloride. Yields $Ba(C_{12}H_6NO_4)_2$ crystallising in brown needles, and a sodium salt, which forms greenish needles, v. sol. water, sl. sol. NaOHAq, fluorescing brick red in dilute alcoholic solution. Resazurin forms $C_{12}H_3Br_4NO_4$ on bromination.

Reactions.—1. AcCl in a sealed tube at 100° forms $C_{12}H_9Cl_2NO_3$ (?) crystallising from HOAc in golden plates and amorphous $C_{26}H_{21}Cl_3N_2O_8$ (?) (Weselsky, *A.* 162, 288; Brunner a. Krämer, *B.* 17, 1854).—2. Conc. H_2SO_4 at 210° and conc. HClAq at 100° form resorufin.—3. On heating with *tin* and conc. HClAq an emerald-green solution is got, from which on cooling 'hydrodiazoresorufin hydrochloride' separates as colourless leaflets or needles, which, when exposed to air, acquire a coppery lustre, and when heated in a current of air produce resorufin. Hydrodiazo-resorufin is dioxyphenoxazine, the formula being



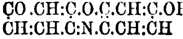
$$C_6H_3(OH)\left\langle\begin{matrix}O\\NH\end{matrix}\right\rangle C_8H_3OH$$

(Nietzki, *B.* 22, 3020). 4. Hot conc. HNO_3 forms 'tetrazoresorcin nitrate' $C_{18}H_6N_7O_{15}$ (?), crystallising in lustrous garnet-red needles, sol. water, alcohol, and ether with indigo-blue colour. According to Brunner a. Krämer (*B.* 17, 1864; 18, 587) these crystals are tri-nitro-resazurin $C_{12}H_6(NO_2)_3NO_4$. By heating them with conc. HNO_3 Weselsky obtained 'tetrazoresorufin nitrate' $C_{36}H_6N_{14}O_{27}$(?), crystallising from NHO_3 in dark-red needles, and from wet ether in purple needles (containing 11 aq). Tin and HClAq acting upon either of these bodies form a red body, probably tri-amido-resorufin hydrochloride, and a colourless body, probably tri-amido-di-oxy-phenoxazine. By passing air through an ammoniacal solution of the colourless body there are formed lustrous green crystals of 'hydroimidotetrazoresorufin' $C_{36}H_{28}N_{14}O_9aq$ (W.) or $C_{12}H_6(NH_2)_3NO_4$ (B.) (possibly tri-amido-resorufin). — 5. *Bromine* added to its solution in NaOHAq forms $(C_{12}H_7Br_2NO_4)HBr$ as a lustrous green mass, forming a blue alcoholic solution with red fluorescence (Brunner a. Krämer, *B.* 17, 1862). Nietzki obtained $C_{12}H_3Br_4NO_4$, which gave $C_{12}H_2NaBr_4NO_4 2aq$, crystallising from dilute alcohol in lustrous green prisms.—6. Oxidised in KOH solution by H_2O_2 to oxyresazurin $C_{18}H_{12}N_2O_7$ (?), which forms almost colourless crystals giving a reddish-yellow solution in alkalis. This compound is also formed by alkaline $KMnO_4$. It is reduced by zinc-dust to $C_{18}H_{16}N_2O_7$ (?), crystallising in colourless needles (Ehrlich, *M.* 8, 425).

Acetyl derivative $C_{12}H_6AcNO_4$. [222°]. Formed by heating the sodium compound with NaOAc and Ac_2O at 100° (Nietzki, *B.* 22, 3024). Ruby-red needles.

Ethyl ether $C_{12}H_6EtNO_4$. [215°]. Formed from the Ag salt, alcohol, and EtI. Dark-red needles. According to Weselsky the formula of the ether [202°] got from resazurin, alcohol, and HCl at 100° is $C_{18}H_8Et_2N_2O_6$.

Resorufin $C_{12}H_7NO_3$ *i.e.*



$$\begin{array}{l}\underset{|}{C}O.CH:\underset{|}{C}.O.\underset{|}{C}.CH:\underset{|}{C}.OH\\ \overset{|}{C}H:CH.\overset{|}{C}:N.\overset{|}{C}.CH:\overset{|}{C}H\end{array}$$

. *Azoresorufin. Diazoresorufin.*

Formation.—1. By heating resazurin with conc. H_2SO_4 at 210°.—2. By heating resorcin with a solution of nitrous acid in H_2SO_4 (Brunner a. Krämer, *B.* 17, 1847).—3. By warming nitroso-resorcin with resorcin and H_2SO_4 (Fevre, *Bl.* [2] 39, 593).—4. By heating resorcin with nitrobenzene and H_2SO_4 at 170°.—5. By the action of zinc-dust on an ammoniacal solution of resazurin (Weselsky a. Benedikt, *M.* 5, 608).—6. By boiling resazurin (1 pt.) with $FeCl_2$ (2 pts.) and fuming HClAq (10 pts.) and ppg. with water (W. a. B.).—7. By action of nitroso-phenol on resorcin or of nitroso-resorcin on phenol in presence of H_2SO_4 (Nietzki, *B.* 22, 3020; 23, 718).—8. By adding MnO_2 to a solution of *p*-amido-phenol and resorcin in conc. H_2SO_4.

Properties. — Small dark-red grains (from dilute HClAq), insol. water and ether, sl. sol. alcohol. Forms a bluish-violet solution in H_2SO_4. Alkalis form a crimson solution with scarlet fluorescence.

Reactions.—1. Reduced by *tin* and HClAq or by *zinc* and HClAq to dioxy-phenoxazine $C_{12}H_9NO_3$, crystallising in nearly colourless needles, which soon become green in the air, and yielding $C_{12}H_6Ac_3NO_3$ [216°] crystallising in colourless needles, sl. sol. hot alcohol.—2. *Bromine* added to the alkaline solution yields the sodium salt $C_{12}H_2Br_4NO_3Na$ 2aq, crystallising in lustrous green needles.—3. *Nitric acid* (S.G. 1·37) forms a body crystallising in green needles, forming a purple solution in water, alcohol, and ether. This body is probably tri-nitro-resorufin. 4. Fuming HCl at 100° forms 'azoresorufyl chloride' $C_{24}H_{16}Cl_4N_2O_5$ (?) crystallising in red plates, sol. ether (Brunner a. Krämer, *B.* 17, 1857). Its alkaline solution exhibits red fluorescence.

Acetyl derivative $C_{12}H_6AcNO_3$. [223°]. Formed by heating resorufin with Ac_2O and NaOAc. Orange scales, v. sol. acetone, sl. sol. alcohol and ether.

Ethyl ether $C_{12}H_8EtNO_3$. [225°]. Orange-red needles (Nietzki).

Nitroso-resorcin *v.* vol. iii. p. 619.

Diresorcin *v.* TETRA-OXY-DIPHENYL.

References.—AMIDO-, AMIDO-DI-IMIDO, BROMO-, DI-BROMO-AMIDO, BROMO-NITRO-, CHLORO-, IODO-, DI-IODO-NITRO-, NITRO-, NITRO-AMIDO-, and NITROSO-RESORCIN.

RESORCIN-AZO- *v.* AZO- COMPOUNDS and DISAZO- COMPOUNDS.

RESORCIN-BENZEÏN *v.* TETRA-OXY-TRI-PHENYL-CARBINOL.

RESORCIN CARBOXYLIC ACID *v.* DI-OXY-BENZOIC ACID.

Resorcin (α)-dicarboxylic acid $C_6H_2(OH)_2(CO_2H)_2$. [276°]. Formed, together with di-oxy-benzoic acid, by heating resorcin (1 pt.) with ammonium carbonate (4 pts.) and water (5 pts.) in a sealed tube (Senhofer a. Brunner, *Bn.* 2, 1266). Minute tables (from water), v. sl. sol. hot water. $FeCl_3$ colours its aqueous solution red.—KHA″aq: needles.—K_2A'' 3aq: needles, v. e. sol. water.—BaA″ 5½aq: needles.—CuA″ 5½aq.—Ag_2A'': amorphous pp.

Resorcin (β)-dicarboxylic acid $C_6H_2(OH)_2(CO_2H)_2$. [250°]. Formed by heating (1,3,5)-di-oxy-benzoic acid with ammonium carbonate and water (S. a. B.). Four-sided prisms (containing aq), sl. sol. cold water. $FeCl_3$ colours its solution violet.—K_2A''.—$Ba(HA'')_2$ 7aq.—BaA″ 4aq: needles.—$Ba_2C_8H_2O_6$ 2aq (dried at 160°).—$PbC_8H_4O_6$ 1½aq.—CuA″ 3½aq.

Resorcin dicarboxylic acid $C_6H_2(OH)_2(CO_2H)_2$[4:2:5:1] (?). [192°]. Formed by oxidising the corresponding aldehyde [127°] (Tiemann a. Lewy, *B.* 10, 2212). Slender needles.

Diresorcin dicarboxylic acid *v.* TETRA-OXY-DIPHENYL DICARBOXYLIC ACID.

RESORCIN ALDEHYDE *v.* DI-OXY-BENZOIC ALDEHYDE.

Resorcin dicarboxylic aldehyde *v.* DI-OXY-ISOPHTHALIC ALDEHYDE.

RESORCIN-INDOPHANE $C_9H_4N_4O_6$. Ppd., as K salt, by warming potassium tri-nitro-resorcin with aqueous KCy (Schreder, *A.* 163, 297). Small lustrous needles, forming a bluish-violet aqueous solution.—$Na_2C_9H_2N_4O_6$ aq.—$K_2C_9H_2N_4O_6$ aq: dark-brown lustrous crystals, exploding when heated.—$BaC_9H_2N_4O_6$ aq.

DIRESORCIN-PHTHALEÏN $C_{32}H_{22}O_{10}$ 5½aq (Link, *B.* 13, 1654) or $C_{20}H_{12}O_6$ (Benedikt a. Julius, *M.* 5, 182). [245°]. Formed by heating diresorcin (tetra-oxy-diphenyl) with phthalic anhydride and $SnCl_4$ or H_2SO_4 at 115°. Silvery plates or needles, forming an indigo-blue solution in alkalis. Converted by heating with zinc-dust and caustic soda into diresorcin-phthalin $C_{32}H_{24}O_{10}$ 8½aq (L.) or $C_{20}H_{14}O_6$ 2aq (B. a. J.), crystallising from water in colourless plates [238°], forming a colourless solution in alkalis.

RESORCIN SULPHONIC ACID $C_6H_3(OH)_2(SO_3H)$. Formed by potash-fusion from the disulphonic acid (H. Fischer, *M.* 2, 337).—KA′ 2aq: crystals.

Resorcin disulphonic acid $C_6H_2(OH)_2(SO_3H)_2$. Prepared by sulphonation of resorcin (Piccard a. Humbert, *B.* 9, 1479; Tedeschi, *B.* 12, 1267). Deliquescent needles (containing 2aq), sol. water and alcohol, insol. ether. $FeCl_3$ gives a red colour. Gives phloroglucin on fusion with potash. Bromine forms tri-bromo-resorcin even in the cold.—K_2A'' aq: needles.—K_2A'' 4aq: deliquescent needles.—Na_2A'' aq.—BaA″ 3aq.—BaA″ 3½aq.—$Ba_2C_6H_2S_2O_8$ 4aq.—CuA″ 10aq: triclinic crystals.—$Ba_2C_6H_2S_2O_8$ 5aq: crystals.—$Pb_2C_6H_2S_2O_8$ 4aq.

Resorcin disulphonic acid $C_6H_2(OH)_2(SO_3H)_2$. Formed from di-amido-benzene disulphonic acid by the diazo- reaction (Limpricht, *B.* 8, 290). Long four-sided needles. BaA″ 2aq: crystalline pp., got by adding alcohol to its aqueous solution.

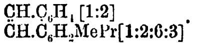
Resorcin trisulphonic acid $C_6H(OH)_2(SO_3H)_3$. Formed by heating the disulphonic acid with fuming H_2SO_4 at 200° (Piccard a. Humbert, *B.* 10, 182). In neutral solution it gives a violet colour with $FeCl_3$.—$Ba_3A'''_2$ 3½aq. Insol. water and HClAq.

References.—IODO-, NITRO-, and NITROSO-RESORCIN SULPHONIC ACID.

RESORCYLIC ACID *v.* DI-OXY-BENZOIC ACID.

RESORCYLIC ALDEHYDE *v.* DI-OXY-BENZOIC ALDEHYDE.

Resorcylic dialdehyde *v.* DI-OXY-ISOPHTHALIC ALDEHYDE.

RETENE $C_{18}H_{18}$ *i.e.* 
$\begin{array}{l} CH.C_6H_4[1:2] \\ \ddot{C}H.C_6H_2MePr[1:2:6:3] \end{array}$.
Mol. w. 234. [98·5°]. (394°) (Schweizer, *A.* 264, 195). V.D. 8·3 (calc. 8·1) (Knecht, *B.* 10, 2074). S. (95 p.c. alcohol) 3 in the cold; 69 at 78°. S.G. (solid) 1·13 at 16°. H.C.v. 2,323,600. H.C.p. 2,326,100. H.F. −13,100 (Berthelot a. Vieille, *A. Ch.* [6] 10, 447). Occurs in scales in fossil pine-stems, accompanying fichtelite in peat bogs, and is a product of the distillation of wood (Fritsche, *J. pr.* 75, 281; Fehling, *A.* 106, 388; Wahlforss, *Z.* [2] 5, 73; Krauss, *A.* 106, 391; Ekstrand, *Bl.* [2] 24, 53; *A.* 185, 75; Bamberger a. Hooker, *A.* 229, 115). Produced by passing acetylene through a red-hot tube (Berthelot, *J.* 1866, 516). White plates, sol. alcohol, v. sol. hot HOAc, ether, and CS_2. Not attacked by potash-fusion or by alkaline $KMnO_4$. Dissolved by fuming HNO_3. It is not attacked by sodium-amalgam or HIAq at 200°.

Reactions.—1. Absorbs *chlorine*, forming $C_{18}H_{18}Cl_2$, which splits up on heating into HCl and chloro-retene $C_{18}H_{17}Cl$, a crystalline body.—2. *Bromine* and water form di-bromo-retene $C_{18}H_{16}Br_2$ [180°] crystallising from CS_2 in colourless tables. Excess of Br at 100° forms viscid $C_{18}H_{16}Br_6$ and crystalline $C_{18}H_{14}Br_4$ [212°].—3. Oxidised by *chromic acid mixture* to retene-quinone, phthalic acid, and HOAc. CrO_3 in HOAc forms retenequinone, retenic acid $C_{18}H_{18}O_2$, and an acid $C_{16}H_{16}O_3$ crystallising from hot alcohol in plates [139°], forming NaA′ and BaA'_2, both crystallising in plates.

Compound with picric acid $C_{18}H_{18}C_6H_2(NO_2)_3OH$. [124°]. S. (95 p.c. alcohol) 2·3 at 10°; 20 at 78°. Orange-yellow needles (from alcohol). Decomposed by water. Crystallises as $(C_{18}H_{18})(C_6H_6)C_6H_3N_3O_7$ from benzene.

Compound with di-nitro-anthraquinone. Dark orange-red needles (from HOAc).

Tetra-hydride $C_{18}H_{22}$. (280° at 50 mm.). Formed by adding Na to a solution of retene in isoamyl alcohol (Bamberger a. Lodler, *B.* 20, 3076). Pale-yellow liquid.

Dodeca-hydride $C_{18}H_{30}$. (336° uncor.). Formed by heating retene with HI and P at 260° (Liebermann a. Spiegel, *B.* 22, 780). Colourless oil with bluish fluorescence. Yields no retenequinone when oxidised by HNO_3.

Perhydride $C_{18}H_{32}$. [48°]. (335° i.V.) at 719 mm. V.D. 8·69 (calc. 8·58). This is probably the constitution of fichtelite (Bamberger a. Strasser, *B.* 22, 3361; Spiegel, *B.* 22, 3369; *cf.* vol. ii. p. 548). By heating with iodine it is converted into $C_{18}H_{30}$ (346° cor.) at 714 mm.

RETENE-FLUORENE *v.* METHYL-ISOPROPYL-FLUORENE.

RETENE-GLYCOLLIC ACID $C_{18}H_{18}O_3$ *i.e.* $C_{16}H_{16}$:C(OH).CO_2H. Formed by boiling retenequinone with NaOHAq (Bamberger a. Hooker, *A.* 229, 132). White crystals, sl. sol. hot water. —AgA′: flocculent pp., sl. sol. hot water.

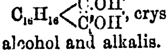
RETENE KETONE *v.* METHYL-ISOPROPYL-DIPHENYLENE KETONE.

RETENEQUINONE $C_{18}H_{16}O_2$ *i.e.*

$\begin{array}{l}CO.C_6H_4\\CO.C_6H_2MePr\end{array}$. *Retistenequinone. Dioxy-retistene.* [192°]. S. (95 p.c. alcohol) ·15 at 0°; 2·2 at 78°. Formed by oxidising retene with CrO_3 in HOAc (Wahlforss, *Z.* [2] 5, 73; Ekstrand, *A.* 185, 75; Bamberger a. Hooker, *B.* 18, 1024; *A.* 229, 117). Orange-red prisms, v. sl. sol. cold alcohol and ether, sl. sol. aniline and HOAc, sol. benzene and chloroform. Not attacked by Cl in the cold. Not affected by hot HNO_3. Conc. H_2SO_4 forms a green solution. Alcoholic potash imparts to its alcoholic solution a claret colour which disappears on shaking with air, but reappears on warming in absence of air.

Reactions.—1. *Bromine* forms $C_{18}H_{14}Br_2O_2$ [252°], crystallising from HOAc in orange prisms. 2. Cold NaOHAq does not dissolve it, but on boiling converts it into retene-glycollic acid.—3. On distillation with *baryta* it yields retene-ketone and oily $C_{21}H_{24}$ (215-220°).—4. Distillation with *zinc-dust* forms retene.—5. HI and P reduce it to retene.—6. In boiling alcoholic solution it is reduced by sodium-amalgam to retene diphenic acid $C_{16}H_{16}(CO_2H)_2$, an unstable resin yielding Ag_2A''.—7. $KMnO_4$ forms oxy isopropyl-diphenylene ketone carboxylic acid.—8. *Phenylene-o-diamine* forms

$C_{16}H_{16}<\begin{array}{l}C:N\\C:N\end{array}>C_6H_4$, crystallising in needles [164°], insol. water, sl. sol. alcohol, v. sol. ether, resinified by strong acids.—9. Alcoholic *ammonia* added to a solution of the quinone in chloroform slowly forms the imide $C_{18}H_{16}O(NH)$, crystallising in unstable golden needles.—10. Aqueous SO_2 forms hydroretenequinone



$C_{16}H_{16}<\begin{array}{l}C.OH\\C.OH\end{array}$, crystallising in white plates, sol. alcohol and alkalis. The same body is got by reducing the quinone with Zn and NaOHAq. It is oxidised by air to retenequinone.

Oxim $C_{18}H_{16}O(NOH)$. [128·5°]. Golden needles (from alcohol), decomposed by acids into the quinone and hydroxylamine. Forms green compounds with iron mordants (Von Kostanecki, *B.* 22, 1347).

RETENE DISULPHONIC ACID $C_{18}H_{16}(SO_3H)_2$. S. c. 40 in the cold. Formed by sulphonation (Ekstrand, *A.* 185, 86). Needles (containing 10 aq), v. sol. water and alcohol. Its aqueous solution is ppd. by H_2SO_4, forming $H_2A''5H_2SO_4$, crystallising in hair-like needles.—$K_2A''\frac{1}{2}$aq (dried at 100°). S. c. 18. Small silky needles.—$Na_2A''\frac{1}{2}$aq (dried at 100°). S. c. 40 in the cold.—BaA″6aq. S. 1·6.—SrA″1½aq. S. 4.—CaA″8aq. S. 5.—MgA″2aq (dried at 100°). S. 4.—CuA″5aq: long needles. S. c. 30.—PbA″aq (dried at 100°). S. 2.

Chloride $C_{18}H_{16}(SO_2Cl)_2$. [175°]. Prisms (from HOAc).

Retene trisulphonic acid $C_{18}H_{15}(SO_3H)_3$. Got by heating retene with fuming H_2SO_4 at 100°. Crystalline mass, v. sol. water, alcohol, and ether; not ppd. by H_2SO_4.—$Ba_3A'''_2$18aq. Needles. S. 7.—$Pb_3A'''_2$18aq: slender needles.

RETENIC ACID $C_{18}H_{18}O_2$. [222°]. A product of oxidation of retene (Ekstrand, *A.* 185, 111). Needles (from alcohol), v. sol. alcohol, ether, and HOAc. May be sublimed.—NaA: plates, m. sol. water.

RETINAPHTHA is TOLUENE.

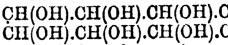
RETINDOLE *v.* INDOLE.

RETISTENE is RETENE.

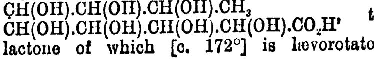
RHAMNETIN is the *Methyl ether* of QUERCETIN (*q.v.*).

RHAMNITE $C_6H_{14}O_5$ *i.e.* CH_3.CH(OH).CH(OH).CH(OH).CH(OH).CH_2OH. [121°]. $[\alpha]_D = 10·7°$. Formed by reducing isodulcite with sodium-amalgam in a solution kept nearly neutral by H_2SO_4 (E. Fischer a. Piloty, *B.* 23, 3104). Triclinic crystals, with sweet taste, v. sol. water and alcohol, sl. sol. chloroform, v. sl. sol. ether. Dextrorotatory. Does not reduce Fehling's solution.

RHAMNOHEPTOSE $C_8H_{16}O_7$ *i.e.*

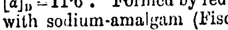


$\begin{array}{l}CH(OH).CH(OH).CH(OH).CH_3\\CH(OH).CH(OH).CH(OH).CHO\end{array}$. $[\alpha]_D = 8°$. Formed by the action of sodium-amalgam on the lactone, [c. 160°], $[\alpha]_D = 55·6°$, of hexa-oxy-octoic acid, which is formed from rhamnohexose by successive treatment with HCy and baryta (Fischer a. Piloty, *B.* 23, 3106). Sweet syrup. Dextrorotatory. Yields $C_8H_{14}O_6(N_2HPh)$ [200°] and $C_8H_{14}O_5(N_2HPh)_2$ [c. 200°]. Converted by treatment with HCy, followed by saponification, into hepta-oxy-ennoic acid



$\begin{array}{l}CH(OH).CH(OH).CH(OH).CH_3\\CH(OH).CH(OH).CH(OH).CH(OH).CO_2H\end{array}$, the lactone of which [c. 172°] is lævorotatory $[\alpha]_D = -51°$.

RHAMNOHEXITE $C_7H_{16}O_6$ *i.e.*



$\begin{array}{l}CH(OH).CH(OH).CH(OH).CH_3\\CH(OH).CH(OH).CH_2(OH)\end{array}$ [c. 173°]. $[\alpha]_D = -11·6°$. Formed by reducing rhamnohexose with sodium-amalgam (Fischer a. Piloty, *B.* 23, 3106). Small colourless prisms (from hot alcohol). Does not reduce Fehling's solution.

RHAMNOHEXOSE $C_7H_{14}O_6$ *i.e.* CH_3.CH(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO. [181°]. $[\alpha]_D = -61°$. Formed by reducing the lactone of isodulcite carboxylic acid with sodium-amalgam in acid solution at a low temperature (Fischer a. Piloty, *B.* 23, 3104). Small tables, sl. sol. alcohol. Its aqueous solution tastes sweet. Yields a di-phenyl-di-hydrazide [200°].

RHAMNOSE *v.* ISODULCITE.

RHATANINE $C_{10}H_{13}NO_3$. S. ·8 at 100°. S (alcohol) ·01 at 15°; ·04 at 78°. Occurs in the extract of rhatany root (Wittstein, *J.* 1854, 656; Ruge, *Viertelj. d. nat. Ges. in Zürich*, 6, Heft 3; Gintl, *Sitz. W.* [2] 60, 668; Kreitmair, *A.* 176, 69). Spherical groups of white needles, insol. ether. Not ppd. by lead acetate or subacetate. Resembles tyrosine. On heating with a little solution of $Hg(NO_3)_2$ it becomes rose-red, and gives a brown pp. on further addition of $Hg(NO_3)_2$. Boiling HNO_3 gives a red colour changing to blue, and finally to a fluorescent green. Sulphuric acid forms a sulphonic acid $C_{10}H_{12}NO_3(SO_3H)$ aq crystallising from alcohol in plates yielding $BaA'_2 2\frac{1}{2}$aq and BaA'_2 5aq.

Salts.—$H_2A''HCl$: monoclinic prisms, decomposed by treatment with water or alcohol.—$(H_2A'')_2H_2PtCl_6$.—Na_2A'': deliquescent amorphous mass.—K_2A''.—BaA'' 2aq.—SrA'' 2aq.—CaA''.—MgA''.—Ag_2A'': minute needles, sl. sol. cold water.—$H_2A''HNO_3$.—$H_2A''H_2SO_4$: trimetric crystals.—$H_2A''H_3PO_4$: small prisms.

RHATANITANNIC ACID $C_{20}H_{20}O_9$ (Raabe, *J.* 1880, 1060). Occurs in rhatany extract from the root-bark of *Krameria triandra* (Wittstein, *J.* 1854, 656; Grabowski, *A.* 143, 274). Amorphous, sol. water. Reduces Fehling's solution. Gives a dark-green colour with $FeCl_3$. Yields phloroglucin and protocatechuic acid on fusion with potash. Boiling dilute H_2SO_4 forms 'rhatania-red' $C_{20}H_{18}O_8$, which yields pyrocatechin on distillation.

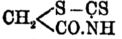
RHINACANTHIN $C_{14}H_{18}O_4$. Occurs in the root of *Rhinanthus communis* (Liborius, *J.* 1881, 1022). Tasteless resin, sol. alcohol. Does not form glucose on boiling with HClAq.

RHINANTHIN $C_{29}H_{52}O_{20}$ (L.) or $C_{61}H_{56}O_{40}$. A glucoside occurring in the seeds of the yellow rattle (*Rhinanthus crista-galli*), and giving rise to the violet colour of bread prepared from rye contaminated with these seeds. Occurs also in the seeds of *Alectrolophus hirsutus* (Ludwig, *Z.* [2] 5, 303; *Ar. Ph.* [2] 142, 199), and in the leaves and stalks of the snap-dragon (*Antirhinum majus*) (Phipson, *C. N.* 58, 99). Stellate groups of prisms, with bitter-sweet taste, v. sol. water and alcohol. Gives a bluish-green solution on warming with alcoholic HCl. Resolved by dilute HClAq into brown amorphous rhinanthogen and a sugar.

RHIZOPOGONIC ACID $C_{28}H_{36}O_4$. [127°]. Obtained from the mushroom *Rhizopogon rubescens* by extracting with ether (Oudemans, *R. T. C.* 2, 155). Red needles, insol. water, v. e. sol. ether, chloroform, and boiling alcohol. Its alkaline solutions are intensely violet.—KA' aq: minute dark-violet crystals.

RHODAMMINES *v.* RHODIUM-AMMONIUM COMPOUNDS, p. 405.

RHODANIDES, another name for *Sulphocyanides* (*q. v.* vol. ii. p. 348).

RHODANIC ACID $C_3H_3NS_2O$ *i.e.* $HS.CH_2.CO.S.CN$ or  $CH_2{<}\begin{smallmatrix}S-CS\\CO.NH\end{smallmatrix}$ (Andreasch, *M.* 10, 73). [169°]. Formed by warming an aqueous solution of chloro-acetic acid (1 mol.) with ammonium sulphocyanide (3 mols.) (Nencki, *J. pr.* [2] 16, 1; *B.* 17, 2279; Ginsberg a. Bondzynski, *B.* 19, 113). Formed also by passing HCl into an alcoholic solution of thioglycollic acid and potassium sulphocyanide (Freydl, *M.* 10, 82). Yellow six-sided prisms and tables, v. sl. sol. cold water, v. sol. alcohol and ether. Acid in reaction. Boiling baryta-water splits it up into HCyS and thioglycollic acid. Water at 200° forms CO_2, H_2S, NH_3, and thioglycollic acid. Reacts with aldehydes in presence of HCl, forming compounds of the type R.CH:C(SH).CO.S.CN. Ethylidene-rhodanic acid $C_5H_5NS_2O$ [148°] forms yellow needles, sol. hot water. Benzylidene-rhodanic acid $C_{10}H_7NS_2O$ [200°] also forms yellow needles, converted by hot H_2SO_4 (4 pts.) into $C_{10}H_7NS_2O_5$, crystallising in needles, yielding NaA', KA', and NH_4A', and converted by HNO_3 into $C_{10}H_6N_2S_2O_7$, crystallising in yellow needles yielding NaA' aq. *o*-Nitro-benzylidene-rhodanic acid $C_{10}H_6N_2S_2O_3$ [189°] crystallises from dilute alcohol, and may be reduced to *o*-amido-benzylidene-rhodanic acid, which yields $C_{10}H_7AcN_2S_2O$ [280°–285°] and $C_{10}H_6Ac_2N_2S_2O$ [189°]. *p*-Nitro-benzylidene-rhodanic acid [252°] is also crystalline (Bondzynski, *M.* 8, 357). $FeCl_3$ added to a hot solution of rhodanic acid forms a brown pp., from which alcohol extracts $C_9H_5N_3S_5O_3$ as a brownish-red powder, forming a red solution in alkalis.

Salts.—CuA'_2 aq: yellowish-green amorphous pp.—$(C_3H_3NS_2O)_2CuCl$: golden needles.

RHODATES. No salts have been isolated the acidic radicle of which is composed of Rh and O; but there is some reason to think that such salts exist in the solution obtained by passing Cl into an alkaline solution of $Rh_2(OH)_6$; *v.* under HYDRATED RHODIUM DIOXIDE, p. 405.

RHODINOL $C_{10}H_{18}O$ *i.e.* $CH_2:C(C_3H_7).CH:CH.CHMe.CH_2OH$. (217°). S.G. $\frac{15}{}$ ·88. Occurs in German and Turkish oil of roses (Eckart, *B.* 24, 4205). Oxidised by chromic acid mixture to an aldehyde, rhodinal, and rhodinolic acid. P_2O_5 yields a terpene. $KMnO_4$ forms valeric, butyric, acetic, oxalic, and carbonic acids and $C_6H_{14}O_5$, possibly an alcohol.

RHODIUM. At. w. 102·7. Mol. w. unknown. Melts at c. 2000° (Pictet, *C. R.* 88, 1317). S.G. 12·1 (Deville a. Debray, *J.* 12, 240). S.H. ·05803 (10° to 97°; specimen contained trace of Ir) (Regnault, *A. Ch.* [3] 63, 1). C.E. ·0000085 at 40° (Fizeau, *C. R.* 68, 1125).

Occurrence.—With the other Pt metals in platinum-ore; the p.c. of Rh varies from 0 to c. 5; as much as 12·3 p.c. was found in a South American ore by Deville a. Debray (*A. Ch.* [2] 29, 137; *cf.* Kern, *C. N.* 35, 88).

Del Rio (*v.* D. a. D., *l.c.*) found an alloy of Rh and Au in Mexico, containing from 34 to 43 p.c. Rh. Rhodium was separated from the other Pt metals in 1803 by Wollaston (*T.* 1804. 419), at the same time as he isolated Pd. The name *rhodium* was given by W. because of the rose-colour of the salts (*ῥόδον* = a rose).

Formation.—1. By reducing $RhCl_3.3NaCl$Aq by Zn, H, formic acid, &c.—2. By strongly heating $RhCl_3.3NH_4Cl$.

Preparation.—Rh is generally prepared by adding iron to the mother-liquors from which Pt has been extracted (*v.* PLATINUM, this vol. p. 286), and then treating the solid so ppd. The processes for the treatment of this residue are many; that described here is the one employed by Claus (*J. pr.* 85, 129), and by Gibbs (*J. pr.* 84, 65; 94, 19), and is a modification of Claus's older method (*cf.* Deville a. Debray, *C. R.* 78, 1782). The platinum-residue—which contains Rh, Ru, Pd, Ir, Cr, Cu, and Pb—is fused at a bright red heat with 1 pt. Pb and 1 pt. PbO; the regulus, after separation of slag, is treated with nitric acid (equal vols. conc. acid and water); the insoluble residue is washed, dried, and mixed with its own weight of NaCl, and this mixture is heated to low redness, in a large porcelain tube, in a stream of Cl, for some time; the treatment with NaCl and Cl is repeated; after cooling, the contents of the tube are lixiviated with water, when $RhCl_3.3NaCl$ dissolves with small quantities of the corresponding salt of Ir and traces of some of the other metals. The solution is heated with HNO_3Aq, to transform $IrCl_3$ into $IrCl_4$, and Ir is then removed, as $IrCl_4.2AmCl$, by fractional ppn. with conc. AmClAq. The filtrate from the last pp. of $IrCl_4.2AmCl$, which is almost quite free from all metals except Rh, is evaporated to dryness with HNO_3Aq, to decompose the AmCl; the residue is mixed with 3 or 4 times its weight of S, and heated to bright redness in a covered porcelain crucible, which is packed in powdered charcoal in a larger earthen crucible. The regulus thus obtained is boiled for some time with *aqua regia*, and then with conc. H_2SO_4; it is then fused, at a low red heat, with 3 or 4 pts. Zn, whereby an alloy of Rh and Zn is formed, with the production of so much heat that part of the Zn is volatilised. After cooling, the alloy is digested with conc. HClAq, to remove impurities, and is then dissolved in *aqua regia*. NH_3Aq is added to this solution till the pp. which forms has dissolved; the solution is boiled, and evaporated until yellow $Rh_2(NH_3)_{10}Cl_6$ separates; the whole is then evaporated to dryness at 100°, and the residue is treated with warm dil. HClAq until the washings show no yellow colour; the residue is dissolved in boiling water, and the liquid is filtered, hot, into dil. HClAq; the small yellow crystals of $Rh_2(NH_3)_{10}Cl_6$ which separate are re-crystallised several times from hot, dil. NH_3Aq, whereby the salt is obtained quite pure. The pure $Rh_2(NH_3)_{10}Cl_6$ is decomposed by heating strongly in a graphite crucible, and the Rh thus obtained is fused in a lime crucible in the O-H flame (*v.* vol. iii. p. 642). The fusion removes the last traces of Os and Si. For other methods of preparing Rh *v.* Bunsen, *A.* 146, 265; Fremy, *C. R.* 38, 1008; Lea, *Am. S.* 38, 81, 248; Schneider, *P. Supp.* 5, 261; Philipp, *D. P. J.* 220, 95; Martius, *A.* 67, 357; Wilm, *Bl.* [2] 34, 679.

Properties.—A very hard, white metal, with a tinge of blue-grey; about as ductile and malleable as Ag. Melts only in the full O-H flame, without volatilising; spits on cooling; is superficially oxidised when very strongly heated in air. Insoluble in acids when compact, but the finely divided metal ppd. from solutions is sol. HNO_3Aq, and also sl. sol. HClAq in presence of air (Wilm, *Bl.* [2] 34, 679). Alloys of Rh with Bi, Cu, Pb, Pt, or Zn are attacked by HNO_3Aq. Rh is obtained as a black porous solid by reducing solutions of Rh compounds by Zn, Hg, EtOH, or HCO_2H (*v.* Claus, *J. pr.* 85, 139; Wilm, *l.c.*). The finely divided Rh obtained by heating the purpureochloride takes up c. 13 p.c. O when heated in a stream of air (RhO requires 13·5 p.c. O), and the O is given up by heating in H.

In its chemical relationships Rh is closely allied to Ru and Pd, and less closely to Os, Ir, and Pt; *v.* NOBLE METALS, vol. iii. p. 628.

The at. w. of Rh has been determined (1) by analyses of $RhCl_3.3KCl$ (Berzelius, *P.* 13, 442 [1828]); (2) by analyses of a large number of different Rh compounds (Claus, *J. pr.* 85, 139 [1862]); (3) by analyses of $Rh_2(NH_3)_{10}Cl_6$ and $Rh_2(NH_3)_{10}Br_6$ (Jörgensen, *J. pr.* [2] 27, 433, 489 [1883]); (4) by reducing pure $Rh_2(NH_3)_{10}Cl_6$ in H, and determining the residual Rh (Seubert a. Kobbé, *A.* 260, 314 [1890]); (5) by determining S.H. of Rh (Regnault, *A. Ch.* [3] 63, 1). No compound of Rh has been gasified. The older values for at. w. of Rh varied from 104·3 to 103. Seubert a. Kobbé have shown that the true value is less than 103.

Reactions and Combinations.—1. Rhodium black *heated in air* combines with O to form RhO, according to Wilm (*B.* 15, 2225). Leidié (*Bl.* [2] 50, 664) says that the products contain from 14·5 to 17·8 p.c. O (RhO requires 13·5 p.c. O).—2. Oxidised to Rh_2O_3, and then to RhO_2, by *fusion with potash and nitre* (Claus, *l.c.*); also by *heating strongly with barium peroxide* (D. a. D., *l.c.*).—3. *Fusion* of Rh black *with potassium-hydrogen sulphate* produces what is probably a double Rh-K sulphate (Claus, *l.c.*).—4. *Heated in chlorine* to c. 400°, $RhCl_3$ is formed (*v.* Leidié, *Bl.* [2] 50, 664).—5. *Mixed with sodium-chloride and heated in chlorine*, $RhCl_3.3NaCl$ is produced; KCl and Cl, and $BaCl_2$ and Cl, act similarly (Berzelius, *P.* 13, 435; Bunsen, *A.* 146, 266).—6. RhS is formed by *heating* Rh black *in vapour of sulphur* (B., *l.c.*).—7. Rh dissolves in *molten phosphoric acid* (Fischer, *P.* 18, 257), also in *molten acid phosphates* (Rose-Finkner, *Hand. d. anal. Chem.* 6th ed., 1, 354).—8. Finely-divided Rh dissolves in *molten zinc* (Jörgensen, *J. pr.* [2] 27, 433, 489).—9. *Hydrogen* is absorbed in large quantities by Rh. The finely divided metal obtained by heating $RhCl_3.3AmCl$ becomes sensibly hot when H is passed over it (Wilm, *l.c.*).—10. Rh black decomposes *chlorine water*, forming HClAq and O, and *solutions of hypochlorites*, forming chlorides and O (Jörgensen, *l.c.*). It also decomposes *hydrogen peroxide*, giving off O.—11. Rh black decomposes *formic acid solution* to H and CO_2; *alcohol in presence of alkali* is oxidised to alkali acetate, and H is given off, at c. 30° (D. a. D., *A. Ch.* [2] 29, 137; 56, 385; *cf.* Hoppe-Seyler, *B.* 16, 117).—12. When Rh black obtained by heating $RhCl_3.3AmCl$ is heated in *coal-gas*, or in *ethylene*, the volume of the Rh increases and C is absorbed (Wilm, *Bl.* [2] 34, 679).

Detection.—Rh may be brought into solution in water, either by repeated fusion with $KHSO_4$, or by mixing with NaCl and heating to low redness in Cl. To detect Rh in solution, Demarçay (*C. R.* 101, 951) recommends to add AmCl to a neutral, or an almost neutral, solution which has been boiled with HClAq, then to add fairly conc. freshly prepared NaClOAq, and then a 20 p.c. acetic acid solution, drop by drop, with constant shaking, till any pp. formed by the NaClOAq dissoves to an orange-coloured solution; on standing, this solution decolourises, deposits a greyish pp., and finally acquires an intense sky-blue colour, which remains for some time. Free HNO_3 or H_2SO_4 should be absent, not much acetic acid should be added, and the temperature should not be raised. By taking two equal portions of the liquid to be tested, diluting one with water to the same bulk as the other occupies when the reagents are added, and comparing the two, ·00019 g. Rh can be detected in 3 c.c. liquid. The other Pt metals give no reaction with NaClOAq under the above conditions.

Rhodium, alloys of. Rh alloys with many metals, by fusion with them. Some of the alloys seem to have definite compositions, *e.g.* Rh_2Pb and $RhZn_2$. Descriptions of the alloys will be found in the papers referred to:—As (Wollaston, *T.* 1804. 419); Bi (W., *l.c.*); Au (W., *l.c.*; van Riemsdyk, *J.* 1880. 1269); Fe (Faraday a. Stodart, *G. A.* 66, 167); Pb (Debray, *C. R.* 90, 1195; Deville a. D., *C. R.* 44, 1101; 94, 1557); Pt (D. a. D., *l.c.*); Ag (W., *l.c.*); Sn (D., *l.c.*; Leidié, *C. R.* 106, 1076); Zn (D. a. D., *l.c.*; Bunsen, *A.* 146, 271; Jörgensen, *J. pr.* [2] 27, 434).

Rhodium, ammonio-salts of, *v.* RHODIUM-AMMONIUM COMPOUNDS, p. 405.

Rhodium, chlorides of. The only chloride of Rh which has been isolated with certainty is $RhCl_3$. The lower chloride $RhCl_2$ probably exists.

RHODIUM DICHLORIDE $RhCl_2$. This chloride probably exists. Berzelius obtained a greyish-red powder, to which he gave this composition, by heating Rh in Cl, warming the product with KOHAq, and treating the hydrated oxide so formed with HClAq, when $RhCl_3$ dissolved and $RhCl_2$ (?) remained (*P.* 13, 437). According to Fellenberg (*P.* 50, 63) $RhCl_2$ is obtained, as a rose-red powder, insol. water, HClAq, or HNO_3Aq, undecomposed by KOHAq, by heating RhS in Cl. Claus (*J.* 1855. 423) and Leidié (*C. R.* 106, 1076; 107, 234) regard the existence of $RhCl_2$ as unproved. According to L., no substance of constant composition is obtained by F.'s method.

(?) Double salt, $Am_4RhCl_6.xH_2O$. The compound to which Wilm gave this composition, and which he said was obtained by adding AmCl to $RhCl_3Aq$ in presence of much *aqua regia* (*B.* 16, 3033), is almost certainly identical with $Am_3RhCl_6.NH_4NO_3.3\frac{1}{2}H_2O$, obtained by Leidié (*v.* AMMONIUM CHLOR-RHODITE, *infra*).

RHODIUM TRICHLORIDE $RhCl_3$ (*Rhodo-chloride. Rhodo-rhodic chloride,* $RhCl_2.RhCl_4$. *Rhodium sesquichloride,* Rh_2Cl_6). $RhCl_3$ is the simplest formula possible, but it is not necessarily molecular. Leidié (*C. R.* 106, 1076; 107, 234) prepared $RhCl_3$ by heating the alloy $RhSn_3$ in a rapid stream of dry, air-free Cl at the B. P. of S, until $SnCl_2$ ceased to be formed, allowing to cool, and removing Cl by a current of CO_2. The chloride is thus obtained as a sealing-wax-red powder. The alloy $RhSn_3$ is formed by fusing 1 part finely divided Rh with 30 to 50 parts Sn, and treating the product for a day or two with fairly conc. HClAq at 0° (Debray, *C. R.* 104, 1470, 1577). $RhCl_3$ was also formed by Jörgensen (*J. pr.* [2] 27, 433) by heating $Cl_2Rh_2(NH_3)_{10}Cl_4$ in a stream of Cl. Leidié (*Bl.* [2] 50, 664) says that $RhCl_3$ is not obtained pure by Claus' method of heating Rh in Cl, as part of the $RhCl_3$ is decomposed at the temperature which must be employed to cause combination of Rh and Cl. Leidié (*l.c.*) could not obtain pure $RhCl_3$ by heating Rh_2S_3 in Cl, nor by heating the double chlorides of Rh and alkali metals with H_2SO_4, as recommended by Claus; in the latter reactions L. obtained alkali sulphate and $Rh_2(SO_4)_3$. $RhCl_3$ is a red powder, insol. water and acids; decomposes to Rh and Cl at c. 450°-500° (L., *l.c.*). When moist $RhCl_3$ is heated *in vacuo*, or in a stream of N, it is partially decomposed at 100°, and wholly at 360°, to Rh_2O_3 and HCl (L., *l.c.*). Slowly reduced by H at low redness (*v.* Claus, *J.* 1855. 423).

HYDRATE OF RHODIUM TRICHLORIDE $RhCl_3.4H_2O$. Said to be formed by Claus (*l.c.*) by dissolving freshly ppd. $Rh(OH)_3$ in HClAq, and evaporating; by Berzelius (*P.* 13, 437) by decomposing K_3RhCl_6Aq by H_2SiF_6Aq, filtering, and evaporating. Described as a dark-red, glassy, deliquescent solid; e. sol. alcohol, insol. ether. Leidié (*Bl.* [2] 50, 664) could not obtain this, nor any definite, hydrate of $RhCl_3$.

Double salts. *Chloro-rhodites* $RhCl_3.3MCl$, or M_3RhCl_6. M = Am, $\frac{1}{2}$Ba, $\frac{1}{2}$Pb, Hg, K, Ag, Na. Also M_2RhCl_5; M = ?Am, and K.

Ammonium chlor-rhodite $2Am_3RhCl_6.3H_2O$ (*Ammonium-rhodium trichloride*). Large, red, rhombic prisms (*v.* Keferstein, *P.* 99, 275); by adding conc. HClAq to Na_3RhCl_6Aq, filtering from NaCl, and adding conc. AmClAq (Claus, *l.c.*; Wilm, *B.* 16, 3033; Leidié, *l.c.*). Sol. water, or dil. AmClAq; insol. alcohol. The salt $Am_2RhCl_5.H_2O$, said to be formed by heating a solution of the preceding salt (Vauquelin, *A. Ch.* 93, 204), could not be obtained by Leidié (*l.c.*).

Double salt with ammonium nitrate, $2(Am_3RhCl_6.NH_4NO_3).7H_2O$. Obtained, as violet-red crystals, by adding HNO_3Aq to Am_3RhCl_6Aq, and then excess of AmClAq, concentrating, and drying the crystals *in vacuo.* Scarcely sol. HNO_3Aq; when boiled with water gives off same gases as are obtained by boiling AmClAq with *aqua regia.*

Potassium chlor-rhodites (1) $K_3RhCl_6.3H_2O$. Dark-red triclinic prisms; by adding conc. KClAq to $RhCl_3Aq$, and allowing to evaporate (Claus, *l.c.*). Obtained by Seubert a. Kobbé (*B.* 23, 2556) by saturating the filtrate from the salt K_2RhCl_5 (*infra*) with HCl, filtering from KCl, and evaporating. Leidié (*l.c.*) failed to obtain this salt.

(2) $K_2RhCl_5.H_2O$ (no water, according to L.). Brown triclinic prisms, sl. sol. water. Gives Rh, KCl, and Cl when heated to redness. Formed by heating a mixture of 1 part spongy Rh with 2 parts KCl, in a stream of Cl, so long as Cl is absorbed, dissolving in water, filtering, and evaporating under reduced pressure (S. a. K., *l.c.*).

Sodium chlor-rhodite $Na_3RhCl_6.9H_2O$. Prepared like the K salt (Berzelius, Claus, Leidié).

The *lead, mercurous,* and *silver* salts are obtained by adding $Pb(NO_3)_2Aq$, $HgNO_3Aq$, or $AgNO_3Aq$, to solution of an alkali salt (Claus, *l.c.*). The *barium* salt is obtained like the K and Na salts (Bunsen, *A.* 146, 276). Compounds of $RhCl_3$ with *methylamine chlorides* are described by Vincent (*Bl.* [2] 44, 513).

Rhodium, cyanides of, *and derivatives,* **v.** vol. ii. p. 346.

Rhodium, hydrosulphide of, RhS_3H_3 (= $Rh_2S_3.3H_2S$). A brownish-black, voluminous pp., obtained by passing H_2S into solution of a Rh salt at c. 100° (Leidié, *Bl.* [2] 50, 664). Insol. acids, or alkali sulphide solutions; decomposed by Br and *aqua regia.* Gives off H_2S, and forms Rh_2S_3 when boiled with much water in N, or when heated with water in a sealed tube to 100°.

Rhodium, hydroxides of, *v.* RHODIUM OXIDES AND HYDRATED OXIDES.

Rhodium, iodide of. The black substance obtained by Jörgensen in making $Rh_2(NH_3)_{10}I_6$ (*v.* IODOPURPUREORHODIUM IODIDE, p. 406) was probably RhI_3; analysis gave 21·8 p.c. Rh, the formula requiring 21·3 p.c. According to Claus (*l.c.*) an iodide of Rh is formed when KIAq is added to solution of a salt of Rh.

Rhodium, oxides and hydrated oxides of. Rh and O combine, when Rh is strongly heated in O, probably with formation of RhO. The only oxides of Rh which have been isolated with certainty are Rh_2O_3 and RhO_2; RhO also probably exists, and there are indications of the formation of RhO_3. The hydrated oxides, or hydroxides, are $Rh_2O_3.3H_2O$ [$=Rh(OH)_3$], and $RhO_2.2H_2O$ [$=Rh(OH)_4$].

RHODIUM MONOXIDE RhO (*Rhodous oxide*). Probably formed when Rh black is heated in a stream of air (Wilm, *B.* 15, 2225). Leidié (*Bl.* [2] 50, 664) says that from 14·5 to 17·8 p.c. O is taken up; RhO requires 13·5 p.c. O. The grey powder obtained by heating $Rh(OH)_3$ was looked on by Claus as probably RhO. Deville a. Debray (*A. Ch.* [3] 61, 83) obtained what they regarded as RhO containing a little PbO by melting Rh with PbO, Pb, and borax, cupelling, and treating the residue with HNO_3Aq. RhO is said to be fairly easily reduced to Rh by heating in H.

RHODIUM SESQUIOXIDE Rh_2O_3 (*Rhodo-rhodic oxide*). This oxide may be formed when Rh black is heated to redness in air. Leidié found from 14·5 to 17·8 p.c. O taken up (*Bl.* [2] 50, 664); Rh_2O_3 requires 18·92 p.c. O. Rh_2O_3 was obtained by Claus (*J. pr.* 76, 24; 80, 282; 85, 129) by heating $Rh(NO_3)_3$ in a Pt crucible till oxides of N ceased to come off; also by fusing Rh with BaO_2 and $Ba(NO_3)_2$. Fremy (*A. Ch.* [3] 44, 385) says that Rh_2O_3 is produced by heating Na_3RhCl_6 to redness in a stream of O. Rh_2O_3 is also formed by heating RhO_3H_3. Rh_2O_3 forms a grey solid; insol. acids; reduced by H to Rh (Claus, *l.c.*). Fremy obtained it as lustrous, metal-like, crystals, somewhat volatile when heated in a stream of O, which decomposed ClAq giving HClAq and O.

HYDRATED RHODIUM SESQUIOXIDE. (1) $Rh_2O_3.3H_2O$ (*Rhodo-rhodic hydroxide*, RhO_3H_3). A black gelatinous pp. formed by adding excess of KOHAq, and a little alcohol, to Na_3RhCl_6Aq. Sl. sol. conc. HClAq (Claus, *l.c.*). (2) $Rh_2O_3.5H_2O$ (*Hydrated rhodo-rhodic hydroxide*, $RhO_3H_3.H_2O$). Obtained by adding KOHAq to solution of $RhCl_3$, the latter being in excess, allowing to stand till the pp. is citron-yellow (the first rose-red pp. contains the hydrate mixed with K_3RhCl_6), and washing with hot water (Claus, *l.c.*). The whole of the KOH cannot be removed from the pp. by washing. Sol. HClAq, HNO_3Aq, H_2SO_4Aq, H_2SO_3Aq, and when freshly ppd. also in acetic acid. Also sol. conc. KOHAq, but reppd. on dilution (Descotils, *Gm.-K.* 3, 1261). Said by Leidié (*C. R.* 107, 234) to be sol. in solution of alkali hydrogen oxalates. Solutions of this hydrate in acids yield the salts Rh_23X on evaporation; $X=2NO_3$, C_2O_4, SO_4, SO_3, &c.

RHODIUM DIOXIDE RhO_2 (*Rhodi-* or *rhodic oxide*). A brown solid; obtained by repeatedly fusing finely divided Rh with KOH and KNO_3. Insol. acids, or boiling KOHAq. Reduced to Rh by H at a high temperature (Claus, *l.c.*).

HYDRATED RHODIUM DIOXIDE $RhO_2.2H_2O$ (*Rhodic hydroxide*, RhO_4H_4). Obtained by Claus (*l.c.*) by leading Cl into a solution of $Rh_2O_3.5H_2O$ in KOHAq till a dark-brown gelatinous pp. was formed, then adding pieces of KOH from time to time, and continuing the passage of Cl until pp. became more compact, and green, and the solution became blue-violet. A greenish solid, sol. HClAq, forming a greenish-blue solution, which evolves Cl and becomes the deep-red colour of $RhCl_3$ solution (*cf.* Jörgensen, *J. pr.* [2] 27, 446).

Rhodic acid and rhodates (?). The blue-violet solution obtained by passing Cl into $Rh_2O_3.5H_2O$ in KOHAq (*supra*) is fairly permanent, but after some time it ppts. a blue powder, gas is given off, and the liquid becomes colourless. When the blue powder is dried it becomes green $RhO_3.2H_2O$. A blue pp. is also obtained by carefully neutralising the blue-violet solution by HNO_3Aq; this powder, when moist, is sol. HClAq, with evolution of Cl; on heating, more Cl is evolved, and the liquid becomes the red colour of $RhCl_3$ solution. Claus (*l.c.*) regarded the blue-violet solution as containing *potassium rhodate*, and the blue pp. he looked on as *rhodium trioxide* or *rhodic anhydride*, RhO_3.

Rhodium, salts of. But few salts are known obtained by replacing H of oxyacids by Rh; the chief are *nitrate*, *nitrite*, *oxalates*, *phosphates*, and *sulphates*; a few double salts are also known.

Rhodium, sulphides of. Rh and S combine when heated, probably forming RhS. Rh_2S_3 is formed by ppn. from Rh salts.

RHODIUM MONOSULPHIDE RhS (*Rhodous sulphide*). Said by Berzelius to be formed by heating finely divided Rh in S vapour; also, according to Vauquelin (*A. Ch.* 88, 167), by heating Am_3RhCl_6 with S. Fellenberg (*P.* 50, 63) obtained RhS by heating dry Rh_2S_3 in CO_2 (?). A white-blue, lustrous solid; heated in air gives spongy Rh; heated in Cl forms $RhCl_2$ and S_2Cl_2 (F., *l.c.*). RhS is insol. *aqua regia*, according to Debray (*C. R.* 97, 1333.) (*v.* also Gibbs, *J. pr.* 91, 171; Lecoq de Boisbaudran, *C. R.* 96, 152).

RHODIUM SESQUISULPHIDE Rh_2S_3 (*Rhodo-rhodic sulphide*). Formed, by passing H_2S into solution of a Rh salt, as a black pp. according to Leidié (*C. R.* 106, 1076, 1533) the pp. is $Rh_2S_3.3H_2S$ (*v.* RHODIUM, HYDROSULPHIDE OF, p. 404), which becomes Rh_2S_3 by heating for some time with water at 100°, in a closed vessel or in N. Leidié (*l.c.*) obtained Rh_2S_3, in black crystalline tablets, by heating $RhCl_3$ to 360° in a stream of H_2S; according to L., this is the only method whereby pure Rh_2S_3 can be prepared. Loses 8 p.c. S when heated in N to dull redness; all S expelled only in O-H flame (L., *l.c.*). Insol. alkali solutions; not acted on by HClAq, HNO_3Aq, BrAq, or *aqua regia* (L., *l.c.*). Forms the *double salt* $Rh_2S_3.3Na_2S$, by adding excess of conc. Na_2SAq to Na_3RhCl_6Aq; decomposed by water, stable in presence of excess of alkali sulphide (Leidié, *l.c.*). M. M. P. M.

RHODIUM - AMMONIUM COMPOUNDS. (*Rhodammines. Ammoniacal rhodium bases.*) When a solution of Rh in *aqua regia* is evaporated with excess of NH_3Aq a compound

$Rh_2Cl_6.10NH_3$ is obtained. By treating this body with moist Ag_2O and water in the cold $Rh_2Cl_4O_2H_2.10NH_3$ is formed; if heat is used, the product is $Rh_2O_6H_6.10NH_3$ These compounds react as definite salts, which exchange their more negative radicles without losing Rh or NH_3. The classification of the rhodium-ammonium compounds generally adopted is similar to that used for the Cr and Co compounds (*v.* vol. ii. pp. 158 and 222). In the following general formulæ M and X represent negative radicles, which may be the same or different

$M_2.Rh_2.10NH_3.X_4$ or $N_4H_6(NH_4)_6(Rh_2M_2).X_4$
Purpureo-rhodium series.

$Rh_2.10NH_3.X_6.2H_2O$ or $N_4H_6(NH_4)_6Rh_2.X_6.2H_2O$
Roseo-rhodium series.

$Rh_2.12NH_3.X_6$ or $N_4H_4(NH_4)_8Rh_2.X_6$
Luteo-rhodium series.

The Rh compounds were investigated by Berzelius (*Lehrbuch*, 5th ed., 3, 956); Vauquelin (*A. Ch.* 88, 167); Claus (*Beiträge zur Chemie der Platinmetalle*, Dorpat, 1854); and more recently by Jörgensen (*J. pr.* [2] 27, 633; 34, 394; 44, 48).

I. Purpureo-rhodium compounds $M_2.Rh_2.10NH_3.X_4$. Changed to roseo salts, without loss of NH_3, by boiling with alkali solution. The two atoms of radicle represented by M_2 are not removed by the ordinary reagents for removing this radicle from salts.

Chloro-purpureo- series (Jörgensen, *l.c.*). *Chloropurpureorhodium chloride* $Cl_2.Rh_2.10NH_3.Cl_4$. This salt is prepared by dissolving the alloy $RhZn_2$ in *aqua regia*, evaporating to dryness, treating the residue with water, filtering, adding excess NH_3Aq, evaporating to dryness at 100°, heating with dil. HClAq, and filtering while hot; the insoluble salt is washed with dil. HClAq, dissolved in boiling water, and the hot solution is filtered into HClAq (1:1 by volume); the purpureo-chloride which separates is washed with dilute HClAq, and then with alcohol. Small lustrous yellow rhombic crystals; isomorphous with chloropurpureo-cobalt chloride (*v.* Topsöe, *J. pr.* [2] 27, 433; Keferstein, *A. Ch.* 99, 275). S.G. 2·079 at 18°. S. ·56 cold water, considerably more sol. hot water. Sol. without decomposition in hot conc. H_2SO_4, also in boiling NaOHAq. Easily reduced to Rh, but not acted on by such oxidisers as *aqua regia* or HClAq and $KClO_3$. Heated in CO_2 gives Rh, NH_4Cl, NH_3, and N; heated in H, gives Rh, NH_4Cl, and NH_3; heated in HCl gas, gives Rh and NH_4Cl; heated in Cl gives $RhCl_3$ and NH_4Cl. Reacts with various substances to exchange Cl_4 for equivalent quantities of other negative radicles. Combines with $PtCl_4$ to form the *double salt* $Cl_2.Rh_2.10NH_3.Cl_4.2PtCl_4$.

Chloropurpureorhodium hydroxide $Cl_2.Rh_2.10NH_3.(OH)_4$. Known only in solution, which is obtained by rubbing the chlorochloride with a little water and moist Ag_2O for a few minutes, and filtering. Reacts strongly alkaline; gives salts by neutralisation with various acids. After warming, the solution contains roseo-chloride, and hydroxide $Rh_2.10NH_3.Cl_2(OH)_4$, along with $Rh_2.10NH_3.(OH)_6$, and gives a pp. with $AgNO_3Aq$.

The other salts of this series are the *chloro-carbonate* $M(CO_3)_2.2aq$, *chloro-nitrate* $M(NO_3)_4$, *silicofluoride* $M(SiF_6)_2$, and *chloro-sulphates* $M(SO_4)_2.4aq$ and $M_2(SO_4)_2.3H_2SO_4$. $M = Cl_2.Rh_2.10NH_3$.

Bromopurpureo- series (Jörgensen, *l.c.*). *Bromopurpureorhodium bromide* $Br_2.Rh_2.10NH_3.Br_4$. Deep-yellow rhombic crystals; S.G. 2·65 at 17·5°; scarcely sol. water. Prepared similarly to the chlorochloride, using HBrAq in place of HClAq; also by dissolving the chlorochloride in 7 p.c. hot NaOHAq, digesting for about an hour at 100°, adding excess conc. HBrAq, washing the pp. which forms with dil. HBrAq and then with alcohol; also by saturating solution of roseo-hydroxide, $Rh_2.10NH_3.(OH)_6$, with dil. HBrAq and heating for some time at 100°. Forms a *double salt* with platinic bromide, $Br_2.Rh_2.10NH_3.Br_4.2PtBr_4$. The *bromo-nitrate*, $Br_2.Rh_2.10NH_3.(NO_3)_4$, and *bromo-silicofluoride*, $Br_2.Rh_2.10NH_3.2SiF_6$, have been isolated.

Iodopurpureo- series (Jörgensen, *l.c.*). *Iodopurpureorhodium iodide* $I_2.Rh_2.10NH_3.I_4$. Prepared by heating the roseohydroxide with excess of HIAq for some time; then transforming the impure product into iodochloride by washing with water, then with alcohol, rubbing repeatedly with dil. HClAq, dissolving in hot water, and filtering into dil. HClAq. The iodo-chloride is then dissolved in hot water and poured into KIAq; the ppd. iodo-iodide is crystallised from hot water. Reddish-yellow, rhombic crystals; S.G. 3·11 at 14·8°; very sl. sol. cold water. Forms a *double salt* with $2PtI_4$. The other salts of this series are the *iodo-chloride* MCl_4, *iodo-nitrate* $M(NO_3)_4$, *iodo-silicofluoride* $M(SiF_6)_2$, and *iodo-sulphate* $M(SO_4)_2.6aq$. $M = I_2.Rh_2.10NH_3$.

Nitratopurpureo- series (Jörgensen, *J. pr.* [2] 31, 49). *Nitratopurpureorhodium nitrate* $(NO_3)_2.Rh_2.10NH_3.(NO_3)_4$. Formed by heating the roseonitrate $Rh_2.10NH_3.(NO_3)_6$ to 100°; also by adding an equal vol. conc. HNO_3Aq to an aqueous solution of the roseonitrate, and heating at 100°. Yellowish-white crystals; deflagrates when heated. The other salts of this series are *nitrato-chloride* MCl_4, and *nitrato-dithionate* $M(S_2O_6)_2$. 2aq. $M = (NO_3)_2.Rh_2.10NH_3$.

Nitritopurpureo- series or *Xantho- series* (Jörgensen, *J. pr.* [2] 31, 49). *Nitritopurpureorhodium nitrate* $(NO_2)_2.Rh_2.10NH_3.(NO_3)_4$ (*Xanthorhodium nitrate*). 5 g. chlorochloride are heated with 50 c.c. water and 30 c.c. NaOHAq (7 p.c.) till dissolved; after cooling, 10 g. crystallised $NaNO_2$ are added and then a slight excess of dil. HNO_3Aq (1 acid : 2 water). The powder which separates after a time is washed with dil. HNO_3Aq, and then with alcohol, and is crystallised from hot water. Octahedral crystals, isomorphous with corresponding Co salt. Insol. alcohol and dilute HNO_3Aq; sl. sol. cold water; easily sol. hot water and conc. HNO_3Aq. No reaction with ordinary reagents for nitrites, *e.g.* KIAq, $KMnO_4Aq$, &c. Conc. H_2SO_4 does not evolve NO_2.

The other salts of this series are: *xantho-bromide* MBr_4, *xanthochloride* MCl_4, *xantho-dithionate* $M(S_2O_6)_2$. 2aq, *oxalate* $M(C_2O_4)_2$, *silicofluoride* $M(SiF_6)_2$, *sulphates* $M(SO_4)_2$ and $M(SO_4)_2.3H_2SO_4$. $M = (NO_2)_2.Rh_2.10NH_3$.

II. Roseorhodium compounds $Rh_2.10NH_3.X_6.2H_2O$. All the atoms of the negative radicle in these salts react similarly; *e.g.* $AgNO_3Aq$ ppts. 6Cl from the chloride. Heated to 100° $2H_2O$ is given off, and purpureo- salts remain. These compounds are generally formed by treating the chloropurpureo- compounds with hot alkali solutions. Many are prepared from the hydroxide by the action of acids (Claus, *l.c.*; Jörgensen, *l.c.*).

Roseorhodium hydroxide $Rh_2.10NH_3.(OH)_6$. Prepared by heating chloropurpureochloride with excess of moist Ag_2O and water for some days, filtering from AgCl, and evaporating *in vacuo*. A yellow deliquescent solid, with strongly alkaline reaction; ppts. metallic hydroxides from salts; decomposes NH_4 salts, giving off NH_3. Neutralises acids, forming roseo- salts.

Roseorhodium bromide $Rh_2.10NH_3.Br_6.2H_2O$. Ppd. by adding conc. HBrAq to solution of the hydroxide; also by boiling chloropurpureochloride with NaOHAq, and then adding excess of conc. HBrAq. Pale-yellow crystals; changes to the purpureo- salt at 100°, or by crystallising from hot water. The other salts of this series are: *carbonate* $M(CO_3)_3.aq$; *iodo-sulphate* $MI_2(SO_4)_2$; *nitrate* $M(NO_3)_6$, and the *double salt* $M(NO_3)_2.PtCl_6$; *phosphate* $M(HPO_4)_3.4aq$, and the *sodium pyrophosphate* $M(NaP_2O_7)_2.23aq$; *sulphate* $M(SO_4)_3.3aq$, and the *double salt* $M(SO_4)_2.PtCl_6$.

III. Luteorhodium compounds $Rh_2.12NH_3.X_6$. These salts are very stable. Their colours are the same as those of corresponding roseo- salts. The chloride can be prepared by heating the chloropurpureochloride with conc. NH_3Aq; most of the other salts are obtained from the chloride (Jörgensen, *J. pr.* [2] 44, 48, 63). The negative radicles are all acted on similarly by reagents.

Luteorhodium chloride $Rh_2.12NH_3.Cl_6$. Prepared by heating chloropurpureochloride with c. 30 times its weight NH_3Aq (25 p.c. NH_3) for several days at 100°–102°, dissolving in hot water, and ppg. by conc. HClAq. S. c. 12 at 8°. Not changed to chloropurpureochloride by digestion with HClAq at 100°. Forms the *double salt* $Rh_2.12NH_3.Cl_6.3PtCl_4.6aq$. The other salts of this series described by Jörgensen are: *bromide* MBr_6, *nitrates* $M(NO_3)_6$ and $M(NO_3)_6.HNO_3$, *phosphate* $M(PO_4)_2.8aq$ and *sodium luteo-pyrophosphate* $M(NaP_2O_7)_2.23aq$, and *sulphate* $M(SO_4)_3.5aq$.

Rhodium-pyridine compounds. Compounds of Rh with pyridine, C_5H_5N, and negative radicles have been prepared by Jörgensen (*J. pr.* [2] 27, 433). The compounds examined contain $8C_5H_5N$, and correspond with the chrom-tetrammonium series of ammoniacal compounds (vol. ii. p. 159), and with the octammine series of ammoniacal Co compounds (vol. ii. p. 225). The composition of these pyridine compounds is represented by the formula $M_4Rh_2(C_5H_5N)_8X_2$; where M = Cl and X = Br, Cl, OH, NO_3 and $\frac{1}{2}SO_4$. The salts resemble the NH_3 compounds generally. The chloride (X = Cl) is prepared similarly to chloropurpureorhodium chloride, using pyridine in place of ammonia; the other salts are prepared from the chloride by the action of acids. $AgNO_3Aq$ ppts. one-third of the halogen only from the chloride and bromide. M. M. P. M.

RHODIZONIC ACID *v.* Di-oxy-diquinoyl.

RHŒADINE $C_{21}H_{21}NO_6$. [232°]. S. (80 p.c. alcohol) ·09. S. (ether) ·08 at 18°. An alkaloid occurring in all parts of the red poppy *Papaver Rhœas*, and in the white seed capsules of the white poppy *Papaver somniferum* (Hesse, *A.* 140, 145; 149, 35; 153, 47). Small white prisms, nearly insol. water, alcohol, and ether. May be sublimed. Tasteless, and not poisonous. Its solution in very weak HCl is colourless, but in conc. HClAq and in H_2SO_4 it forms purple solutions, the base being partially decomposed. The colourless solution is ppd. by tannin and by $HgCl_2$.

Salts.—$B'_2H_2PtCl_6$ 2aq: yellow amorphous pp.—B'HI 2aq: mass of minute prisms.

Rhœagenine $C_{21}H_{21}NO_6$. [223°]. S. (80 p.c. alcohol) ·07. S. (ether) ·06. Formed by boiling rhœadine with dilute H_2SO_4. Small crystals (from alcohol), sl. sol. ether, alcohol, and water, v. sol. dilute acids. Its alcoholic solution turns litmus blue. Cannot be sublimed. Not coloured by acids. Its salts taste bitter.—$B'_2H_2PtCl_6$.—B'HI: short prisms, m. sol. hot water.

RIBONIC ACID $C_5H_{10}O_6$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CH(OH).CO_2H$. *Tetra-oxy-valeric acid.* Formed by heating $CH_2(OH).CH(OH).CH(OH).CH(OH).CO_2H$, arabonic acid, with pyridine in a closed vessel at 130° (E. Fischer a. Piloty, *B.* 24, 4216). When set free from its salts it changes into the lactone.—HgA'_2: needles.—CdA'_2. $[\alpha]_D = 0·6°$. Needles.

Lactone $C_5H_8O_5$. [72°–76°]. $[\alpha]_D = -18°$. Colourless prisms, v. e. sol. water and alcohol, v. sl. sol. ether. Converted by heating with pyridine and water at 135° into arabonic acid. HNO_3 yields tri-oxy-glutaric acid. Phenyl hydrazine forms $C_5H_9O_5(N_2H_2Ph)$ [164°].

RIBOSE ×$C_5H_{10}O_5$. Formed by reducing the lactone of ribonic acid with sodium-amalgam (Fischer a. Piloty, *B.* 24, 4220). Colourless syrup. Yields a phenyl-hydrazide [155°] and a *p*-bromo-phenyl-hydrazide $C_{11}H_{15}O_4N_2Br$ [165°].

RICINELAIDIC ACID $C_{18}H_{34}O_3$. [53°]. Formed by the action of nitrous acid on ricinoleïc acid (Boudet, *A.* 4, 16; Playfair, *A.* 60, 322; Bouis, *A. Ch.* [3] 44, 82; Ulrich, *Bl.* [2] 9, 225). Got also by saponifying ricinelaidin. White silky needles, v. sol. alcohol and ether. Reddens litmus. Yields *n*-heptoic acid on oxidation with HNO_3 (Krafft, *B.* 21, 2735). Alkaline $KMnO_4$ yields two tri-oxy-stearic acids [120°] and [116°] (Grüssner a. Hazura, *M.* 10, 196; Mangold, *M.* 13, 326). Forms oily $C_{18}H_{34}Br_2O_3$, converted by KOHAq in the cold into $C_{18}H_{33}BrO_3$, whence alcoholic potash forms an acid melting at 71°.

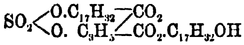
Salts.—BaA'_2: unctuous powder.—AgA': white powder, sol. NH_3Aq.

Ethyl ether EtA'. [16°]. Crystalline.

Amide $C_{18}H_{35}NO_2$. [93°] (Rowney, *Chem. Gaz.* 1855, 361).

Reference.—Bromo-ricinelaidic acid.

RICINELAIDIN. [45°] (Bouis); [66°] (Boudet). Formed by the action of nitrous fumes on castor oil. Solid, v. sol. alcohol and ether. Split up by boiling KOHAq into glycerin and potassium ricinelaidate. Yields heptoic aldehyde (œnanthol) on dry distillation (Bertagnini, *A.* 85, 282). Yields octyl alcohol and potassium sebacate on distillation with potash (Bouis).

RICINIC ACID $C_{18}H_{34}O_3$ *i.e.* $C_{17}H_{32}(OH).CO_2H$. [81°]. (252° at 15 mm.). Formed by distilling barium ricinoleate *in vacuo* (Krafft, *B.* 21, 2736). Plates (from dilute alcohol). Yields, on oxidation by HNO_3, *n*-heptoic acid and an acid [c. 103°] not volatile with steam. Converted by HCl into diricinic acid $C_{17}H_{32}(OH).CO.O.C_{17}H_{32}.CO_2H$, triricinic acid $C_{17}H_{32}(OH).CO.O.C_{17}H_{32}.CO.O.C_{17}H_{32}.CO_2H$, and polyricinic acids. Sulphuric acid forms these acids, as well as $SO_3H.O.C_{17}H_{32}.CO_2H$, $SO_3H.O.C_{17}H_{32}.CO.O.C_{17}H_{32}.CO_2H$, &c. H_2SO_4 acting on castor oil forms the compound  $SO_2<\begin{matrix}O.C_{17}H_{32}-CO_2\\ O.\ C_3H_5<CO_2.C_{17}H_{32}OH\end{matrix}$ and the above acids, constituting Turkey red oil. The polyricinic acids are converted by boiling KOHAq but not by Na_2CO_3 into ricinic acid. Hot water decomposes the polyricino-sulphuric acids into H_2SO_4 and polyricinic acids (Juillard, *Bl.* [3] 6, 638).

RICININE. An alkaloid occurring, according to Tuson (*C. J.* 17, 195; *C. N.* 22, 229; *cf.* Werner, *C. N.* 22, 203), in the seeds of the castor oil plant (*Ricinus communis*). Rectangular prisms or laminæ, insol. water, nearly insol. ether, sol. alcohol.

RICINISOLIC ACID *v.* TRI-OXY-STEARIC ACID.

RICINOLEÏC ACID $C_{18}H_{34}O_3$ *i.e.* $CH_3.[CH_2]_5.CH(OH).CH:CH[CH_2]_8.CO_2H$ (?). [17°]. Occurs as glyceride in castor oil (Bussy a. Lecanu, *J. Ph.* 13, 70; Saalmüller, *A.* 64, 108; Svanberg a. Kolmodin, *J. pr.* 45, 431; Bouis, *A. Ch.* [3] 44, 103; 48, 99; Petersen, *A.* 118, 69). Prepared by saponification of castor oil by KOH or HCl and purified by means of its Ca or Ba salt (Claus, *B.* 9, 1916; Krafft, *B.* 21, 2731). Crystalline mass, miscible with alcohol and ether. Its alcoholic solution is alkaline in reaction. Does not absorb oxygen from the air. Yields $C_{18}H_{33}AcO_3$. Yields polymerides when heated with water in closed vessels (Scheurer-Kestner, *C. R.* 113, 201).

Reactions.—1. Oxidised by HNO_3 to azelaic acid $C_9H_{16}O_4$, oxalic acid, and heptoic acid.—2. Alkaline $KMnO_4$ forms two isomeric tri-oxy-stearic acids (Dieff, *J. pr.* [2] 39, 345; *B.* 20, 1211; Hazura a. Grüssner, *M.* 8, 475; Mangold, *M.* 13, 326).—2. *Nitrous acid* forms ricinelaidic acid.—3. Yields methyl hexyl ketone (173°) and an acid $C_{18}H_{34}O_3$ [81°] on distillation of the Ba salt.—4. The Na salt on distillation with NaOH yields methyl hexyl ketone, *sec*-octyl alcohol and sodium sebacate $Na_2C_{10}H_{16}O_4$.—5. *Bromine* forms oily $C_{18}H_{34}Br_2O_3$, converted by alcoholic potash into $C_{18}H_{33}BrO_3$, whence Br forms oily $C_{18}H_{33}Br_3O_3$, converted by alcoholic potash at 120° into ricinostearolic acid $C_{18}H_{32}O_3$, which combines with bromine forming unstable oily $C_{18}H_{32}Br_4O_3$.—6. PCl_5 forms $C_{18}H_{32}Cl_2O$.—7. HI and P give $C_{18}H_{33}IO_2$.

Salts.—BaA'_2: soft scales (from alcohol), sl. sol. water.—SrA'_2: small grains (from alcohol).—CaA'_2 (dried at 100°). [80°].—MgA'_2: slender needles, v. sol. alcohol.—PbA'_2. [100°]. Crystalline mass, v. sol. ether.—ZnA'_2.—AgA': curdy pp.

Ethyl ether EtA'. Oil.

Amide $C_{17}H_{33}.CONH_2$. [66°]. Nodules (from alcohol).

References.—BROMO- and OXY- RICINOLEÏC ACID.

RICINOLIC ACID *v.* TRI-OXY-STEARIC ACID.

RICINOSTEAROLIC ACID $C_{18}H_{32}O_3$. [51°]. Formed by heating the dibromide of ricinoleïc acid with alcoholic potash (Ulrich, *Z.* 1867, 547). Groups of needles (from alcohol), v. sol. ether. Volatile.—BaA'_2: plates (from alcohol) [135°].—AgA': granular pp.

RICINOSTEAROXYLIC ACID $C_{18}H_{32}O_4$. [78°]. Formed by heating ricinostearolic acid with moist Ag_2O (Ulrich, *Z.* 1867, 550). Dendritic groups of needles (from alcohol), v. sol. ether.—BaA'_2.—AgA'; granular pp. decomposed by hot alcohol.

ROBININ $C_{25}H_{30}O_{16}$. [195°]. Occurs in the blossoms of the acacia (*Robinia pseudacacia*) (Zwenger a. Dronke, *A. Suppl.* 1, 257). Thin yellow needles (containing 5½ aq). Neutral in reaction. Tasteless, sl. sol. cold water and alcohol, insol. ether. Sol. alkalis, forming yellow solutions. The ammoniacal solution turns brown in air. $FeCl_3$ gives a brown colour. Its alcoholic solution is ppd. by lead subacetate. Reduces hot Fehling's solution. HNO_3 forms oxalic and picric acids. Split up by boiling dilute acids into quercetin and a sugar.

ROCCELLIC ACID $C_{17}H_{32}O_4$. [132°]. S. (boiling alcohol of S.G. ·819) 55. Occurs in various species of *Roccella* (Heeren, *S. J.* 59, 346; Liebig, *P.* 21, 31; Schunck, *A.* 61, 64; Hesse, *A.* 117, 332). Four-sided prisms, insol. water, v. sol. alcohol and ether, sl. sol. warm benzene. Sol. Na_2CO_3Aq and borax.

Salts.—BaA'' (dried at 100°).—CaA''aq: amorphous pp.—$Pb_3A''_2(OH)_2$2aq: white powder.—Ag_2A'': amorphous pp.

Ethyl ether Et_2A''. Oil.

Anhydride $C_{17}H_{30}O_3$. Got by heating the acid above 220°. Oil, v. sol. hot alcohol and ether.

Anilide $C_{17}H_{30}O_2(NHPh)_2$. [55°]. Got by heating the acid with aniline at 190°. Colourless laminæ (from alcohol), insol. water, NH_3Aq, and HClAq.

ROCCELLININ $C_{18}H_{16}O_7$. Occurs in *Roccella tinctoria* (Stenhouse, *A.* 68, 69). Silky needles (from alcohol), nearly insol. cold alcohol and ether. Its solutions in alkalis are not coloured by air. Not decomposed by boiling KOHAq. Does not pp. metallic salts.

ROCHELLE SALTS. *Potassium-sodium tartrate*; *v.* TARTRATES.

ROSANILINE $C_{20}H_{21}N_3O$ *i.e.* $([4:1]C_6H_4(NH_2))_2C(OH).C_6H_3Me(NH_2)[1:3:4]$. *Tri-amido-di-phenyl-tolyl-carbinol.* Formed by oxidation of a mixture of aniline, *o*-toluidine, and *p*-toluidine (Hofmann, *J. pr.* 77, 190; 87, 226; *Pr.* 12, 2; Mühlhäuser, *D. P. J.* 266, 455, 503, 547). $SnCl_4$, As_2O_5, HNO_3, $Hg(NO_3)_2$, $FeCl_3$, and nitrobenzene may be used as oxidising agents. For the production of a red colouring matter it is essential that there should be present a base with methyl in the *p*- position to amidogen (*p*-toluidine, (1,3,4)-xylidine, or mesidine), and also a base with H in the *p*- position to amidogen (*e.g.* aniline, *o*-toluidine, or (1,3,2)-xylidine) (Rosenstiehl, *C. R.* 82, 415; 94, 1319; 95, 238; 98, 433; *A. Ch.* [6] 2, 360). When nitro-benzene is used as oxidising agent it appears to be itself reduced to benzene and

nitrogen, and not to take part in the formation of rosaniline. Thus, when chloro-nitro-benzene, nitro-aniline, or di-nitro-benzene is used, a substituted rosaniline (*e.g.* chloro-rosaniline) is not formed (Lange, *B.* 18, 1918). Colourless needles or plates, obtained by ppg. a solution of one of its salts with NH_3Aq and recrystallising. Nearly insol. water, sl. sol. NH_3Aq, m. sol. alcohol, insol. ether. Turns red in air. Dyes silk and wool in acid, neutral, and even in slightly ammoniacal solutions.

Reactions.—1. Reduced by ammonium sulphide or powdered zinc to tri-amido-di-phenyl-tolyl-methane (leucaniline) (Hofmann, *Pr.* 12, 2).—2. Yields alkyl derivatives on heating with *alkyl iodides* and phenyl derivatives on heating a salt with aniline (Hofmann, *Pr.* 13, 9). Benzyl chloride, methyl iodide, and MeOH form $C_{20}H_{16}(C_7H_7)_3N_3MeI$, crystallising in lustrous green needles (Hofmann, *B.* 6, 263).—3. The hydrochloride, heated with *water* at 235°, forms NH_4Cl, phenol, red crystals of $C_{20}H_{20}N_2O_2$ [176°], and colourless crystals, which turn red in air and then crystallise from alcohol in red needles $C_{20}H_{19}NO_3$ (Liebermann, *B.* 5, 144; 6, 951).—4. The hydrochloride, heated with dilute HClAq at 240°, yields aniline and toluidine (L.).—5. *Water* at 270° forms di-oxy-benzophenone, di-amido-phenyl-tolyl-ketone, oxy-amido-phenyl-tolyl-ketone, phenol, and NH_3 (Liebermann, *B.* 6, 951; 11, 1435; 16, 1927).—6. *Potassium cyanide* added to rosaniline acetate in alcohol yields $C_{21}H_{20}N_4$, a white crystalline powder, sol. HClAq, and reppd. by NH_3Aq. It separates from alcohol in monoclinic crystals. It forms crystalline salts.—7. A solution of a rosaniline salt is decolourised by SO_2, and the solution is turned red, and afterwards violet, by aldehydes, and gradually deposits copper-coloured scales of alkylidene derivatives (Schiff, *Bl.* [2] 7, 518). Thus œnanthol forms $C_6H_{13}.CH{:}C_{20}H_{17}N_3$, which yields $B'HAsO_2$ and $B'H_2PtCl_6$.—8. *Œnanthol* reacts with rosaniline acetate in the cold, forming $(C_7H_{14})_3(C_{20}H_{16}N_3)_2$ (Schiff, *Bl.* [2] 5, 291).—9. By exhaustive chlorination it yields CCl_4 and per-chloro-benzene (Merz a. Weith, *B.* 16, 2876).—10. Boiling Ac_2O yields a tetra-acetyl derivative as a reddish amorphous powder. The same body is got by treating tri-acetyl-tri-amido-di-phenyl-tolyl-methane with $K_2Cr_2O_7$ and HOAc (Renouf, *B.* 16, 1303). A mono-acetyl derivative $C_{20}H_{18}AcN_3$, got by heating rosaniline hydrochloride with acetamide, is reddish-brown and yields dark-blue B'HCl with metallic lustre (Beckerhinn, *J.* 1870, 768).—11. May be sulphonated by H_2SO_4 containing SO_3 at 130° (Schoop, *Chem. Zeit.* 11, 572).—12. By diazotisation followed by reduction with tin and HCl in the cold it is converted into 'roshydrazide,' the hydrochloride of which forms green crystals, and dyes cotton brownish-red (Ziegler, *B.* 20, 1557).—13. Br forms a tetra-bromo-rosaniline (?) crystallising from benzene in prisms (Caro a. Graebe, *A.* 179, 203).—14. *Aldehyde* forms a blue product which is converted by $Na_2S_2O_3$ into aldehyde green $C_{22}H_{27}N_3S_2O$, an amorphous green mass, sol. alcohol and ppd. by ether (Cherpin; Usèbe, *J. pr.* 92, 337; Hofmann, *B.* 3, 761; Gattermann, *B.* 22, 227).

Salts.—These are derived from the anhydrous base $C_7H_7N{:}C(C_6H_4.NH_2)_2$.—$C_{20}H_{19}N_3HCl$. Red crystals with green lustre. Insol. ether, sl. sol. water, m. sol. alcohol. Its solution in water or alcohol is crimson. Dyes wool and silk magenta. The absorption-spectrum has been studied by Hartley (*C. J.* 51, 169).—$C_{20}H_{19}N_3 3HCl$. Ppd. by conc. HClAq. Yellowish-brown needles, more sol. alcohol and water than B'''HCl.—Decomposed by much water, forming B'''HCl.—$C_{20}H_{19}N_3 4HCl$ or $(C_7H_6NH_3Cl).CCl(C_6H_4NH_3Cl)_2$. Got by passing dry HCl into rosaniline powder (Rosenstiehl, *Bl.* [3] 9, 122). Reddish-brown and hygroscopic, forming a magenta solution. Fumes in air, giving off HCl. After keeping it is not completely soluble.—$C_{20}H_{19}N_3 4HBr$. Resembles the preceding salt.—$C_{20}H_{19}N_3HOAc$. Large crystals with green metallic lustre; v. sol. water and alcohol.—$(C_{20}H_{19}N_3)_2H_2PtCl_6$. Amorphous.—$(C_{20}H_{19}N_3)_2 3H_2PtCl_6$.—$C_{20}H_{19}N_3HBr$. Sl. sol. water.—$C_{20}H_{19}N_3HI$. Green needles, v. sol. water.—$C_{20}H_{19}N_3HNO_3$: small crystals.—$(C_{20}H_{19}N_3)_2H_2SO_4$ (dried at 130°). Crystals with green lustre. Does not form an alum with $Al_2(SO_4)_3$ (Wood, *C. N.* 38, 1).—$C_{20}H_{19}N_3C_6H_3N_3O_7$. Red needles, very slightly sol. water.—$(C_{20}H_{19}N_3)_2H_2C_2O_4$ aq.—Tannate: ppd. by adding tannin to an aqueous solution of a salt of rosaniline. Red mass, insol. water, sol. alcohol and HOAc (E. Kopp, *J.* 1862, 694).—Aurinate: Got by heating equivalent quantities of rosaniline and aurin with alcohol (Dale a. Schorlemmer, *C. J.* 43, 186). Hexagonal crystals with green lustre (Dyson, *C. J.* 43, 471). More sol. alcohol than either constituent. Dyes silk magenta.—Phenate $C_{20}H_{19}N_3C_6H_6O$. Got by heating rosaniline with phenol, dissolving in alcohol, and ppg. with water (Dyson, *C. J.* 43, 470).

Para-rosaniline $C_{19}H_{19}N_3O$ *i.e.* $([1{:}4]C_6H_4(NH_2))_3COH$. *Tri-amido-tri-phenyl-carbinol.*

Formation.—1. From tri-nitro-tri-phenyl-methane by oxidation by CrO_3 and HOAc followed by reduction of the resulting tri-nitro-tri-phenyl-carbinol with zinc-dust and HOAc (E. a. O. Fischer, *B.* 11, 195, 473, 612, 1079, 1598; *A.* 194, 242).—2. By heating a mixture of aniline and *p*-toluidine with arsenic acid (Rosenstiehl, *A. Ch.* [5] 8, 192); formed therefore in the preparation of rosaniline (Graebe, *B.* 12, 2241).—3. By heating *p*-nitro-di-amido-tri-phenyl-methane with $FeCl_2$ at 170° (O. Fischer, *B.* 15, 678).—4. By heating *p*-nitro-benzylidene bromide with aniline (Zimmermann a. Müller, *B.* 17, 2936).—5. Hy heating aurin with NH_3Aq at 180° (Dale a. Schorlemmer, *B.* 10, 1016).—6. By heating di-amido-di-phenyl-methane (from aniline and formic aldehyde) with aniline, aniline hydrochloride, and nitro-benzene or arsenic acid.

Properties.—Crystalline plates. Nearly colourless; sl. sol. water; absorbs CO_2 from air. Its solution in conc. HClAq is coloured grass-green by a crystal of $KClO_3$.

Reactions.—1. Yields *o*-toluidine and di-amido-benzophenone [237°] on boiling with HClAq for a long time (Wicnelhaus, *B.* 19, 110). 2. HIAq at 190° forms aniline and *p*-toluidine 3. *Nitrous acid* forms the tri-diazo- derivative, which on boiling is converted into aurin.—4. Reduced by *zinc-dust* and HClAq to tri-amido-tri-phenyl-methane.—5. KCy added to its hydrochloride in presence of alcohol forms 'hydro-

cyanpararosaniline' $C_{19}H_{17}N_3HCN$, crystallising from hot alcohol in colourless prisms, forming $B'H_3Cl_3$ 2aq.—6. Pararosaniline (5 g.) is slowly converted by conc. HClAq (55 g.), water (55 g.), and aldehyde (22 g.) in the cold into aldehyde-blue, a dark-blue hygroscopic powder, ppd. by adding NaCl to the product after dilution with water (Gattermann, *B.* 22, 227). Aldehyde blue yields, on distillation, a solid base $C_{10}H_9N$.

Salt.—$C_{10}H_{18}N_3Cl$. S. ·24 at 9°.

Tri-methyl-rosaniline *v.* TRI-METHYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL.

Hexa-methyl-pararosaniline *v.* HEXA-METHYL-TRI-AMIDO-TRI-PHENYL-CARBINOL.

Phenyl-rosanilines *v.* HEXA-PHENYL-TRI-AMIDO-TRI-PHENYL-CARBINOL and TRI-PHENYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL.

ROSEÏNE. A name for salts of ROSANILINE.

ROSEMARY OIL. S.G. $\frac{15}{\ }$ ·905. $\alpha = +42'$ to $+9°\,48'$ in 100 mm. (Schimmel, *Ph.* [3] 21, 940; 22, 328). Obtained by steam-distillation from *Rosmarinus officinalis* (Kane, *Trans. Irish Acad.* 18, 135; Lallemand, *A.* 114, 197; *A. Ch.* [3] 57, 404; Gladstone, *J.* 1863, 549; Montgolfier, *Bl.* 1876, 18; Bruylants, *J. Ph.* [4] 29, 508). Contains a terpene (165°), dextrorotatory camphor, borneol, and cineol $C_{10}H_{18}O$ (176°–179°) (Weber, *A.* 238, 89). The cineol forms a hydrochloride $(C_{10}H_{18}O)_2HCl$, a tetra-bromide [124°], and the iodide $C_{10}H_{18}I_2$ [79°].

ROSE OIL. Obtained by steam-distillation from rose leaves. Contains a stearoptene $C_{16}H_{34}$ [34°] (365°) which is not attacked by chromic acid mixture and appears to be a paraffin (Markownikoff, *B.* 23, 3191; *J. pr.* [2] 48, 311; *cf.* Blanchet, *A.* 7, 154; Gladstone a. Dale, *C. J.* 17, 1; Salkülünski, *N. R. P.* 24, 129; Bauer, *D. P. J.* 204, 253; Flückiger, *Z.* [2] 6, 126; Panajotoff, *B.* 24, 2700; Eckart, *B.* 24, 4205). Rose oil also contains rhodinol (*q.v.*). Bulgarian oil of roses contains roseol $C_{10}H_{20}O$ (225° cor.), which is oxidised by $KMnO_4$ to $C_{10}H_{19}(OH)_3$ (240°) S.G. $\frac{0}{0}$ 1·0445; $\frac{20}{0}$ 1·0343; and is reduced by HI to $C_{10}H_{22}$ (159°) S.G. $\frac{0}{0}$ ·7700; $\frac{20}{0}$ ·7554 (Ladenburg, *J. pr.* [2] 48, 293).

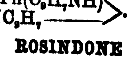
ROSEOCOBALT SALTS *v.* COBALTAMINES, vol. ii. p. 226.

ROSEOCHROMIUM SALTS *v.* CHROM-AMMONIUM SALTS, vol. ii. p. 160.

ROSEORHODIUM SALTS *v.* RHODIUM-AMMONIUM COMPOUNDS, this vol. p. 407.

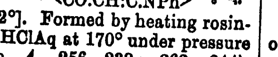
ROSEWOOD OIL. The oil got by steam-distillation from the wood of *Convolvulus scoparius* contains a terpene $C_{10}H_{16}$ (249°) (Gladstone a. Dale). Rosewood also contains a black resin $C_{21}H_{21}O_6$ [95°] S.G. $\frac{15}{\ }$ 1·266, which is insol. water, sol. alcohol, and gives a blood-red colour with H_2SO_4 (Terreil a. Wolff, *Bl.* [2] 33, 435).

ROSINDOLES. Red colouring matters, greatly resembling rosaniline, formed by heating indoles with BzCl, and by oxidation of benzylidene derivatives of indoles (E. Fischer a. Wagner, *B.* 20, 815). Thus methyl-ketole yields dimethyl rosindole, $C_{25}H_{20}N_2$, which may possibly be



$$\left.\begin{array}{l}CPh(C_9H_7NH)\\ NC_9H_7\text{———}\end{array}\right>.$$

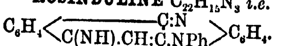
ROSINDONE



$$C_6H_4\left<\begin{array}{l}\text{————}C{:}N\\ CO.CH{:}C.NPh\end{array}\right>C_6H_4.$$

Rosindulone. [262°]. Formed by heating rosinduline with conc. HClAq at 170° under pressure (Fischer a. Hepp, *A.* 256, 238; 262, 244). Formed also from oxy-naphthoquinone and phenyl-*o*-phenylene-diamine (Kehrmann, *J. pr.* [2] 43, 269; *B.* 24, 586). Red hexagonal tables, insol. hot water, m. sol. boiling alcohol, forming a scarlet solution with brick-red fluorescence. Reduced to naphthophenazine by distilling in a current of H over zinc-dust. Converted by *p*-toluidine at 130° into *p*-tolyl-rosinduline. Oxidised by CrO_3 to rosindonic acid $C_{22}H_{14}N_2O_3$, which crystallises in colourless needles, sl. sol. alcohol, insol. water, v. sol. ether.

ROSINDULINE $C_{22}H_{15}N_3$ *i.e.*



$$C_6H_4\left<\begin{array}{l}\text{————}C{:}N\\ C(NH).CH{:}C.NPh\end{array}\right>C_6H_4.$$

[199°].

Formed by heating benzene- azo- (α)-naphthylamine with aniline and alcohol at 165° under pressure (Fischer a. Hepp, *A.* 256, 236). Formed also by heating phenyl-*o*-phenylene-diamine with oxy-naphthoquinone imide, HOAc, and alcohol at 100° (Kehrmann, *J. pr.* [2] 43, 269; *B.* 24, 587). Reddish-brown plates, v. sol. alcohol and ether, insol. water. Conc. H_2SO_4 forms a green solution, becoming red on dilution. The alcoholic solutions exhibit reddish-yellow fluorescence.—B'HCl $3\frac{1}{2}$aq: red needles.

Rosinduline. This name has also been given to the phenyl derivative of the preceding body (*v.* vol. iii. p. 9).

ROSOLIC ACID *v.* TRI-OXY-DI-PHENYL-TOLYL-CARBINOL and TRI-OXY-TRI-PHENYL-CARBINOL.

ROTTLERIN $C_{11}H_{10}O_3$? [200°]. A yellow substance occurring in the fruit of *Rottlera tinctoria*, which grows in India (Anderson, *N. Ed. P. J.* [2] 1, 300; Jawein, *B.* 20, 182). It is identical with Mallotoxin (*q. v.*).

RUBAZONIC ACID $C_{20}H_{17}N_5O_2$. Formed by oxidation of oxy-amido-phenyl-methyl-pyrazole (Knorr, *A.* 238, 137). Got also by boiling pyrazole-blue with NH_3Aq. Prepared from the phenyl-hydrazide of oxy-phenyl-methyl-pyrazole by reduction with zinc-dust and HOAc, followed by oxidation with $FeCl_3$ (Buchka a. Sprague, *B.* 22, 2551). Insol. water and dilute acids, v. sol. ether and benzene. Its solutions in alkalis are deep violet, but on boiling become yellow.

RUBERYTHRIC ACID $C_{26}H_{28}O_{14}$ *i.e.* $C_{14}H_6O_2(OH).O.C_{12}H_{14}O_3(OH)_7$. *Rubianic acid.* [260°]. Obtained from madder-root by extracting with boiling absolute alcohol (Rochleder, *A.* 80, 321; 82, 205; Schunck, *A.* 66, 176; Liebermann a. Bergami, *B.* 20, 2241). Lemon-yellow needles, v. sol. hot water, v. sl. sol. alcohol, insol. ether. Its alcoholic solution is yellow. Alkalis form blood-red solutions. It does not ferment with yeast. Boiling dilute acids split it up into alizarin and sugar. Ac_2O and NaOAc yield $C_{26}H_{20}Ac_8O_{14}$, crystallising in yellow needles [230°].—$C_{26}H_{27}KO_{14}$.—BaA'_2 aq.

RUBIAN $C_{28}H_{34}O_{15}$. A glucoside in madder root, split up by acids, alkalis, or the madder-ferment (erythrozym) into glucose, alizarin, and other bodies (Schunck, *P. M.* [4] 12, 200, 270; *J. pr.* 59, 465). Amorphous resin, v. sol. water, m. sol. alcohol, insol. ether. Its solutions are very bitter. Yields ruberythric acid on treatment with baryta. It is probably a mixture of ruberythric acid and other bodies.

RUBIANIC ACID *v.* RUBERYTHRIC ACID.

RUBIDINE. A general name for homologues of pyridine of the formula $C_{11}H_{17}N$, *e.g.* DI-METHYL-ISOBUTYL-PYRIDINE.

Rubidine $C_{11}H_{17}N$. (230°). S.G. ^{22} 1·017. Occurs in coal-tar (Thenius, *Rep. Chim. app.* 4, 181). Liquid, sl. sol. water, miscible with alcohol and ether. Its salts redden in the air. Bleaching-powder gives a red colour. Colours acidified fir-wood red. — $B'_2H_2PtCl_6$: reddish crystalline powder.

RUBIDIUM. Rb. At. w. 85·2. Mol. w. unknown. Melts at c. 38·5° (Bunsen, *A.* 125, 367). S.G. c. 1·52 (B., *l.c.*). Refraction-equivalent 12·1 (Gladstone, *Pr.* 18, 49); 11·6 (Kannonikoff, *J. R.* 1884 [1] 119). Chief lines in emission-spectrum are two in the red, Rb_δ and Rb_γ, 7800 and 6297; and two in the violet, Rb_β and Rb_α, 4216 and 4206 (Kirchoff a. Bunsen, *P.* 113, 337; Lecoq de Boisbaudran, *Spectres lumineux* [1874] 46; *v.* also *B. A.* 1884. 438). Beketoff (*J. R.* 1888. 363) gives $[Rb^2,O] = 94,900$.

Occurrence.—Never free. Salts are widely distributed, but in very small quantities, along with salts of Cs, and frequently also salts of Li, K, and Na. Many *lepidolites* contain Rb salts amounting to c. ·24 p.c. Rb (K. a. B., *P.* 113, 337; 119, 1; Grandeau, *A. Ch.* [3] 67, 155; Allen, *Am. S.* [2] 34, 367). Traces of Rb salts have been found in specimens of *orthoclase* (Erdmann, *J. pr.* 86, 377, 448; Laspeyres, *A.* 134, 349; *petalite* (Grandeau, *l.c.*); *micas* (Schrötter, *J. pr.* 85, 458); *basalt* (Engelbach, *A.* 135, 126); *carnallite* (Erdmann, *l.c.*); in *alum* obtained on the island of Volcano (Cossa, *Acc. dei Lincei*, 11, 9); *saltpetre* (Dieulafait, *C. R.* 98, 1545). Small quantities of Rb salts, varying from c. ·0002 to c. ·03 g. RbCl per litre, occur in mineral springs (*v.* Bunsen, *A.* 122, 347: Grandeau, *A. Ch.* [3] 67, 155; Schrötter, *J. pr.* 85, 458; Redtenbacher, *J. pr.* 85, 458; Böttger, *J. pr.* 89, 378). Traces of Rb salts have been found in *sea water* (Sonstadt, *C. N.* 22, 25, 44); in *fumaroles* giving out boric acid (Hofmann, *J. C. T.* 1863. 354); in *coffee*, *tea*, *cocoa*, and *tobacco* (Grandeau, *l.c.*); in the ashes of *beetroot* (G., *l.c.*; Lefèvre, *C. R.* 55, 430); in the *ashes of various plants* (von Than, *A. Suppl.* 2, 84); in normal human *urine* (Schiaparelli a. Peroni, *G.* 10, 390). According to Lockyer a well-marked Rb line occurs in the solar spectrum (*Pr.* 27, 279).

Historical.—In 1860 Bunsen applied the method of spectroscopic analysis, then being worked out by him along with Kirchoff, to the examination of the residue obtained by evaporating very large quantities of the water from a mineral spring at Dürkheim. Two red lines appeared which were not known to belong to any element. By further investigation Bunsen separated the chloride of the element, and on electrolysing the molten chloride he obtained metallic globules, which rose to the surface and took fire. By strongly heating an intimate mixture of the carbonate of the new element with finely divided charcoal and distilling into a receiver under rock-oil, Bunsen obtained the metal in some quantity. The name rubidium was given because of the characteristic lines in the red part of the spectrum (*ruber* = dark red) (*v.* Bunsen, *A.* 113, 337; 122, 347).

Formation.—1. By distilling the mixture of Rb_2CO_3 and C obtained by carbonising Rb.H tartrate (Bunsen, *l.c.*; Setterberg, *A.* 211, 100).—2. By distilling a mixture of RbOH and Al (Beketoff, *J. R.* 1888. 363).—3. By passing a strong electric current through molten RbCl, the positive electrode being graphite, and the negative an iron wire, globules of Rb rise to the surface, and there take fire. If the negative electrode is surrounded with H (*v.* Lithium, vol. iii. p. 148), a smalt-blue substance is formed, which dissolves in water with formation of RbOH and H; this blue solid is probably a lower chloride than RbCl, perhaps Rb_2Cl (Bunsen, *l.c.*).

Preparation.—The saline residues from the manufacture of lithium compounds from Saxon lepidolite (at Struve's works in Leipzig) were found by Bunsen (*l.c.*), Heintz (*J. pr.* 87, 310), and Erdmann (*J. pr.* 86, 294) to be rich in Rb salts. The specimen examined by Bunsen contained 19·75 p.c. RbCl. Cossa (*B.* 11, 811) recommended the natural alum from the island of Volcano as a good raw material for preparing Rb salts.

1. Bunsen's method (*A.* 122, 351) for separating Rb is based on the different solubilities in water of the platinochlorides of K, Rb, and Cs; these solubilities at 17° are in the ratio of 15:2:1. One kilo. of the saline residue from the preparation of Li compounds from Saxon lepidolite is dissolved in 2·5 kilos. water, and ppd., when cold, by 30 g. Pt in *aqua regia*. After settling the liquid is drawn off, and the pp. is boiled 25 times in succession with small quantities of water (1·5 kilos. in all), each portion being poured into the liquid which was drawn off from the pp. by the $PtCl_4$. The 4 kilos. of liquid and washings are evaporated to 2·5 kilos. While this evaporation is proceeding, the washed platinochloride pp. is dried at 100°, heated nearly to redness in a stream of H until a mixture of Pt with RbCl, and perhaps a little CsCl, remains (if the solid melts reduction is incomplete); and the RbCl is dissolved out in hot water. The Pt which remains is dissolved in *aqua regia*, and added to the liquid which has been evaporated. The pp. is washed with small quantities of water as before, dried, and reduced in H, the supernatant liquid and washings being evaporated. The reduced Pt is dissolved and added to the liquid, and so on. These processes are repeated seven or eight times. From 1 kilo. material Bunsen obtained ·125 kilo. RbCl, containing 3-4 p.c. KCl and a little CsCl. To separate KCl, the approximately pure RbCl is dissolved in water (36 g. in 1 litre), heated to boiling, and a boiling solution of $PtCl_4$ (30 g. Pt in *aqua regia*, diluted to 1 litre) is added; the pp. is washed repeatedly with water at 40°–50°, then dried, and reduced in H; the RbCl is dissolved in water, and the Pt in *aqua regia*, and these processes are repeated until the RbCl shows no trace of the red lines of K in the spectroscope. Finally, Bunsen separated CsCl by transforming the chlorides into carbonates, and treating the powdered salts with boiling absolute alcohol until the insoluble RbCl ceased to show the blue lines of Cs in the spectroscope (RbCl is insoluble, while CsCl dissolves, in absolute alcohol). This process has been modified by Heintz (*J. pr.* 87, 310), Grandeau (*A. Ch.* [3] 67, 155), Piccard (*J. pr.* 86, 449), Böttger (*J. pr.* 89, 378), Schrötter (*J. pr.* 85, 458), de Boisbaudran (*Bl.* [2] 17, 551), and others.

2. Redtenbacher's method (*J. pr.* 95, 148) is

based on the different solubilities of the alums of K, Rb, and Cs; the solubilities in water, at 17°, are as 22:4:1. The method has been modified by Stolba (*J. pr.* 99, 49), Godeffroy (*A.* 181, 176), Petersen (*D. P. J.* 224, 176), Cossa (*B.* 11, 811), Setterberg (*A.* 211, 100), Robinson a. Hutchins (*C. N.* 49, 253). The mother-liquor from which Li_2CO_3 has been separated by Schrötter's method (vol. iii. p. 149) is evaporated with H_2SO_4Aq, with addition of $Al_2(SO_4)_3$, whereby Rb and Cs alums are obtained mixed with K alum. Or lepidolite may be decomposed by heating with H_2SO_4 and CaF_2, the residue boiled with five or six volumes water, KOH added equal to 5 p.c. of the quantity of lepidolite used, the whole boiled with water, and filtered hot, when the alums crystallise out on cooling (Stolba, *l.c.*). The alums are dissolved in half their weight of boiling water, half as much cold water is added, and after stirring the whole is let cool to 45°, when almost all the Rb and Cs alums separate, leaving much K alum in solution. The solution in water, and cooling, are repeated, temperature being allowed to fall to 40°; the alum which separates is dissolved in water equal to half the weight of the original quantity of mixed alums, boiled for some time, and allowed to cool to 60° while being stirred. The crystals which separate are almost pure Cs alum; the mother-liquor, when evaporated, yields almost pure Rb alum.

To prepare the metal, RbCl or Rb alum can be transformed into RbOH, and Rb prepared therefrom; or the RbOH may be dissolved in the proper quantity of tartaric acid to form RbH tartrate, which may then be charred, and Rb obtained from the mixture of Rb_2CO_3 and C so formed.

To prepare RbOH, the RbCl is converted into Rb_2SO_4 by H_2SO_4Aq, the Rb_2SO_4 is dissolved in water, boiled, BaOAq is added, the liquid being kept boiling. $BaSO_4$ is removed by decantation, and the liquid is evaporated to dryness in a silver dish as quickly as possible. RbOH is obtained from Rb alum by dissolving in hot water, ppg. Al_2O_3 by slight excess of NH_3Aq, filtering hot, evaporating to dryness in a Pt dish, strongly heating till $(NH_4)_2SO_4$ is removed, and then proceeding to decompose the Rb_2SO_4 by BaOAq as already described. RbOH is mixed with Al clippings in the ratio 2RbOH:Al (= 1 part Al to 7·5 parts RbOH), and the mixture is heated to full redness in a furnace, in an iron cylinder, connected by an iron tube with a glass receiver. The Rb distils over, and appears like Hg in the receiver. As H is given off, the Rb is surrounded by a non-oxidising atmosphere ($4RbOH + 2Al = Rb_2O.Al_2O_3 + 2Rb + 2H_2$). From 28 to 33 p.c. of the Rb in RbOH is obtained (Beketoff, *J. R.* 1888. 363; abstracts in *C. J.* 58, 108, and *B.* 21, *Ref.* 424). For a description of the method of preparing Rb from Rb_2CO_3 and C *v.* Bunsen (*A.* 125, 367) and Setterberg (*A.* 211, 100). An explosive compound similar to the compound of K and CO (this vol. p. 300) is liable to be formed.

For a method of separating Rb from Cs and K, based on the formation of double compounds of RbCl with $SbCl_3$, and with $SnCl_4$, *v.* Muthmann (*B.* 26, 1019 [1893]).

Properties.—A very lustrous, white metal, with an extremely faint tinge of yellow. Soft as wax, even at −10°; melts very easily (c. 38·5°). Lighter than water. Bunsen (*A.* 125, 367) made one determination of S.G., which gave 1·52, but the result is not final. Heated in absence of O, the metal distils below redness, forming a blue vapour. Rb dissolves in liquid NH_3 (Seeley, *C. N.* 23, 169). When exposed to air Rb is at once covered with a greyish-blue film, which is supposed to be a suboxide; much heat is produced, and the metal soon takes fire. Decomposes cold water very rapidly, with evolution of H, which takes fire. Rb is the most positive element next to Cs. It closely resembles K in its chemical relations (*v.* ALKALIS, METALS OF THE, vol. i. p. 114). The at. w. of Rb has been determined (1) by determining Cl in RbCl by Bunsen (*P.* 113, 339; 115, 584 [1861]), Piccard (*J. pr.* 86, 454 [1862]), and Godeffroy (*A.* 181, 189 [1875]); (2) by determining V.D. of RbCl and RbI at c. 1200° (Scott, *Pr. E.* 14, 410). The S.H. of Rb has not been determined; but from observations of the molecular heats of RbCl and Rb_2CO_3, and comparisons of these with those of the corresponding salts of metals that have normal atomic heats, it is probable that the atomic heat of Rb is c. 6·4, and, therefore, that the S.H. is c. ·075. The atom of Rb is monovalent in the gaseous molecules RbCl and RbI.

Reactions and Combinations.—1. Rapidly oxidises in *air*; much heat is produced, and the metal ignites. Beketoff (*J. R.* 1888. 363) gives $[Rb^2,O] = 94{,}900$.—2. Decomposes cold *water*, with rapid evolution of H and production of RbOHAq; Beketoff (*l.c.*) gives $[Rb,H^2OAq] = 96{,}400$, with formation of RbOHAq and H.—3. Burns in vapour of *chlorine*, *bromine*, *iodine*, *sulphur*, and *arsenic*, forming compounds with those elements (Bunsen, *l.c.*).

Detection and Estimation. — Phosphomolybdic acid gives a yellow pp. insol. acids (Debray, *Bl.* [2] 5, 404). Silicotungstic acid ($SiW_{12}O_{42}H_8.xH_2O$) ppts. Rb salts, but not salts of K (Godeffroy, *B.* 9, 1365). As Cs salts are ppd. by $SbCl_3$ in conc. HClAq, added to solutions containing conc. HCl (as $6CsCl.SbCl_3$), while Rb salts give no pp., Rb can be separated from Cs salts by addition of HClAq and $SbCl_3$ in HClAq (G., *B.* 8, 9). Rb is best detected by the spectroscope. The most characteristic lines are in the blue-violet, $Rb_\alpha (\lambda = 4206)$, and $Rb_\beta (\lambda = 4216)$: ·0002 mgm RbCl can be detected (Bunsen, *l.c.*). Rb is determined in the form of RbCl. For the separation of Rb from K, and estimation of the Rb, *v.* Bunsen (*l.c.*). Bunsen determined RbCl in presence of CsCl by finding the sum of the two chlorides, then estimating the total Cl, and calculating the quantity of each salt.

Rubidium, amalgam of. When conc. RbClAq is electrolysed, using Hg as negative electrode, a solid, white, lustrous, crystalline amalgam is formed. Decomposes cold water rapidly; becomes oxidised superficially in air, and then deliquesces with formation of RbOH. Is electropositive to K amalgam (Bunsen, *A.* 122, 347).

Rubidium, bromide of. RbBr. Formula probably molecular, from analogy of RbCl and RbI. Formed by burning Rb in Br. Also by saturating HBrAq with Rb_2CO_3, and evaporating

White, lustrous, regular octahedra. S. 98 at 5°, 104·8 at 16° (Reissig, *A.* 127, 33). Melts at c. 683° (Carnelley, *C. J.* 33, 279). Combines with IBr, to form RbBr.IBr; and with Br to form $RbBr.Br_2$ (Wells a. Wheeler, *Am. S.* [3] 43, 475).

Rubidium, chloride of. RbCl. Mol. w. 120·57. V.D. at 1200°-1500° 69·7 (Scott, *Pr. E.* 14, 410). Melts at c. 710° (Carnelley, *C. J.* 33, 279). By burning Rb in Cl. Also by saturating HClAq with Rb_2CO_3, evaporating, and crystallising from water. Also by reducing Rb_2PtCl_6 in H, and dissolving out RbCl in water (*cf. Preparation*, p. 411). White, lustrous, cubical crystals; unchanged in air; decrepitates when heated, and then melts, and volatilises at a very high temperature. S. 76·38 at 1°, 82·89 at 7°; sol. alcohol (Bunsen, *l.c.*). Molten RbCl is a good conductor of electricity (Hampe, *Chem. Zeitung*, 1887. No. 54). *Double compounds*: RbCl combines with many metallic chlorides; some at any rate of the products, *e.g.* the platino- and platini-chlorides Rb_2PtCl_4 and Rb_2PtCl_6, are best regarded as Rb salts of acids containing metals and Cl. The following compounds have been prepared: M = RbCl. — $6M.SbCl_3$ (1); $3M.2SbCl_3$ (6); $6M.BiCl_3$ (1); $2M.CdCl_2$, $M.CdCl_2.xH_2O$ (1); $2M.CrCl_3.aq$ (2); $2M.CuCl_2$ (1); $M.AuCl_3$ (3); $3M.FeCl_3$ (1), $2M.FeCl_3.aq$ (2); $2M.MnCl_2.3aq$ (1); $2M.HgCl_2$, $2M.HgCl_2.2aq$, $M.2HgCl_2$, $M.4HgCl_2$ (1); $2M.NiCl_2$ (1); $2M.PtCl_2$ (4), $2M.PtCl_4$ (5); $3M.TlCl_3$ (2); $2M.SnCl_4$ (1); $2M.ZnCl_2$ (1).

References to above.—(1) Godeffroy, *B.* 8, 9; (2) Neumann, *A.* 244, 329; (3) Rosenbladt, *B.* 19, 2535; (4) Nilson, *Bl.* [2] 27, 210; (5) Bunsen, *A.* 122, 347; (6) Muthmann, *B.* 26, 1019, 1425.

RbCl also combines with IBr to form RbCl.IBr; with ICl, to form RbCl.ICl; with BrCl, to form RbCl.BrCl; and with Br to form $RbCl.Br_2$ (Wells a. Wheeler, *Am. S.* [3] 43, 475).

Rubidium, cyanide of. Setterberg (*A.* 211, 100) probably obtained a cyanide of Rb by passing dry HCN into an alcoholic solution of RbOH. Reissig (*A.* 127, 33) failed to obtain the salt free from products of decomposition.

Rubidium, ferrocyanide of; *v.* vol. ii. p. 335.

Rubidium, fluoride of, RbF. Formula probably molecular, from analogy of RbCl and RbI. S.G. 3·202 at 16·5° (Clarke, *Am. S.* [3] 13, 293). Melts at c. 753° (Carnelley, *C. J.* 33, 279). Forms a *double compound* with uranyl fluoride, $4RbF.UO_2F_2.6aq$ (Ditte, *C. R.* 91, 166).

Rubidium, hydroxide of, RbOH. A white, brittle solid, with slight greyish tinge; very alkaline and caustic; easily sol. water, with production of much heat; sol. alcohol. Formed by decomposing H_2O by Rb; also by boiling Rb_2SO_4Aq till air is driven out, adding BaOAq gradually, keeping the liquid boiling till $BaSO_4$ ceases to be formed, decanting from $BaSO_4$, which separates out rapidly, and evaporating in a silver dish. Melts below redness; is not decomposed by heating. When molten attacks Pt. Beketoff (*J. R.* 1888. 363) gives [Rb,O,H] = 164,800; $[Rb^2O,H^2O] = 69,900$.

Rubidium, iodide of, RbI. Mol. w. 211·53. V.D. 110·8 at 1200°-1500° (Scott, *Pr. E.* 14, 410). Melts at c. 642° (Carnelley, *C. J.* 33, 279). Lustrous, white, regular octahedra; unchanged in air. S. 137·5 at 6·9°, 152 at 17·4°. Formed by saturating HIAq with Rb_2CO_3, evaporating, and crystallising from water. Also by heating Rb in I vapour (Reissig, *A.* 127, 33). RbI combines with I to form $RbI.I_2$ (Wells a. Wheeler, *Am. S.* [3] 43, 475).

Rubidium, oxides of. No oxide of Rb has been isolated. Rb burns in air, possibly with formation of an oxide and peroxide similar to K_2O and K_2O_4. The greyish-blue film which is formed on the surface of the metal when exposed to the air is perhaps a suboxide. According to Beketoff (*J. R.* 1888. 363), the thermal value of $[Rb^2,O]$ is 94,900.

Rubidium, salts of. The principal salts formed by replacing H of oxyacids by Rb are *borate*, *carbonates*, *chlorate* and *perchlorate*, *chromate* and *dichromate*, *molybdate*, *nitrate*, *oxalate*, *silicotungstate*, *sulphate*, and *thiosulphate* (*v.* Carbonates, Nitrates, &c.).

Rubidium, silicofluoride of. Rb_2SiF_6. White, regular crystals. S.G. 3·338 at 20°. S. c. ·16 at 20°, 1·35 at 100°. By ppg. hot Rb alum solution by $CuSiF_6$ (Stolba, *J. pr.* 102, 1).

M. M. P. M.

RUBIJERVINE *v.* Jervine.

RUE OIL. The essential oil (c. 229°) obtained by distilling *Ruta graveolens* contains methyl ennyl ketone $C_{11}H_{22}O$ (224°), a ketone $C_{12}H_{24}O$ (232°), and a small quantity of terpene (Gerhardt, *C. R.* 26, 225, 361; Cahours, *C. R.* 26, 262; Greville Williams, *T.* 1858 [1] 99; *A.* 107, 374; Hallwachs, *A.* 113, 108; Harbordt, *A.* 123, 293). By boiling oil of rue with nitric acid (S.G. 1·2) an acid $C_9H_{18}N_2O_4$ may be obtained (Chiozza, *A.* 85, 225; Alexejeff, *Z.* 1865, 736). This acid is a heavy oil, forming KA′ and NaA′, crystallising from alcohol in greenish-yellow tables (Limpach, *A.* 190, 298).

RUFICOCCIN *v.* Carminic acid.

RUFIGALLIC ACID *v.* Hexa-oxy-anthraquinone.

RUFIN $C_{21}H_{20}O_8$. A product of the action of heat on phlorizin (Mulder, *Rev. Scientif.* 3, 50; Stas, *A.* 30, 198). Dark-red resin, sol. alcohol, nearly insol. ether and water. Its alkaline solutions are red. Ac_2O forms $C_{21}H_{19}AcO_8$ (Schiff, *A.* 156, 5).

RUFIOPINE is Tetra-oxy-anthraquinone.

RUFOL *v.* Di-oxy-anthracene.

RUTHENAMMINES *v.* Ruthenium-ammonium compounds, p. 418.

RUTHENATES *v.* Ruthenium, salts of oxyacids of, p. 417.

RUTHENITES *v.* Ruthenium, salts of oxyacids of, p. 417.

RUTHENIUM. At. w. 101·4. Mol. w. unknown. Melts at highest temperature attainable by O-H flame, which is above 2000° (Deville a. Debray, *A. Ch.* [3] 56, 385). S.G. 12·26 at 0° (crystallised) (D. a. D., *C. R.* 83, 928); older determinations varied from 8·6 to 11·4. Joly (*C. R.* 116, 430) gives S.G. of Ru melted in an electric furnace as 12·63 at 0° referred to water at 4°. S.H. ·0611 from 0° to 100° (Bunsen, *P.* 141, 1). C.E. at 40° (linear) ·00000963 (Fizeau, *C. R.* 68, 1125).

Occurrence.—In many platinum ores; Ru is a constant ingredient of *osmiridium* (vol. iii. p. 47), the quantity varying from 3 to 6 p.c. (*v.* Claus, *A.* 56, 257; 59, 234; Gibbs, *Am. S.* [2] 29,

427; 31, 63; 34, 341). Wöhler found Ru_2S_3 in *laurite*, a rare mineral occurring in Borneo and in Oregon (*J. pr.* 98, 226).

In 1828 Osann (*P.* 13, 283; 14, 329; *cf.* 64, 197) thought he had discovered three new metals in the portion of a Pt ore insol. in *aqua regia*; to these metals he gave the names *polin*, *pluranium*, and *ruthenium* (from *Ruthenia* = Russia). In 1845 Claus (*A.* 56, 257; 59, 234; *cf.* 63, 359) examined the substance called ruthenium oxide by Osann, and found it to consist chiefly of SiO_2, TiO_2, Fe_2O_3, and ZrO_2; from this material Claus isolated a new metal, to which he assigned Osann's name, *ruthenium*.

Formation. — 1. By reducing Ru_2O_3 by heating in H or C.—2. By strongly heating $(NH_4)_2RuCl_6$, $(NH_4)_2RuCl_5$, $Ru(NH_3.NH_3Cl)_2$, or $Ru(NH_3.NH_3Cl)_2.HgCl_2$.—3. By heating $RuSn_2$ in a graphite boat in a stream of HCl.

Preparation.—Deville a. Debray (*C. R.* 82, 926) prepared pure Ru by heating the ordinary metal in a stream of O till every trace of Os was removed as OsO_4 (vol. iii. p. 646), fusing with KOH and KNO_3, dissolving in water, saturating with Cl, and distilling off RuO_4 into KOHAq, by heating in a stream of Cl on a water-bath, ppg. Ru_2O_3 by adding alcohol to the solution of $KRuO_4$, heating the pp. in coal-gas till reduced to Ru, melting in a graphite crucible with 5 to 6 parts pure tin, treating with boiling HClAq, washing and drying the crystalline $RuSn_2$ which remained, and heating this strongly in a graphite boat in a stream of HCl.—2. Osm-iridium is mixed with 2 parts KNO_3 and 1 part KOH, and the mixture is heated to redness in a large silver crucible, embedded in MgO in an earthenware crucible; the molten portion is poured off, and the residue is heated with more KNO_3 and KOH. The fused mass is lixiviated with water; the orange solution, which contains KOH and K salts of HNO_2, HNO_3, H_2OsO_4, and H_2RuO_4, is neutralised by HNO_3Aq, when a black pp. forms containing $OsO_2.xH_2O$ and $Ru_2O_3.xH_2O$. This pp. is filtered off, the filtrate being set aside, and is washed and boiled with HClAq and HNO_3Aq in a retort connected with a receiver which is kept very cold; the boiling is continued till a drop of the distillate, when brought alternately into the oxidising and reducing parts of the Bunsen flame, ceases to give a bright flash in the former, *i.e.* until OsO_4 ceases to distil off. The residue, which contains $RuCl_3$ and $RuCl_4$, is dissolved in a little water, excess of NH_4Cl is added to the hot conc. solution, the liquid is poured off from $(NH_4)_2RuCl_5$, evaporated and mixed with more NH_4Cl, when $(NH_4)_2RuCl_6$ ppts. Excess of NH_4Cl is removed from the pps. by washing with alcohol. By strongly heating the pps. Ru is obtained. The solution filtered from the pp. of $OsO_2.xH_2O$ and $Ru_2O_3.xH_2O$ contains OsO_4 and RuO_4; it is made strongly acid by HClAq, OsO_4 is distilled off, the solution is evaporated till most of the KNO_3 crystallises out, the mother-liquor is evaporated to dryness, the residue is dissolved in water, and Ru_2S_3 is ppd. by adding $(NH_4)_2SAq$ and then acidifying; after washing and drying, the Ru_2S_3 is roasted, and the Ru_2O_3 so formed is reduced by heating in H, or by strongly heating in a graphite crucible; or the Ru_2O_3 may be dissolved in HClAq, and NH_4-Ru chlorides obtained from this solution and decomposed by heat (Claus, *J. pr.* 85, 129; Carey Lea, *Am. S.* [2] 38, 83).

For other methods of separating Ru from osm-iridium *v.* Deville a. Debray (*A. Ch.* [3] 56, 385; *C. R.* 83, 927; Fremy, *A. Ch.* [3] 44, 385; Gibbs, *Am. S.* [2] 34, 343; 37, 61). Debray obtained *ruthenium in crystals* by dissolving the spongy metal in molten lead, heating strongly, and, after cooling, dissolving out the lead (with which Ru does not alloy) in HNO_3Aq (*C. R.* 90, 1195).

Properties.—A white, lustrous, hard, heavy, brittle metal. As obtained by heating the double ammonium chlorides, Ru forms a white spongy mass; the metal formed by reducing the oxide by H appears in white porous fragments, which can be powdered; after fusion in an electric furnace Ru appears greyish (Joly, *C. R.* 116, 430). Next to Os, Ru is the most infusible metal; small pieces can be melted at the highest temperature of the O-H flame (D. a. D., *A. Ch.* [3] 56, 385); a little RuO_4 is formed and then decomposed to RuO_2 (D. a. D., *C. R.* 80, 457). Insoluble in all acids if in compact pieces; very finely divided Ru dissolves slightly and slowly in boiling *aqua regia*. Not attacked by molten $KHSO_4$; oxidised to K_2RuO_4 by fusion with KOH, KNO_3, or $KClO_3$. Ru dissolves in molten Zn or Pb; treatment with HNO_3Aq leaves the Ru undissolved. Small quantities of Ru when alloyed with Pt metals soluble in acids go into solution, with the Pt metals, in these acids. Finely divided Ru combines with O, when heated in O or in air.

Ru is closely related to Rh and Pd, and less closely, but very distinctly, to Os, Ir, and Pt; *v.* NOBLE METALS, vol. iii. p. 628.

The atomic weight of Ru has been determined (1) by determining the ratio of Ru to KCl in K_2RuCl_5 (Claus, *P.* 65, 218 [1845]; (2) by analyses of the salts $M_2Ru(NO)Cl_5$, where M = K, Na, and NH_4 (Joly, *C. R.* 107, 994; 108, 946 [1889]; (3) by determining V.D. of RuO_4 (Debray a. Joly, *C. R.* 106, 328); (4) by measuring S.H. of Ru (Bunsen, *P.* 141, 1). Claus's determinations gave values from 102·2 to 104·8 for the at. wt.

The only compound of Ru whose mol. weight is known in the gaseous state is RuO_4; the valency of the atom of Ru cannot be determined from this datum.

Reactions and Combinations.—1. Finely divided Ru, when heated to redness in *air* or in *oxygen*, rapidly absorbs 18·5 p.c. O (Claus, *J. pr.* 42, 364); after 10 hours, c. 23 p.c. O has combined (D. a. D., *C. R.* 87, 441); the product is a mixture of RuO_2 and Ru (Claus failed to obtain a lower oxide than RuO_2 in this way). Crystals of RuO_2 are obtained by heating the metal in a tube in a rapid stream of O; according to Debray and Joly (*C. R.* 106, 1494), RuO_4 is formed and then decomposed (*v.* RUTHENIUM TETROXIDE, p. 417).—2. Heated in *chlorine*, a small portion is changed to a chloride; mixed with *sodium chloride and heated in chlorine*, Na_2RuCl_5 is formed (Claus, *l.c.*).—3. Spongy Ru is said to form HClAq when placed in *chlorine water*; and to produce chlorides in solutions of *hypochlorites*, O being given off (Schönbein, *J. pr.* 98, 76).—4. Very finely divided Ru dissolves slightly when kept in *boiling aqua regia* for some time, $RuCl_3$ being formed.—5. M_2RuO_4

soluble in water. is formed by fusing Ru with caustic *alkalis*, *alkali chlorates*, or *alkali nitrates*. *Alkaline earth nitrates* or *chlorates* also form ruthenates (*v.* Ruthenates, p. 417).

Detection.—A few mgms. of the substance to be tested are heated, in a spoon of Pt, with excess of KNO_3 until the whole melts and ceases to give off gas; when cold, the mass is dissolved in water, when a strongly coloured orange-yellow solution is obtained; a little HNO_3Aq is added to this solution, followed by HClAq, and warming till the voluminous black pp., produced by HNO_3Aq, dissolves to an orange-yellow solution; H_2S is passed into this liquid, until it appears black from the presence of suspended Ru sulphide (or oxysulphide); on filtering, an azure-blue liquid is obtained, probably containing $RuCl_2$ (Bunsen, *A.* 146, 265). For estimation *v.* Deville a. Debray (*C. R.* 83, 927).

Ruthenium, alloys of. An alloy with *iridium* was obtained by Deville a. Debray (*A. Ch.* [3] 56, 385). A crystalline alloy with *tin*, $RuSn_3$, is formed by melting Ru with 10 to 15 parts Sn, and when cold treating with HClAq. The tin is removed, and crystalline Ru remains, by heating, in a graphite boat, in HCl gas (D. a. D., *l.c.*; *v.* also *C. R.* 83, 927). Ru alloys with *zinc*; much heat is produced (D. a. D., *l.c.*). Ru dissolves in molten lead, but separates out again on cooling (Debray, *C. R.* 90, 1195).

Ruthenium, ammonio-salts of; *v.* Ruthenium-ammonium compounds, p. 418.

Ruthenium, chlorides of. Two chlorides, $RuCl_2$ and $RuCl_3$, are obtained by heating finely divided Ru in a stream of Cl. No other chloride has been isolated; the existence of double compounds of $RuCl_4$ with alkali chlorides is doubtful. The molecular weights of the chlorides are not known.

Ruthenium dichloride $RuCl_2$. (*Ruthenous chloride. Ruthenoso-chloride.*) Prepared by heating very finely divided Ru in a stream of Cl. Action begins at c. 360° (Joly, *C. R.* 114, 291) with formation of $RuCl_3$, which is removed by subliming, and the temperature is kept at dull redness for an hour or two; the residue is powdered, and again heated in Cl; and this treatment is repeated several times (Claus, *A.* 59, 234). A black crystalline mass; insoluble water, acids, or alkali solutions. The azure-blue liquid formed by the action of reducers, such as Zn or H_2S, on solutions of $RuCl_3$, was thought by Claus (*l.c.*) to contain $RuCl_2$.

Ruthenium trichloride $RuCl_3$. (*Rutheno-*, or *ruthenoso-ruthenic*, *chloride. Sesquichloride of ruthenium.*) Obtained, as a brown, crystalline, very hygroscopic solid, by dissolving $Ru(OH)_3$ (Claus, *A.* 59, 234), or RuO_4 (Joly, *C. R.* 107, 994), in HClAq, and evaporating to dryness. Joly (*C. R.* 114, 291) obtained $RuCl_3$ by heating finely divided Ru at 360° to 440° in a mixture of CO and Cl, the Cl being in excess. Claus says that $RuCl_3$ is sol. water, with partial decomposition to an insol. oxychloride; and that, on heating, the solution decomposes with separation of a black powder (partly oxychloride, partly RuO_3H_2), the colouring power of which is so great that 1 mgm. suffices to make 500 c.c. water appear quite black. Joly (*C. R.* 114, 291) says that $RuCl_3$, prepared by heating Ru in Cl and CO, is insol. cold water, acid solutions, CCl_4, CS_2, $CHCl_3$, Et_2O, or PCl_3; it is decomposed slowly by hot water; slowly dissolved by digesting with 50 times its weight of absolute alcohol, in a sealed tube. Solution in alcohol is purple-violet; slowly decomposes in moist air, more rapidly at 60°, giving $RuCl_2.OH$ (*v.* Ruthenium hydroxychloride, p. 416). $RuCl_3$ absorbs NH_3 to form $2RuCl_3.7NH_3$; another compound containing NH_3, viz. $Ru_2Cl_4(OH)_2.7NH_3.3H_2O$, is formed by throwing $RuCl_3$ in small successive quantities into cold saturated NH_3Aq and then heating to 40° (Joly, *C. R.* 115, 1299).

Double salts. *Chlor-ruthenites*, $RuCl_3.2MCl$, or M_2RuCl_5; $M = NH_4$, K, Na (Claus, *A.* 59, 234; 63, 359). Formed by evaporating RuO_3H_3 in HClAq nearly to dryness, dissolving in water, and adding conc. solution of the alkali chloride; also by heating a mixture of Ru with KCl or NaCl in Cl (Joly, *C. R.* 107, 994). The *potassium salt*, which seems to be the most definite, is a brownish-violet, crystalline powder, scarcely sol. cold water, somewhat sol. boiling water, insol. alcohol of 80 p.c.

Joly (*C. R.* 108, 854) obtained *ruthenium nitrosochloride* $RuCl_3.NO.H_2O$, by heating $RuCl_3$ with a large excess of HNO_3Aq, and evaporating at 120°. Heated *in vacuo*, or in CO_2, at 440°, gives off NO, and leaves a mixture of $RuCl_3$ and RuO_2. Solution of the nitrosochloride is not ppd. by alkalis in the cold; but on boiling with enough alkali to combine with 3Cl, a brown gelatinous pp. of nitroso-oxide, $Ru_2O_3.2NO.2H_2O$, is obtained. For compounds of $RuCl_3$ with NO and alkali chlorides, *v. Nitroso-chlor-ruthenates*, *infra*.

Ruthenium tetrachloride $RuCl_4$. (*Ruthenichloride. Ruthenic chloride.*) Claus (*A.* 59, 234) supposed that a solution of RuO_4H_4 in HClAq contained this chloride; he also described various alkali *chlor-ruthenates*, M_2RuCl_6, obtained by adding alkali chlorides to the supposed solution of $RuCl_4$. Joly, however (*C. R.* 107, 994), has shown that Claus' salts contain NO; and he asserts that the compound used by C. and supposed to be RuO_4H_4 itself contained NO. Joly failed to obtain either $RuCl_4$ or the salts M_2RuCl_6. The compounds described by C. as M_2RuCl_6, but shown by J. to be $M_2Ru(NO)Cl_5$, may be called nitrosochlor-ruthenates.

Nitrosochlor-ruthenates, $M_2Ru(NO)Cl_5(RuCl_3.NO.2MCl)$. M = Am, K, Na. These salts were obtained by Joly (*C. R.* 107, 994) by heating $RuCl_3$ in HNO_3Aq for some time and adding alkali chlorides, also by adding alkali nitrites to warm solutions of $RuCl_3$ in HClAq. According to Joly, the salts described by Claus as M_2RuCl_6 are in reality nitrosochlor-ruthenates. These salts yield NO when heated with $CaCO_3$. Solutions of these salts are not ppd. by alkalis in the cold; on boiling with alkali sufficient to combine with 3Cl, a pp. of $Ru_2O_3(NO)_2.2aq$ is slowly formed (J., *C. R.* 108, 854). The group NO evidently forms part of the acidic radicle of the salts (*cf.* Ruthenium-ammonium compounds, p. 418).

Potassium nitrosochlor-ruthenate, $K_2Ru(NO)Cl_5$. Prepared by fusing Ru with KOH and KNO_3, dissolving in HClAq, and evaporating somewhat till excess of KCl and KNO_3 crystallise out; by evaporating the mother-liquor a mixture of K_2RuCl_5 and $K_2Ru(NO)Cl_5$ is obtained, from which water dissolves the latter salt. Purified by crystallisation from water, wherein the salt is fairly soluble. Black, orthorhombic prisms; transparent when in thin crystals. Solution in water is violet-red.

Ruthenium, cyanide of, and *derivatives*; *v.* vol. ii. p. 346.

Ruthenium, hydroxides of; *v.* RUTHENIUM, OXIDES AND HYDRATED OXIDES OF, *infra*.

Ruthenium, hydroxychloride of, $Ru(OH)Cl_2$. Described by Joly (*C. R.* 114, 291) as a solid, obtained by heating, in moist air to 60°, a solution of $RuCl_3$ in absolute alcohol. Very sol. water; the deep indigo-blue solution slowly deposits RuO_3H_3.

Ruthenium, iodide of, RuI_3. This compound is formed, according to Claus (*A.* 59, 234), as a black pp. by adding KI to K_2RuCl_5Aq.

Ruthenium, nitrosochloride of, $Ru.NO.Cl_3$, *v.* under RUTHENIUM TRICHLORIDE.

Ruthenium, nitrosopentoxide of, $Ru_2(NO)_2O_3.2H_2O$, *v.* under RUTHENIUM PENTOXIDE.

Ruthenium, oxides and hydrated oxides of. Claus described four oxides of Ru: RuO, Ru_2O_3, RuO_2, and RuO_4; and the hydrated oxides $Ru_2O_3.3H_2O$ and $RuO_2.2H_2O$. According to Debray and Joly, RuO and Ru_2O_3 have not been isolated, but the oxides Ru_2O_5 and Ru_4O_9 exist, besides RuO_2 and RuO_4. According to Joly, Claus' $RuO_2.2H_2O$ contains NO. Ru combines with O when melted in the O-H flame, with formation of RuO_2; it is probable that RuO_4 is formed, and then decomposed to $RuO_2 + O_2$.

RUTHENIUM MONOXIDE RuO. (*Ruthenous oxide.*) According to Claus (*A.* 59, 234), this oxide is formed, as a dark-grey, metal-like solid, by calcining $RuCl_2$ mixed with rather more than an equivalent of Na_2CO_3 in a stream of CO_2, and washing with water as long as anything dissolves. Debray and Joly (*C. R.* 106, 328, 1424) could not obtain this oxide.

RUTHENIUM SESQUIOXIDE Ru_2O_3. (*Ruthenooxide.*) When Ru black is strongly heated in a Pt crucible, c. 18·5 p.c. O is rapidly taken up; O is then slowly absorbed till from 23 to 24 p.c. has combined, and a blue-black mass is formed. This blue-black solid is Ru_2O_3, according to Claus (*A.* 56, 257; 59, 234); according to D. a. J. (*l.c.*) it is a mixture of Ru and RuO_2.

HYDRATED RUTHENIUM SESQUIOXIDE $Ru_2O_3.3H_2O$ or RuO_3H_3. (*Black ruthenium hydroxide.*) A black powder; prepared by ppg. solutions of $RuCl_3$ by alkali, or by alkali carbonate, phosphate, or borate (Claus, *A.* 59, 234). Also ppd. from an aqueous solution of $Ru(OH)Cl_2$ (*v. Hydroxychloride, supra*). Even after washing for several days the pp. retains c. 1 p.c. alkali. Reduced, but incompletely, by H at ordinary temperature. Insol. KOHAq or NaOHAq, sl. sol. NH_4Aq (Claus, *l.c.*); sol. in acids. The only salts of oxyacids derived from this oxide which have been prepared are $Ru(NO_2)_3.3KNO_2$ and the corresponding Na salt (Claus, *J.* 1863. 697; Gibbs, *Am. S.* [2] 29, 427; 31, 63; 34, 341).

RUTHENIUM DIOXIDE RuO_2. (*Ruthenic oxide.*) Formed by strongly heating Ru sulphide, or $Ru(SO_4)_2$, in air (Claus, *A.* 59, 234). $Ru(SO_4)_2$ is obtained by ppg. $RuCl_3$ solution by H_2S, and oxidising the pp. by HNO_3. RuO_2 is also formed, as a crystalline sublimate, by roasting osmiridium containing Ru in a porcelain tube (Fremy, *A. Ch.* [3] 44, 385). Also obtained by strongly heating finely divided Ru for some time in a stream of O (D. a. D., *A. Ch.* [3] 56, 385; *C. R.* 83, 927; 87, 441). The whole of the Ru is not converted into RuO_2, but some metal remains unoxidised (D. a. J., *C. R.* 106, 1494). At a very high temperature RuO_4 is formed, and at a lower temperature this is resolved into RuO_2 and O (D. a. D., *C. R.* 80, 457; D. a. J., *C. R.* 106, 1424). D. a. J. (*C. R.* 106, 328) obtained RuO_2, partly amorphous and partly crystalline, by heating RuO_4 to 107°; also by heating Ru_4O_9 to 440°.

Dark-violet, quadratic crystals; isomorphous with *rutile* (Fremy, *l.c.*; D. a. J., *l.c.*). S.G. 7·2 (D. a. D., *A. Ch.* [3] 56, 385). Insol. acids, sol. molten KOHAq. Easily reduced by H. The only salt of an oxyacid corresponding with RuO_2 which has been isolated is $Ru(SO_4)_2$ (Claus, *l.c.*).

HYDRATED RUTHENIUM DIOXIDE $RuO_2.5H_2O$ or $RuO_4H_4.3H_2O$. The existence of this compound is doubtful. Claus (*A.* 59, 234) gave this composition to the gelatinous, yellow-brown pp. formed by decomposing K_2RuCl_6Aq by Na_2CO_3; but Joly has shown that Claus' K_2RuCl_6 contains NO (*cf.* RUTHENIUM TETRACHLORIDE, p. 415). Claus also obtained hydrated RuO_2 by evaporating $Ru(SO_4)_2Aq$ with KOHAq; but as the sulphate employed was obtained by oxidising Ru sulphide by HNO_3, it may have contained NO. Joly (*C. R.* 107, 994) gives the formula $Ru_2O_3(NO)_2.2H_2O$ to to the brown gelatinous pp. formed by boiling $Ru(NO)Cl_3$ or $K_2Ru(NO)Cl_5$ with KOHAq or K_2CO_3Aq. It seems probable that Claus' $RuO_2.5H_2O$ is the same as the nitroso- compound obtained by Joly (*cf. infra Hydrated nitroso-pentoxide*).

RUTHENIUM PENTOXIDE $Ru_2O_5 (= RuO_2.RuO_3)$. When RuO_4Aq stands for some time in a closed vessel, a black pp. settles down and a black crystalline crust forms on the sides of the vessel, while O is set free and escapes when the vessel is opened. The composition of the pp. and crystalline crust after drying at 100° is given by Debray a. Joly as Ru_2O_5 (*C. R.* 106, 328). This oxide is also obtained by allowing a dilute solution of a ruthenate to stand for a long time, or by adding a dilute acid to such a solution. Ru_2O_5 dissolves in HClAq, giving off Cl; heated to 360° Ru_4O_9 is formed.

Hydrated nitroso-pentoxide $Ru_2O_3(NO)_2.2H_2O$. A black solid, formed by boiling $Ru(NO)Cl_3$ or $K_2Ru(NO)Cl_5$ (*v. Nitrosochloride*, and *Nitrosochlor-ruthenates*, p. 415) with sufficient alkali or alkaline carbonate to combine with 3Cl, and drying the pp. at 150° (Joly, *C. R.* 108, 854). Slowly decomposes when heated to 360° in CO_2, giving Ru_4O_9; above 440° decomposes violently, giving off N oxides; reduced by H below 100°, giving off NH_3. Sol. in acids, forming nitroso-salts.

RUTHENIUM NONOXIDE $Ru_4O_9 (= 3RuO_2.RuO_3)$. This composition was given by D. a. J. (*C. R.* 106, 328) to the black, lustrous, crystalline crust obtained by heating RuO_4Aq to 100°. The same oxide is formed by heating Ru_2O_5 to 360°. Heated to 440° this oxide gives amorphous RuO_2 and O.

RUTHENIUM TRI-OXIDE RuO_3. (*Ruthenic anhydride.*) This oxide has not been isolated, but salts derived from it are known. RuO$_3$ is the hypothetical anhydride of ruthenic acid (H$_2$RuO$_4$), which has not been isolated. For the salts corresponding with this oxide *v. Ruthenates*, under RUTHENIUM, SALTS OF OXYACIDS OF, *infra*.

RUTHENIUM HEPTOXIDE Ru$_2$O$_7$. (*Per-ruthenic anhydride.*) This oxide, the hypothetical anhydride of the non-isolated per-ruthenic acid (HRuO$_4$), has not been prepared. For the salts corresponding with this oxide *v. Per-ruthenates*, under RUTHENIUM, SALTS OF OXYACIDS OF, *infra*.

RUTHENIUM TETROXIDE RuO$_4$. (Sometimes called *per-ruthenic acid*, and frequently *ruthenic acid*.) Mol. w. 165·24. V.D. 83·3 at 100° and 106 mm. pressure (Debray a. Joly, *C. R.* 106, 328).

Formation.—1. By passing Cl into a solution of the product of fusing Ru with KOH and KNO$_3$.—2. By the action of KClO$_3$ and HCl, not *aqua regia*, on K$_2$RuCl$_5$Aq (Claus, *A.* 59, 234).—3. By heating finely divided Ru in a stream of O to c. 1000°, and cooling rapidly by means of ice. If the temperature is allowed to fall slowly the RuO$_4$ formed decomposes explosively at c. 108° (Debray a. Joly, *C. R.* 106, 100).

Preparation.—A mixture of 1 part finely divided Ru, with 8 parts KOH and 1 part KNO$_3$, is heated to dull redness in a silver crucible till fused; the product, when cold, is dissolved in 16 parts water; the solution is placed in a tubulated retort connected, by a long tube, with a very well cooled receiver (the connecting tube being also cooled), and a rapid stream of Cl is passed into the solution; a considerable amount of heat is produced, and RuO$_4$ passes over and solidifies in the receiver (Deville a. Debray, *A. Ch.* [5] 4, 537). To free the preparation from water D. a. J. (*C. R.* 106, 328) place it in a tube with fused CaCl$_2$, contract the tube in the middle, pump out the air, and seal off the tube. The RuO$_4$ slowly sublimes into the upper part, which is then separated from the rest. The RuO$_4$ is finally distilled *in vacuo* into tubes which have been very carefully cleansed from all traces of organic matter, and dried by heating to redness in a stream of H. RuO$_4$ may be obtained in well-formed crystals by subliming *in vacuo* at the ordinary temperature.

Properties.—(D. a. J., *C. R.* 106, 328.) Golden yellow crystals, melting at 25·5° to an orange-red liquid, which solidifies slowly to a vitreous solid. Smell resembles that of ozone; the vapour causes coughing, but does not affect the eyes (Claus, *J. pr.* 80, 282). Sublimes at 3 to 4 mm. pressure on the slightest rise of temperature; the vapour is golden yellow. Decomposes at 106°-107° without boiling. The vapour-pressure of the crystals is almost *nil* at 0°, 20 mm. at 42°, and 182 mm. at 100·8°. May be distilled in water-vapour containing Cl or HClO. Gradually reduced to RuO$_2$ by sunlight (Joly, *C. R.* 113, 693). Dissolves in water, forming a golden-yellow solution, which gradually decomposes with ppn. of Ru$_2$O$_5$.xH$_2$O. RuO$_4$ attacks Hg, and slowly acts on glass. RuO$_4$ does not form corresponding salts, either by reacting with acids or alkalis. Moist RuO$_4$ is very easily reduced, *e.g.* by contact with paper.

Reactions.—1. Decomposed by *heat*; no action below 106°; at 107° sudden decomposition occurs, with a smoky flame and formation of amorphous RuO$_2$ on the walls of the vessel, and crystalline RuO$_2$ from the part that has melted (D. a. J., *l.c.*). According to D. a. J. (*C. R.* 106, 100), RuO$_4$ is formed when O is passed over spongy Ru at c. 1000°, and the product is rapidly cooled. If cooling is allowed to take place slowly the RuO$_4$ decomposes at c. 108°.—2. Dissolves in *water*; solution keeps unchanged for some time, but slowly deposits Ru$_2$O$_5$.xH$_2$O. Decomposition is more rapid at higher temperatures; at 100° Ru$_4$O$_9$.xH$_2$O is formed (D. a. J., *l.c.*).—3. Solution in water, or moist RuO$_4$, is quickly reduced by *alcohol and several other organic compounds* (Claus, *J. pr.* 80, 282).—4. With *solutions of alkalis* forms ruthenates and per-ruthenates, with evolution of O. *Alcoholic solution of potash* ppts. Ru$_2$O$_3$.3H$_2$O.—5. Heated with *hydrochloric acid*, Cl is given off and RuCl$_3$ formed in solution.—6. *Hydrogen sulphide* gradually throws down a black pp. of an oxysulphide, from RuO$_4$Aq (Claus, *l.c.*).

Ruthenium, oxyacids of. No oxyacid of Ru has been isolated, but some salts of the hypothetical acids H$_2$RuO$_4$ and HRuO$_4$ are known (*v.* RUTHENIUM, SALTS OF OXYACIDS OF, *infra*).

Ruthenium, oxysulphide of. A current of H$_2$S passed into RuO$_4$Aq slowly ppts. all the Ru as a black substance, which is said by Claus (*J. pr.* 80, 282) to be an oxysulphide, whose composition varies according to the quantity of H$_2$S passed in. The pp. suddenly glows when dried at 100°, and burns, giving off SO$_2$.

Ruthenium, salts of. Very few salts are known obtained by replacing the H of oxyacids by Ru. The double nitrites Ru(NO$_2$)$_3$.3MNO$_2$, where M = K or Na, are the only salts which have been prepared corresponding with Ru$_2$O$_3$; and Ru(SO$_4$)$_2$ is the only salt of RuO$_2$ which has been isolated; the double sulphite RuSO$_3$.K$_2$SO$_3$ corresponds with RuO.

Ruthenium, salts of oxyacids of. A few salts of the hypothetical acid H$_2$RuO$_4$, and two salts of the hypothetical acid HRuO$_4$, have been isolated.

RUTHENATES, M$^I_2$RuO$_4$. Salts of hypothetical H$_2$RuO$_4$ (formerly called *ruthenites*). These salts are formed by heating Ru, or an oxide of Ru, with an oxide, hydroxide, nitrate, or chlorate of an alkali metal (Claus, *A.* 56, 257; 59, 234), or of an alkaline earth metal (Deville a. Debray, *A. Ch.* [3] 56, 385). Ruthenates in solution are easily reduced by organic bodies, with ppn. of black Ru$_2$O$_3$.3H$_2$O; acids added to conc. solutions form per-ruthenates, M^{I}RuO$_4$.

Barium ruthenate BaRuO$_4$.aq. Obtained by adding RuO$_4$ to BaOAq. The solution is at first green, probably from formation of per-ruthenate; a black pp. is thrown down, which soon changes to the cinnabar-coloured crystalline Ba salt. This salt is also formed by adding BaCl$_2$Aq to a solution of the K salt (Debray a. Joly, *C. R.* 106, 1494).

Potassium ruthenate K$_2$RuO$_4$.aq (D. a. J., *l.c.*). 50 g. RuO$_4$, melted under water, are slowly added to 70 g. KOH in 500 c.c. water at 60°; temperature is kept at 60° until the evolution of O has ceased, when the solution is evaporated *in vacuo*; long, black, orthorhombic prisms, reflecting green light, are formed (for crystalline measurements v. D. a. J. (*l.c.* p. 1497). After drying *in vacuo*, the crystals absorb moisture and CO_2 from the air. Unchanged at 106° *in vacuo*; loses H_2O at 200°, and may then be heated to 400° without decomposition. Very sol. water; solution is orange yellow; it soon decomposes in air, depositing $Ru_2O_5.xH_2O$, and probably forming $KRuO_4Aq$. Organic bodies dipped into the solution become black from deposition of $Ru_2O_3.3H_2O$. Acids hasten formation of $KRuO_4Aq$ and Ru_2O_5; from conc. K_2RuO_4Aq acids ppt. $KRuO_4$, which decomposes to Ru_2O_5 and RuO_4 (D. a. D., *C. R.* 83, 927).

The *magnesium*, *silver*, and *strontium* salts are obtained by adding $MgCl_2Aq$, $AgNO_3Aq$, and $SrCl_2Aq$ respectively to K_2RuO_4Aq. The *sodium* salt has not been isolated; it cannot be separated from excess of soda.

PER-RUTHENATES, M^IRuO_4. Salts of hypothetical $HRuO_4$ (formerly called *ruthenates*). Obtained by the action of Cl on ruthenates, or of acids on conc. solutions of ruthenates. Alkalis produce ruthenates from solutions of per-ruthenates.

Potassium per-ruthenate $KRuO_4$ (Déville a. Debray, *C. R.* 83, 927). 50 g. RuO_4, melted under water, are slowly added to 60 g. KOH in 250 c.c. water at 60°; O is evolved, and the solution becomes green; after O ceases to come off, the liquid is allowed to cool in a closed vessel; the cold (red) liquid, which contains K_2RuO_4, is poured off, and the crystals of $KRuO_4$ that adhere to the sides of the vessel are dried *in vacuo* on an unglazed porcelain plate. Black, opaque, quadratic pyramids (for crystallographic measurements v. D. a. J., *C. R.* 106, 1496). Unchanged in air after drying *in vacuo*; decomposes suddenly at 440°, giving off O (? with formation of K_2RuO_4 and RuO_2). Cl reacts in the cold to form RuO_4 and KCl. Slightly sol. water; solution is blackish-green and soon decomposes, KOH being formed. Alkalis added to $KRuO_4Aq$ produce K_2RuO_4Aq, with evolution of O.

The *sodium* salt, $NaRuO_4.aq$, has been isolated; it forms black crystals. Addition of chlorides of alkaline earths to solution of $KRuO_4$, or $NaRuO_4$, ppts. $M^{II}RuO_4$, not $M^{II}(RuO_4)_2$, and the solutions contain RuO_4.

Ruthenium, sulphides of. No sulphide of Ru has been isolated with certainty. Claus could not obtain a sulphide by heating Ru with S in CO_2 (*A.* 56, 257; 59, 234). The pps. formed by H_2S in solutions of Ru compounds vary in composition, and contain free S. By ppg. $RuCl_3$ solution by H_2S, and heating the solid in CO_2, S and H_2O are given off, and a greyish-black metal-like substance remains, which is perhaps Ru_2S_3 (C., *l.c.*). The pp. which H_2S produces in RuO_4Aq is probably an *oxysulphide* (*q.v.*). The mineral *laurite*, from Borneo and Oregon, contains Ru_2S_3 with Os sulphide (Wöhler, *A.* 139, 116; 191, 374). M. M. P. M.

RUTHENIUM-AMMONIUM COMPOUNDS. (*Ruthenammines. Ammoniacal ruthenium bases.*) These compounds have not been obtained by treating Ru chlorides with NH_3Aq. The starting-point for the compounds described by Claus was $RuCl_4.2NH_4Cl$. By treatment with NH_3Aq, Claus obtained $RuCl_2.4NH_3.3aq$, and from this he prepared various salts $RuX_2.4NH_3$, where X = monovalent acidic radicle (*N. Petersb. Acad. Bull.* 1, 97; 2, 158). By evaporating a solution of the base $Ru(OH)_2.4NH_3$ *in vacuo* over H_2SO_4, Claus obtained a new base, to which he gave the formula $Ru(OH)_2.2NH_3.4aq$; he did not prepare any salts of this base. Joly (*C. R.* 107, 994) found that Claus' $RuCl_4.2NH_4Cl$ is a nitroso- compound, and has the composition $RuCl_3NO.2NH_4Cl$. Joly also showed (*C. R.* 108, 1300) that Claus' $RuCl_2.4NH_3$ has the composition $RuCl_2.NO.OH.4NH_3$, and that the salts obtained by Claus belong to the form $RuX_2.NO.OH.4NH_3$. Whether the base described by Claus as $Ru(OH)_2.2NH_3$ contains NO or not has not been determined; it is described here provisionally.

The nomenclature adopted in this article must be looked on as only provisional.

NITROSO-RUTHENI-DIAMMINES, $X.NO.Ru(NH_3.NH_3R)_2$; R may or may not be the same as X. (Joly, *C. R.* 108, 1300; 111, 969.) Described by Claus as *ammonium ruthenoso-diammonium compounds*, $N_2H_4(NH_4)_2Ru.X_2$, or *ruthenoso-diammines*, $Ru(NH_3.NH_2X)_2$.

Series I. *Hydroxy-compounds*, $OH.NO.Ru(NH_3.NH_3R)_2$. The *chloride*, R = Cl, was obtained (Joly, *C. R.* 108, 1300) by boiling $Ru(NO)Cl_3$ (described under RUTHENIUM TRICHLORIDE, p. 415) with excess of NH_3Aq, until the liquid became golden yellow, and deposited orange-yellow crystals of the salt. The *bromide* R = Br, and *iodide* R = I, were prepared similarly. The *carbonate* $R = \frac{1}{2}CO_3$, *nitrate* $R = NO_3$, and *sulphate* $R = \frac{1}{2}SO_4$, were prepared by the reaction of the chloride with Ag salts. By reacting on the chloride with moist Ag_2O, Joly obtained a strongly alkaline liquid which probably contained the *hydroxide*, R = OH. The chloride forms a *double compound* with $PtCl_4$.

Series II. *Chloro-compounds*, $Cl.NO.Ru(NH_3.NH_3R)_2$ (Joly, *C. R.* 111, 969). The *chloride*, R = Cl, was obtained by dissolving the hydroxy-chloride in much HClAq, evaporating, and crystallising from boiling water; it combines with $PtCl_4$. The *bromide* and *iodide*, R = Br and I, were obtained similarly to the chloride.

Series III. *Nitrato-compounds*, $NO_3.NO.Ru(NH_3.NH_3R)_2$. The *nitrate*, $R = NO_3$, was formed by the action of $AgNO_3Aq$, or boiling HNO_3Aq, on the chloro-chloride (J., *l.c.*).

Series IV. *Sulphato-compounds*, $SO_4.2[NO.Ru(NH_3.NH_3R)_2]$. Two *sulphates*, the normal salt where $R = \frac{1}{2}SO_4$ and the acid salt $2(SO_4.2[NO.Ru(NH_3.NH_3)_2SO_4]).H_2SO_4$, were obtained by the action of H_2SO_4Aq on the chloro-chloride.

These compounds give off NH_3 when heated in KOHAq, and separate Ru nitroso-hydroxide $Ru(OH)_3NO$, from which nitroso- salts are obtained by the action of acids.

??RUTHENOS-AMMINES, $Ru(NH_3X)_2$, or *ruthenos-diammonium compounds*, $NH_2(NH_4)Ru.X_2$. The only compound of this class which has been isolated is the *hydroxide*, $Ru(NH_3.OH)_2.4aq$, obtained by Claus (*N. Petersb. Acad. Bull.* 1, 97; 2, 158) by evaporating, over H_2SO_4 *in vacuo*, a solution of the base to which he gave the formula $Ru(NH_3.NH_3.OH)_2$. As the compound from which Claus obtained the supposed ruthenos-ammine hydroxide has been found to contain NO, it is probable that the product of evaporation was also a nitroso- compound.

M. M. P. M.

RUTIN $C_{42}H_{50}O_{25}$. [above 190°]. S. ·59 at 100°. S. (boiling alcohol) 20. S. (ether) ·29. Extracted by alcohol or HOAc from the leaves of the garden rue (*Ruta graveolens*) (Weiss, *Pharm. Centr.* 1842, 903; Borntrüger, *A.* 53, 385; Förster, *B.* 15, 217). Occurs also in capers, the flower-buds of *Capparis spinosa* (Rochleder a. Hlasiwetz, *A.* 82, 197; 96, 123; Zwenger a. Dronke, *A.* 123, 145), in safflower (Stein, *J. pr.* 58, 399; 88, 280), in rose leaves (Filhol, *J.* 1863, 594), and in the leaves of the buckwheat (*Polygonum Fagopyrum* (Schunck, *C. J.* 53, 262). Crystallises from water in pale-yellow needles (containing 8aq). Sol. alkalis, forming a yellow solution, from which it is reppd. by acids. $FeCl_3$ gives a dark-green colour. Lead acetate added to its alcoholic solution forms a yellow pp. $Pb_2C_{42}H_{44}O_{25}$. Does not reduce Fehling's solution. Decomposed by boiling dilute H_2SO_4 into quercetin (1 mol.) and isodulcite (3 mols.).

RUTYL. A name sometimes used for decoyl $C_{10}H_{19}O$ or decyl $C_{10}H_{21}$.

RUTYLENE *v.* DECINENE.

RUTYLIDENE *v.* HENDECINENE.

S

SACCHARIC ACID $C_6H_{10}O_8$ *i.e.* $CO_2H.CH(OH).CH(OH).CH(OH).CH(OH).CO_2H$. Mol. w. 210. Formed by the action of nitric acid (6 pts. of S.G. 1·15) on dextrose (glucose), and therefore on cane sugar and on milk sugar (Scheele, *Opuscula*, ii. 203; Trommsdorff, *A.* 8, 36; Guérin-Varry, *A. Ch.* [2] 49, 280; 52, 318; 65, 332; Erdmann, *A.* 21, 1; Hess, *A.* 26, 1; Thaulow, *A.* 27, 113; Liebig, *A.* 30, 313; 113, 1; Heintz, *P.* 61, 315; 105, 211; 106, 93; 111, 265, 291; *A.* 51, 185; Tollens, *B.* 21, 2149). Formed also by oxidation of dextrin, maltose, and dextrose by Br, and subsequent addition of $ZnCO_3$ (Herzfeld, *A.* 220, 353), and by the action of Br on glycuronic acid (Thierfelder, *B.* 19, 3148).

Preparation.—1. Dextrose (5 g.) is evaporated with HNO_3 (30 c.c. of S.G. 1·15) to a thick syrup. The syrup is dissolved in water (20 c.c.) and neutralised with K_2CO_3; HOAc is then added and the solution evaporated until the acid K salt crystallises out (Tollens, *A.* 249, 218).—2. Starch (100 g.) is ground up with water (100 c.c.), poured into HNO_3 (500 c.c. of S.G. 1·15), and heated on the water-bath till red fumes begin to come off. The temperature is then lowered and kept at 65° until syrupy. The product is converted as above into the acid K salt (20 g.), which is dissolved in water, neutralised with ammonia, and ppd. by $AgNO_3$. The Ag salt is then decomposed by HCl (Sohst a. Tollens, *A.* 245, 4).

Properties.—Brittle deliquescent mass, v. sol. water and alcohol, v. sl. sol. ether. Dextrorotatory, $[\alpha]_D$ varying from 8° to 38°. Reduces auric chloride and ammoniacal $AgNO_3$ (forming a mirror) but not Fehling's solution (Kiliani, *B.* 14, 2529).

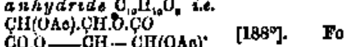
Reactions.—1. Oxidised by HNO_3 to dextrotartaric, racemic, and oxalic acids.—2. *Potash* at 250° yields acetic and oxalic acids.—3. PCl_5 forms chloromuconic acid $C_6H_4Cl_2O_4$ [260°] (Bell, *B.* 12, 1272).—4. Boiling dilute (30 p.c.) HClAq forms dehydromucic acid (S. a. T.; Schrötter, *M.* 9, 442).—5. HIAq and P at 150° forms some adipic acid (De la Motte, *B.* 12, 1572).—6. The ammonium salt decomposes at 160° into CO_2, NH_3, and pyrrole (Bell a. Lapper, *B.* 10, 1961). The ethylamine salt yields, in like manner, ethyl-pyrrole.—7. *Phenyl-hydrazine acetate* at 100° forms $C_4H_4O_4(CO.N_2H_2Ph)_2$, a yellowish substance [210°], insol. water, alcohol, and ether; not decomposed by alcoholic potash (Maquenne, *Bl.* [2] 48, 721).

Salts.—KHA'': trimetric crystals; $a:b:c = 1·763:1:2.234$. S. 1·1 at 7°.—K_2A'': crystalline crusts, v. sol. water.—$(NH_4)HA''$. S. 1·29 at 15°; 24·4 at 100°. Four-sided prisms.—BaA'': minute crystals, v. sl. sol. water.—$BaA''3aq$: amorphous.—$CaA''aq$.—$SrA''1\frac{1}{2}aq$.—$MgA''3aq$: crystalline, m. sol. hot water.—$ZnA''aq$.—CdA''.—PbA''.—$Pb_2C_6H_6O_8$.—$Pb_3C_{12}H_{14}O_{16}$.—$Pb_4C_{12}H_{10}O_{16}$.—$Pb_2C_6H_4O_8$.—Pb_2Cl_2A''.—$Bi_2C_6H_4O_8\,2aq$.—Ag_2A'': white pp.

Ethyl ether Et_2A''. Crystalline mass, v. sol. water and alcohol.—$(Et_2A'')_2CaCl_2$. Prisms, v. sol. water, sl. sol. alcohol, insol. ether.

Tetra-acetyl derivative of the ethyl ether $C_6H_4Ac_4Et_2O_8$. [61°]. Monoclinic tables (from alcohol), insol. Aq, v. e. sol. hot alcohol.

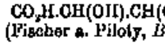
Anhydride $C_6H_8O_7$ *i.e.*



$$CH(OH)<\begin{matrix}CH(OH)\\CO\;.\;O\end{matrix}>CH.CH(OH).CO_2H.$$

Saccharolactone. [132°]. Formed by allowing syrupy saccharic acid to stand over H_2SO_4 for some days (Sohst a. Tollens, *A.* 245, 5). Thin plates (from water). Yields pyromucic acid on heating. Reduced in acid solution by treatment with sodium-amalgam to glycuronic acid $CO_2H.CH(OH).CH(OH).CH(OH).CH(OH).CHO$ (Fischer a. Piloty, *B.* 23, 937; 24, 521).

Di-acetyl derivative of the double anhydride $C_{10}H_{10}O_8$ *i.e.*



$$\begin{matrix}CH(OAc).CH.O.CO\\CO.O\text{——}CH-CH(OAc)\end{matrix}$$

[188°]. Formed from Ac_2O, acid potassium saccharate, and H_2SO_4 (Maquenne, *Bl.* [2] 48, 720; *cf.* Baltzer, *Bl.* [2] 10, 263; *A.* 149, 238). White plates, v. sl. sol. alcohol and ether.

Amide $C_6H_8O_4(NH_2)_2$. Amorphous powder.

Isosaccharic acid $C_6H_{10}O_7$. [185°]. $[\alpha]_D = 46°$ at 20°. Formed by careful oxidation of glucosamine hydrochloride by dilute HNO_3 (S.G. 1·2) (Tiemann, *B.* 17, 246; 19, 1258, 1273). Trimetric crystals (from water), v. sol. water and alcohol, sl. sol. ether. Dextrorotatory. Converted by heat into CO_2 and pyromucic acid. Reduced by HI to adipic acid. Heated in a current of dry HCl it yields furfurane ($\alpha\alpha'$)-dicarboxylic acid. PCl_5 forms $C_4H_2ClO(CO_2H)_2$, which yields Et_2A'' [40°].—

KHA″ ½aq: v. sol. water.—$(NH_4)_2A''$.—BaA″.—CaA″.—SrA″.—PbA″ 2aq.—CuA″.—Ag_2A''.

Ethyl ether Et_2A''. [73°]. (250°). $[\alpha]_D = +35{\cdot}5°$. Needles, v. sol. water. Yields a tetra-acetyl derivative $C_4H_4(OAc)_4(CO_2Et)_2$ [47°] v. sol. water and alcohol.

Amide of the anhydride $C_4H_4O(OH)_2(CONH_2)_2$ [226°]. $[\alpha]_D = 7{\cdot}2°$.

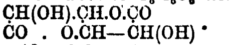
Anilide of the anhydride. [231°].

Acetyl derivative $C_4H_4(OAc)_4(CO_2H)_2$ aq. [101°]. Needles (from water).

Parasaccharic acid $C_6H_{10}O_8$. Formed, together with glycyrrhetin, by boiling glycyrrhizin with dilute H_2SO_4 (Habermann, *C. C.* 1880, 253). Hygroscopic mass, sol. water and alcohol. Its salts are amorphous.

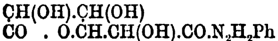
Metasaccharic acid $C_6H_{10}O_8$. The salt CaA″ aq, got by boiling an aqueous solution of the dianhydride with $CaCO_3$, forms crystals, sl. sol. water. KA′ and $Ag_2C_6H_8O_8$ have also been prepared (Fischer, *B.* 23, 2621). Solutions of metasaccharates turn deep red when exposed to air.

Dilactone $C_6H_6O_6$ *i.e.*



$$\begin{array}{l}\text{ÇH(OH).ÇH.O.ÇO}\\ \text{CO . O.CH—CH(OH)}\end{array}$$

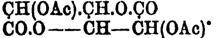
. *l-Mannosaccharic acid.* [68°]. S. 5·5 at 15°. $[\alpha]_D = -202°$ (Fischer, *B.* 24, 541). Formed by oxidation of arabinose-carboxylic (mannonic) acid $C_6H_{12}O_7$ by digesting its lactone with HNO_3 (S.G. 1·2) for 24 hours at 50° (Kiliani, *B.* 20, 341, 2710; 21, 1422). Long colourless needles (containing 2aq), sl. sol. alcohol, insol. ether. Readily reduces Fehling's solution. Reduced by HI to *n*-adipic acid. Sodium-amalgam reduces it to mannite. Phenyl hydrazine hydrochloride and sodium acetate solution in the cold form



$$\begin{array}{l}\text{ÇH(OH).ÇH(OH)}\\ \text{CO . O.CH.CH(OH).CO.}N_2H_2\text{Ph}\end{array}$$

[192°] crystallising in minute plates (containing ½aq), v. e. sol. hot water. Phenyl hydrazine hydrochloride and boiling sodium acetate solution forms $C_4H_4(OH)_4(CO.N_2H_2Ph)_2$, crystallising in minute plates [213°], v. sl. sol. water.

Di-acetyl derivative of the dilactone



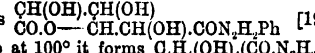
$$\begin{array}{l}\text{ÇH(OAc).ÇH.O.ÇO}\\ \text{CO.O——CH—CH(OAc)}\end{array}$$

. [155°]. Formed by adding a few drops of H_2SO_4 to a mixture of the dilactone and Ac_2O (Kiliani, *B.* 22, 524). Prisms, v. sol. hot HOAc.

Amide $C_4H_4(OH)_4(CO.NH_2)_2$. [190°]. Formed from the lactone and NH_3Aq. Monoclinic tables.

Dextro-metasaccharic acid. *d-Mannosaccharic acid* $C_6H_{10}O_8$. Salts.—CaA″: crystalline powder.—BaA″: minute tables, m. sol. water.—SrA″.—CdA″: minute tables, v. sl. sol. water.

Lactone $C_6H_6O_6$. [180°–190°]. $[\alpha]_D = 202°$ at 23°. Formed by oxidation of mannose, of mannite, or of *d*-mannonic acid by HNO_3 (S.G. 1·2) at 50° (Fischer a. Wirthle, *B.* 24, 539; Easterfield, *C. J.* 59, 306). Long needles (from alcohol or water), v. sol. hot water. Readily reduces Fehling's solution. Turns yellow on boiling with potash. Phenyl-hydrazine acetate in the cold forms



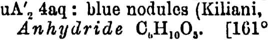
$$\begin{array}{l}\text{ÇH(OH).ÇH(OH)}\\ \text{CO.O—CH.CH(OH).CON}_2\text{H}_2\text{Ph}\end{array}$$

[191°], while at 100° it forms $C_4H_4(OH)_4(CO.N_2H_2Ph)_2$ [212°], almost insol. hot water.

Amide $C_6H_{12}N_2O_6$. [189°]. Formed from the lactone and NH_3Aq in the cold. Crystals.

Inactive metasaccharic acid $C_6H_{10}O_8$. *i-Mannosaccharic acid.* The salts of this acid greatly resemble those of the preceding acid.

Lactone $C_6H_6O_6$. [c. 190°]. Formed by mixing equal parts of the dextro- and lævo-lactones in aqueous solution. Formed also by oxidising *i*-mannonic lactone (E. Fischer a. Stanley Smith, *B.* 23, 2622; 24, 544). The aqueous solution is inactive to light, and gradually becomes acid on standing. Phenyl-hydrazine acetate reacts, forming in the cold



$$\begin{array}{l}\text{ÇH(OH).ÇH(OH)}\\ \text{CO.O —CH.CH(OH).CON}_2\text{H}_2\text{Ph}\end{array}$$

[190°–195°] and at 100° $C_4H_4(OH)_4(CON_2H_2Ph)_2$ [220°–225°].

Amide. [185°].

SACCHARIN. The lactone of saccharinic acid (*v. infra*). The name has also been applied to the imide of SULPHOBENZOIC ACID.

SACCHARINIC ACID $C_6H_{12}O_6$ *i.e.*

$CH_2(OH).CH(OH).CH(OH).CMe(OH).CO_2H$.

Formed by boiling an aqueous solution of dextrose, lævulose, or invert sugar with lime (Péligot, *Bl.* [2] 36, 226; *C. R.* 90, 1141; Scheibler, *B.* 13, 2212). On setting the acid free it changes, especially on heating, into the anhydride. The salts are v. e. sol. water.—KA′: monoclinic tables.—NaA′. $[\alpha]_D = -17{\cdot}2°$.—$CaA'_2$ (dried at 100°). Formed by boiling the lactone with water and $CaCO_3$. Amorphous. $[\alpha]_D = -5{\cdot}7°$.—CuA'_2 4aq: blue nodules (Kiliani, *B.* 15, 2955).

Anhydride $C_6H_{10}O_5$. [161°]. $[\alpha]_D = 94°$. S. 13 at 15°. *Electrical conductivity*: Walden, *B.* 24, 2028. H.C. 656,900. H.F. 252,100 (Stohmann, *J. pr.* [2] 45, 313).

Preparation.—A cold solution of 1 kg. of invert sugar in 9 litres of water is treated with 100 g. of powdered lime and allowed to stand, agitating at intervals. After 14 days 400 g. more CaO_2H_2 is added, and the mixture again allowed to stand for one or two months, until it no longer reduces Fehling's solution. It is then saturated with CO_2, the remaining Ca precipitated with oxalic acid, and the filtrate evaporated nearly to a syrup. The saccharin which separates is recrystallised from hot water; the yield is 100 g. (Kiliani, *B.* 15, 2954).

Properties.—Prisms, with bitter taste, v. sol. hot water. Dextrorotatory. Converted by alkalis into lævorotatory salts of saccharinic acid. May be volatilised almost without decomposition. Can be extracted by ether, even from solutions containing Na_2CO_3. Does not ferment with yeast. Does not reduce Fehling's solution, even after long boiling with dilute H_2SO_4. Not attacked by dilute HNO_3. Conc. HNO_3 forms oxalic acid and saccharonic acid $C_6H_{10}O_7$. 1 g. reduces 4·6 g. of $KMnO_4$. Oxidised by moist Ag_2O to formic, acetic, and glycollic acids. Boiling HIAq reduces it to the lactone of γ-oxy-isohexoic acid $CH_3.CH(OH).CH_2.CHMe.CO_2H$, which is further reduced by HI at 200° to $CHMePr.CO_2H$ (Liebermann a. Scheibler, *B.* 16, 1821; Kiliani, *A.* 218, 371). I and KOH give iodoform. Potash-fusion forms formic and lactic acids (Hermann a. Tollens, *B.* 18, 1333). Boiling HClAq has no action. Phenyl-hydrazine forms $C_6H_{11}O_5(N_2H_2Ph)$ [165°], crystallising from alcohol in needles, v. sol. water (Fischer a. Passmore, *B.* 22, 2733). Phenyl cyanate at 165° forms $C_{34}H_{30}N_4O_9$, crystallising in silky needles

[230°-240°], v. sol. hot aniline, sl. sol. alcohol (Tesmer, *B.* 18, 2607).

Isosaccharinic acid $C_6H_{12}O_6$ *i.e.* $CH_2(OH).CH(OH).CH_2.C(OH)(CO_2H).CH_2OH$? Formed by the action of lime on malt-extract at 20° or on milk-sugar (Cuisinier, *Bl.* [2] 38, 512). The free acid at once splits up into water and lactone. The Na salt is lævorotatory.—CaA'_2. S. 1 in hot water. Crystalline powder.

Lactone $C_6H_{10}O_5$. *Isosaccharin.* [95°]. $[\alpha]_D = 63°$ in a 10 p.c. aqueous solution; = 74° in HOAc. Electrical conductivity: Walden, *B.* 24, 2028. Prepared by allowing a solution of milk-sugar (1 kilo) in water (9 litres) mixed with slaked lime (450 g.) to stand for 6 weeks; filtering; saturating the filtrate with CO_2; boiling, again filtering, and evaporating to 500 c.c. The calcium isosaccharinate (170 g.) which then crystallises is decomposed by oxalic acid (Kiliani, *B.* 18, 631). Large crystals, v. e. sol. water, alcohol, and ether. Dextrorotatory. Does not ferment with yeast or reduce Fehling's solution.

Reactions.—1. Reduced by HI and P to the lactone of oxy-hexoic acid, and finally to $CHPrMe.CO_2H$.—2. Oxidised by HNO_3 to di-oxy-propane tricarboxylic acid $C_3H_3(OH)_2(CO_2H)_3$, which is split up by heat into CO_2 and $\alpha\gamma$-di-oxy-glutaric acid $CH_2(CH(OH).CO_2H)_2$ (Kiliani, *B.* 18, 2514).—3. *Phenyl cyanate* at 165° forms $C_{34}H_{30}N_4O_9$ [181°] a white amorphous powder (Tesmer, *B.* 18, 2609).

Anilide $C_{12}H_{17}NO_5$. [165°]. Formed by heating the lactone with aniline at 115° (Sorokin, *Bl.* [2] 47, 168; *J. pr.* [2] 37, 318). Needles, v. sol. water. Decomposed by acids and alkalis into aniline and isosaccharin.

Metasaccharinic acid $C_6H_{12}O_6$ *i.e.* $CH_2(OH).CH(OH).CH(OH).CH(OH).CH_2.CO_2H$. Formed, together with isosaccharinic acid, by the action of lime on a cold solution of milk-sugar, its Ca salt being contained in the mother-liquor from which calcium isosaccharinate has crystallised (Kiliani, *B.* 16, 2625; 18, 642). The free acid splits up at once into water and lactone.—CaA'_2 2aq: crusts of minute prisms, v. sl. sol. cold water.—CuA'_2 2aq: groups of minute green plates.

Lactone $C_6H_{10}O_5$. *Metasaccharin.* [142°]. $[\alpha]_D = -48°$. Large trimetric plates; $a:b:c$ = ·624:1:·899. V. sol. cold water and alcohol, v. sl. sol. ether. Lævorotatory.

Reactions.—1. Reduced by HI to the lactone of oxy-*n*-hexoic acid.—2. Oxidised by HNO_3 to tri-oxy-adipic acid.—3. *Phenyl cyanate* at 165° forms $C_{34}H_{30}N_4O_9$, a white amorphous powder [205°-210°] (Tesmer, *B.* 18, 2608).

SACCHAROLACTONE *v. Anhydride* of SACCHARIC ACID.

SACCHARONIC ACID $C_6H_{10}O_7$ *i.e.* $CO_2H.CH(OH).CH(OH).CMe(OH).CO_2H$. Formed by heating saccharin (1 pt.) with HNO_3 (3 pts. of S.G. 1·375) at 35°, diluting, adding $CaCO_3$, filtering, evaporating, and extracting with ether (Kiliani, *A.* 218, 361). The product so obtained is the lactonic acid; the free acid at once splits up into water and lactone.—Na_2A''. Formed by boiling the anhydride with Na_2CO_3Aq. Crystalline. — $(NH_4)_2A''$.—CaA'': gummy. — Ag_2A'': flocculent pp.

Lactonic acid $C_6H_8O_6$. *Saccharone.* $[\alpha]_D = -6°$. Formed as above. Large trimetric crystals (containing aq), v. sl. sol. ether. Conc. HIAq converts it into a dibasic acid $C_6H_8O_4$ [139°] crystallising from water in small prisms, and finally to α-methyl-glutaric acid. Does not reduce Fehling's solution.—NaA' aq. Formed from saccharone (2 mols.) and Na_2CO_3Aq (1 mol.). Trimetric prisms with neutral reaction.—NH_4A': crystals. Its aqueous solution is ppd. by lead subacetate, but not by lead acetate or $AgNO_3$.

SACCHARUMIC ACID $C_{14}H_{18}O_{11}$. A product of the action of baryta on dextrose (Reichardt, *Vierteljahrschrift pr. Pharm.* 19, 384, 503). Yellowish-brown powder with bitter taste, v. sol. water and alcohol, sl. sol. ether. Its solution becomes dark on exposure to air or on addition of alkalis. — BaH_2A^{iv}. — Ba_2A^{iv} 5aq: pp. — Cu_2A^{iv} 3aq: greyish-brown pp. — Pb_2A^{iv}. — $Pb_3C_{14}H_{12}O_{11}$.

SACCULMIC ACID $C_{11}H_{10}O_4$? Formed, together with sacculmin, by boiling cane-sugar (300 g.) with H_2SO_4 (15 g.) and water (420 g.) (Stein, *A.* 30, 84; Sestini, *G.* 10, 121). The yield of the two bodies is about 10 p.c. of the sugar used. Glittering black mass, sl. sol. water and alcohol, insol. ether. The alcoholic solution is red, with reddish-brown reflex. Sol. KOHAq and reppd. by acids. $AgNO_3$ gives brown amorphous $C_{44}H_{30}AgO_{16}$. $BaCl_2$ ppts. brown $C_{22}H_{18}BaO_8$ aq. Chlorine passed into water in which sacculmic acid or sacculmin is suspended gives yellow flocculent di-chloro-oxy-sacculmide $C_{11}H_8Cl_2O_6$. Di-chloro-oxy-sacculmide boiled with KOHAq forms oxysacculmic acid $C_{11}H_8O_6$, which is sol. water, but insol. water containing H_2SO_4. $CuSO_4$ gives in its aqueous solution a brown pp. of $C_{44}H_{30}CuO_{21}$. Bromine and water form amorphous orange $C_{44}H_{26}Br_6O_{22}$ (Sestini, *G.* 12, 292).

Sacculmin $C_{44}H_{38}O_{15}$. Formed as above. Black amorphous mass, insol. KOHAq. Reacts with chlorine water in the same way as sacculmic acid. According to Conrad and Guthzeit (*B.* 18, 443; 19, 2844), sacculmin and sacculmic acid are mixtures of variable composition.

SAFFLOWER *v.* CARTHAMIN.

SAFFRANINE (PHENO-) $C_{18}H_{16}N_4O$. *Phenosaffranine.* The hydrochloride may be represented as $C_6H_3(NH_2)<\genfrac{}{}{0pt}{}{N\overline{}}{NPhCl}>C_6H_3NH_2$ (Bernthsen, *B.* 20, 179, 2690; *cf.* Andresen, *B.* 19, 2215; Nietzki, *B.* 19, 3017, 3163; Witt, *B.* 19, 3121), or by $C_6H_4<\genfrac{}{}{0pt}{}{N\overline{}}{NCl(C_6H_4NH_2)}>C_6H_3(NH_2)\left[\begin{smallmatrix}2 & \\ 1 & 4\end{smallmatrix}\right]$ (Witt).

Formation.—1. Formed by gently warming phenylene-*p*-diamine (1 mol.) with aniline (2 mols.) and $K_2Cr_2O_7$ (Nietzki, *B.* 16, 466). A blue compound $C_6H_4<\genfrac{}{}{0pt}{}{N\overline{}}{NCl(NHPh)}>C_6H_3NH_2$ (?) is first formed, and changes at 100° into the red saffranine (Barbier a. Vignon, *Bl.* [2] 48, 338 772; *C. R.* 105, 939). The blue compound is reduced by zinc and hydrochloric acid to $C_6H_4<\genfrac{}{}{0pt}{}{NH}{NH}>C_6H_3.NH_2$, which is oxidised by air to amido-phenazine. According to Nietzki, however, the blue intermediate compound is the indamine $C_6H_4(NH_2).N:C_6H_4:NH_2Cl$ and yields di-amido-diphenylamine on reduction.—2. From benzene-azo-aniline (amido-azo-benzene) by treatment with nitro-benzene, Fe, and HClAq

(B. a. V.).—3. By oxidising a mixture of $NH(C_6H_4.NH_2[1:4])_2$ (1 mol.) and aniline (1 mol.) with $K_2Cr_2O_7$ (B.).

Properties.—Golden plates. When freshly precipitated by baryta from the sulphate it is $C_{18}H_{15}N_4OH$, but after frequent recrystallisation from hot water it approximates to $C_{18}H_{14}N_4$ (Nietzki a. Otto, *B.* 21, 1590). V. sol. hot water, sol. alcohol, almost insol. ether. Conc. H_2SO_4 gives a green colour, changing to blue and red on dilution. Conc. HClAq gives a blue colour. $NaNO_2$ added to a solution of saffranine hydrochloride forms the diazo- compound $C_{18}H_{15}N_5Cl_2$, which gives a blue solution and yields $C_{18}H_{15}N_5Cl_22AuCl_3$. This diazo- compound on boiling with alcohol forms $C_{18}H_{13}N_3$, the salts of which form red aqueous solutions and dye wool and silk a bluer shade than saffranine. The base $C_{18}H_{13}N_3$ is also got by adding H_2SO_4 till the colour is violet, then adding excess of $NaNO_2$ and boiling: it yields $B'HNO_3$, $B'H_2SO_4$, and a violet acetyl derivative. Alcoholic potash forms NH_3 and saffranol. Zinc-dust and HCl give leuco-saffranine and, on long boiling, $C_{18}H_{19}N_3O$ [130°], crystallising from water in long needles yielding $C_{18}H_{18}AcN_3O$ [173°] and converted by nitrous ether into $C_{18}H_{18}N_2O$ [117°], crystallising from alcohol in needles.

Salts. — $(C_{18}H_{15}N_4Cl)_2PtCl_4$. — $C_{18}H_{15}N_4Cl$. Flat needles with green lustre, sl. sol. cold, v. sol. hot water, insol. HClAq.—$B'HNO_3$. Almost insol. HNO_3.

Di-acetyl derivative $C_{18}H_{14}Ac_2N_4$.—B'HCl. Got by heating saffranine hydrochloride with Ac_2O and NaOAc (Nietzki, *B.* 16, 468). Lustrous brown plates, forming a violet solution in alcoholic soda.—B'HI.

Di-methyl-saffranine. The chloride of this substance $C_{20}H_{19}N_4Cl$ is formed, together with $N_2(C_6H_4NMe_2)_2$, by the action of *p*-nitroso-di-methyl-aniline (1 mol.) on aniline (1 mol.) in alcoholic solution at 100° (Barbier a. Vignon, *C. R.* 105, 672). An isomeric (?) di-methyl-saffranine got by oxidising a mixture of $C_6H_4(NH_2)NMe_2$ and aniline yields $B'_2H_2PtCl_6$ and $B'HNO_3$ (Nietzki, *B.* 16, 869 ; 19, 3163). An isomeride is formed by heating benzene-azo-xylidine with aniline at 150° (Menton, *A.* 263, 337). Crystalline, forming a rose-red aqueous solution. A tetramethyl-saffranine $C_{22}H_{22}N_4$ is got by oxidising di-methyl-phenylene-green mixed with aniline acetate (Bindschedler, *B.* 16, 867). It yields B'HCl, v. e. sol. water and $B'HNO_3$ aq.

Ethyl-saffranine $C_{18}H_{13}EtN_4$. Formed by boiling *p*-phenylene-ethyl-diamine with aniline, $K_2Cr_2O_7$, and dilute HOAc (Schweizer, *B.* 19, 150). Formed also by oxidising phenylene-*p*-diamine, aniline, and ethyl-aniline with $K_2Cr_2O_7$ and dilute HOAc (S.). The hydrochloride forms bluish-green hygroscopic crystals, sol. water and alcohol, insol. ether. Its solutions exhibit olive-green fluorescence.—$B'_2H_2PtCl_6$: dark lustrous needles.

Di-ethyl-saffranine $C_{22}H_{24}N_4$. Formed by oxidising a mixture of $C_6H_4(NH_2)(NEt_2)$ (1 mol.) and aniline (2 mols.) with $K_2Cr_2O_7$ (Nietzki, *B.* 16, 470). Formed also by oxidising a mixture of phenylene-*p*-diamine, aniline, and di-ethyl-aniline with $K_2Cr_2O_7$ (N.). The alcoholic solution is fluorescent. The hydrochloride is sol. HClAq. $NaNO_2$ added to its solution in HClAq gives a greenish-blue colour due to the diazo-chloride which forms $C_{22}H_{23}N_5Cl_2PtCl_4$. — $B'_2H_2PtCl_6$: green needles.

Acetyl derivative $C_{18}H_{11}Et_2AcN_4$. The hydrochloride is ppd. as glittering brown needles on adding NaCl to its aqueous solution. —$B'_2H_2PtCl_6$.

Tetra-ethyl-saffranine $C_{26}H_{32}N_4$ or $C_{26}H_{33}N_4.OH$. Formed by oxidising a mixture of phenylene-di-ethyl-*p*-diamine, aniline, and di-ethyl-aniline with $K_2Cr_2O_7$ (N.).—$B'_2H_2PtCl_6$.

Para-saffranine $C_{20}H_{18}N_4$. Prepared by dissolving mauveïne in dilute acetic acid and boiling with PbO_2. NaOH is added to slight excess, and the red filtrate boiled with some powdered zinc and $CaCO_3$ and then NaCl added. Commercial saffranine contains some para-saffranine (Perkin, *C. J.* 35, 728).

Properties.—Red-brown pp., dissolving in water or alcohol. It is isomeric or identical with commercial saffranine, prepared from equal molecules of tolylene *p*-diamine, *o*-toluidine, and aniline. Salts.—B'HCl.—$B'HNO_3$. These salts dye silk a shade more scarlet than saffranine.

Saffranine $C_{21}H_{20}N_4$ or $C_{21}H_{21}N_4OH$. Formed from *o*-toluidine by treatment with nitrous acid and oxidation of the product with $K_2Cr_2O_7$ (Mène, *C. N.* 25, 215; Hofmann a. Geyger, *B.* 5, 526; Dale a. Schorlemmer, *C. J.* 35, 683). Obtained by heating toluene-azo-*o*-toluidine with *o*-toluidine hydrochloride at 150°–160° (Witt, *B.* 10, 873), and by adding K_2CrO_4 to a hot solution of tolylene-*p*-diamine hydrochloride (1 mol.) and *o*- or *p*-toluidine hydrochloride (2 mols.) (Witt, *B.* 12, 939; Bindschedler, *B.* 13; 207). The commercial saffranine (saffranine hydrochloride) can be purified by recrystallisation from water containing HCl, or by treatment with alcohol (Böttger, *N. R. P.* 23, 181). Reddish-brown crystals, v. sol. water and alcohol, insol. ether. Conc. HCl changes the colour of its solution through violet to blue. H_2SO_4 turns it blue and finally green. Decolourised by zinc and HClAq. Saffranine is also decolourised by glucose and NaOHAq on heating, and hence may be used as a test for sugar in urine (Crismer, *C. C.* 1888, 1510); the colour is restored by atmospheric oxidation. Commercial saffranine (·5 g.) is fatal when administered to dogs by subcutaneous injection (Weyl, *B.* 21, 2191).—B'HCl. Thin reddish crystals, sol. water and alcohol, insol. ether and NaClAq.—$B'_2H_2PtCl_6$. Yellowish-red crystalline powder, almost insol. water, alcohol, and ether. —×B'HBr: minute needles.—$B'HNO_3$. Slender reddish-brown needles, v. sl. sol. cold water.—Sulphate: needles, m. sol. water.—$B'C_6H_3N_3O_7$: brownish-red insoluble needles.

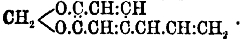
Substances of the saffranine class are formed by heating $NH(C_6H_4NH_2)_2$ with (4,3,1)- and (4,2,1)- xylidine and with (5,4,2,1)-cumidine, but not with mesidine, (5,4,3,1)-cumidine, or (5,2,1)-, (6,2,1)-, (5,3,1)-, and (3,2,1)-xylidine (Nietzki, *B.* 19, 3163).

Saffranol $C_{18}H_{10}N_2(OH)_2$. Formed by boiling saffranine hydrochloride with alcoholic potash for 3 days (Nietzki a. Otto, *B.* 21, 1593). Ppd. as yellowish needles by adding HCl to its solution in alkalis. Nearly insol. water, alcohol, and HOAc. Conc. H_2SO_4 forms a brown solution. Yields a crystalline diacetyl derivative.

SAFFRON. The dried stigmas of *Crocus sativus*, used as a colouring matter. It contains crocin (*q.v.*), crocose (*q.v.*), picrocrocin (*q.v.*), polychroite, and an oil $C_{10}H_{14}O$ (209°) miscible with alcohol and ether but decomposed by water (Quadrat, *J. pr.* 56, 68; Weiss, *J. pr.* 101, 65).

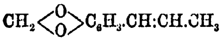
Polychroite $C_{48}H_{60}O_{18}$. Dried saffron is washed with ether and extracted with water. The extract is mixed with alcohol and filtered, and the filtrate ppd. by ether. Orange deliquescent mass, v. sol. water, insol. alcohol. Yields glucose on boiling with dilute acids.

SAFROLE $C_{10}H_{10}O_2$ *i.e.*

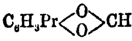


$CH_2<\begin{array}{l}O.\underset{|}{C}.CH:\underset{|}{CH}\\ O.\overset{|}{C}.CH:\overset{|}{C}.CH.CH:CH_2\end{array}$ · *Shikimole.* [8°]. (232°). S.G. $\frac{18}{}$ 1·0956 (S.); $\frac{11\cdot3}{}$ 1·0963 (Gladstone, *C. J.* 59, 290). V.D. 81 (obs. and calc.). $\mu_D = 1{\cdot}539$ at 11° (G.). $R_\infty = 45{\cdot}57$ (Brühl, *B.* 21, 477). H.C.v. 1,243,800. H.C.p. 1,244,700. H.F. 40,300 (Stohmann a. Langbein, *J. pr.* [2] 46, 533). The chief constituent of the essential oil of sassafras (*Sassafras officinalis*) (Grimaux a. Ruotte, *A.* 152, 88; J. Schiff, *B.* 17, 1935; Poleck, *B.* 17, 1940; 19, 1094; 22, 2861). Occurs also in the oil obtained from the leaves and fruit of *Illicium religiosum* (Eykman, *R. T. C.* 4, 36, 45; *B.* 22, 2757; 23, 864), and in the oil of the camphor tree, *Cinnamomum camphora* (Flückiger, *Ph.* [3] 17, 989). Monoclinic crystals, sol. alcohol and ether. Smells like oil of sassafras. Inactive to light. Oxidised by dilute $KMnO_4$ to CO_2, formic, oxalic, and piperonylic acids, and piperonal. Alcoholic potash converts it into isosafrole. Does not react with hydroxylamine or BzCl. Does not combine with $NaHSO_3$. Bromine forms $C_{10}H_5Br_5O_2$ [170°] S. (chloroform) 7.

Isosafrole $C_{10}H_{10}O_2$ *i.e.*

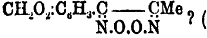


$CH_2<\begin{array}{c}O\\ O\end{array}>C_6H_3.CH:CH.CH_3$. (247°). V.D. 80·3 (obs.); 81 (calc.). H.C.v. 1,233,600. H.C.p. 1,234,500. H.F. 50,500. Formed by boiling safrole (100 g.) with KOH (250 g.) in alcohol (500 c.c. of 94 p.c.) for 24 hours (Schiff; Ciamician a. Silber, *B.* 23, 1160). Liquid, even at −18°, miscible with alcohol, ether, HOAc, and benzene, insol. water and alkalis. Conc. H_2SO_4 forms an intensely red solution. Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to piperonal and acetic aldehyde. Alkaline $KMnO_4$ gives piperonylic acid. Bromine in CS_2 forms $C_{10}Br_3H_9O_2$ [110°], crystallising from ligroïn in colourless needles. Sodium reduces it in alcohol solution to $C_{10}H_{12}O_2$ or

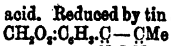


$C_6H_3Pr<\begin{array}{c}O\\ O\end{array}>CH_2$ (228°), a liquid miscible with alcohol and ether. Isosafrole is converted by treatment with KOH and MeOH into a compound, apparently different from methyl-eugenol, but yielding isovanillic acid on oxidation, and [4:2:1] $C_6H_3(C_3H_5)(OAc)_2$ on treatment with Ac_2O (Ciamician a. Silber, *B.* 25, 1470).

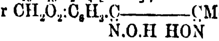
Nitrosite $C_{10}H_8N_2O_4$ *i.e.*



$CH_2O_2:C_6H_3.\begin{array}{c}\underset{|}{C}\text{——}\underset{|}{C}Me\\ N.O.O.N\end{array}$? (Angeli, *B.* 24, 3994; 25, 1956). Mol. w. 224 (by Raoult's method). [124°]. Ac_2O forms a white modification [124°]. Alcoholic potash forms an isomeride [185°] which yields a mono-acetyl derivative [129°], and a benzoyl derivative [146°]. $KMnO_4$ oxidises it to piperonylic acid. Reduced by tin and HClAq to $C_{10}H_8N_2O_3$ or



$CH_2O_2:C_6H_3.\begin{array}{c}\underset{|}{C}-\underset{|}{C}Me\\ N.O.N\end{array}$? [86°]. Mol. w. 197 (by Raoult's method). Zinc and HOAc yield $C_{10}H_{10}O_3$, probably represented by $(CH_2O_2)C_6H_3.CH_2.CO.CH_3$ [38°], which yields a phenyl-hydrazide $C_{10}H_{10}O_2(N_2HPh)$ [97°]. Another product of the action of zinc and HOAc is $C_{20}H_{18}N_2O_4$ [180°]; and a third is $C_{10}H_{10}N_2O_4$ or



$CH_2O_2:C_6H_3.\begin{array}{c}\underset{|}{C}\text{————}\underset{|}{C}Me\\ N.O.H\ \ HON\end{array}$? [159°], which yields a di-acetyl derivative [138°].

SAGAPENUM. A gum resin imported from Egypt and Persia, consisting of yellow agglomerated granules, smelling like garlic and having an acrid bitter taste. Softens in the hand. Yields umbelliferone on distillation. HNO_3 forms styphnic acid. Potash-fusion forms resorcin (Brandes, *N. Tr.* 2, 2, 97; Pelletier, *Bull. Pharm.* 3, 481; Johnston, *Tr.* 1840, 361). After moistening with alcohol it dissolves in H_2SO_4, forming a brown liquid. Sagapenum is only partially soluble in alcohol and ether, but the ethereal extract is not clouded by addition of alcohol. $FeCl_3$ colours its solutions black (Hirschsohn, *J.* 1875, 859; *Ar. Ph.* [3] 10, 481; 11, 54, 152, 247, 312, 434; *C. C.* 1877, 182).

SAGE OIL. Obtained in the south of Europe by distilling sage (*Salvia officinalis*) with water, the plant being cut down in the autumn (M. M. P. Muir, *C. J.* 33, 292; 37, 678; *cf.* Rochleder, *A.* 44, 4; Herberger, *R. P.* 34, 138; Hlasiwetz, *J. pr.* 51, 355). Contains a terpene (156°), salviol (*q.v.*), $C_{10}H_{18}O$ (c. 200°), a camphor $C_{10}H_{16}O$, probably a little cymene, and, especially when prepared from English plants, cedrene, $C_{15}H_{24}$ (c. 260°). The amount of salviol and of camphor is very small at first and increases with the age of the oil, being formed by oxidation of the terpenes. Pure salviol, pure sage terpene, and pure cedrene do not resinify when singly exposed to heat and light; but a mixture of these rapidly darkens.

SAGO. Balls of starch got from the pith of certain species of *Sagus* and *Cycas* by stirring with water, allowing to settle, and rubbing the deposit through sieves.

SALAMANDRINE $C_{34}H_{60}N_2O_5$. An alkaloid obtained from the poisonous secretion of the cutaneous glands of the salamander (*Salamandra maculata*). Crystalline, v. sol. water and alcohol (Zalesky, *Bl.* [2] 6, 344). Alkaline in reaction. Poisonous.—$B'H_2Cl_2$: needles.

SALICIN $C_{13}H_{18}O_7$ *i.e.* $C_6H_{11}O_5.O.C_6H_4.CH_2OH$. Mol. w. 286. [201°] (Schiff, *B.* 14, 304). S. 3·3 at 11° (Piria, *A.* 96, 378). $[\alpha]_D = -62{\cdot}6°$ (Tiemann, *B.* 18, 1600; *cf.* Hesse, *A.* 176, 116; Sorokin, *J. pr.* [2] 37, 331). Occurs in the bark of several species of willow and poplar, *e.g.* *Salix helix*, *S. amygdalina*, *Populus tremula*, *P. græca* (Leroux, *A. Ch.* [2] 43, 440; Braconnot, *A. Ch.* [2] 44, 296; Pelouze a. Gay-Lussac, *A. Ch.* [2] 44, 220; 48, 111; Piria, *A. Ch.* [2] 69, 281; [3] 1[illegible], 257; Bouchardat, *C. R.* 18, 299; 19, 602, 1179; 20, 610, 1635; Gerhardt, *A. Ch.* [3] 7, 215; Tischhauser, *A.* 7, 280). Occurs also in castoreum (Wöhler, *A.* 67, 360).

Formation.—1. By digesting an aqueous solution of helicin with sodium-amalgam (Lisenko, *Z.* 1864, 577) or with zinc and H_2SO_4 (Michael, *Am.* 5, 172).—2. By boiling populin with lime-water (Piria).

Preparation.—Willow bark (6 lbs.) is boiled with water; the filtrate evaporated (to 18 lbs.); mixed while hot with PbO (2 lbs.); digested for 24 hours and filtered; the filtrate evaporated to a syrup and left to crystallise (Duflos, *A.* 8, 200; *cf.* Peschier, *A. Ch.* [2] 44, 418; Erdmann, *B. J.* 33, 1, 136).

Properties.—Trimetric tables; a:b:c = ·927:1:2·494. Sol. water and alcohol, insol. ether. Lævorotatory. Tastes bitter. Neutral to litmus. Its solutions are not ppd. by lead acetate or subacetate, by gelatin, or by tannin. Conc. H_2SO_4 gives a red colour. IClAq forms a crystalline body (Stenhouse, *C. J.* 17, 327). After injection of salicin, salicylic aldehyde and salicylic acid are found in the urine (Laveran a. Millon, *A. Ch.* [3] 13, 145; Ranke, *J. pr.* 56, 1).

Reactions.—1. Decomposed at 240° into saliretin and glucosan.—2. Split up by *emulsin* and *saliva* at 40° into glucose and saligenin (Piria; Städeler, *J. pr.* 72, 350).—3. Boiling dilute H_2SO_4 forms glucose and saliretin.—4. Oxidised by *chromic acid mixture* to CO_2, formic acid, and salicylic aldehyde.—5. Cold dilute HNO_3 forms helicin. Hot conc. HNO_3 forms picric acid.—6. *Potash-fusion* forms salicylic acid.—7. Boiling NaOHAq forms saliretin.—8. HCl and $KClO_3$ give tetra-chloroquinone.

Metallic derivatives. — $C_{13}H_{17}NaO_7$. Formed from salicin and NaOEt in alcohol (Perkin, *C. N.* 18, 110). Crystalline. — $Pb_2C_{13}H_{14}O_7$. Got by adding NH_3Aq to a hot conc. solution of salicin, and then adding lead subacetate. Bulky white pp.

Acetyl derivative $C_{13}H_{14}Ac_4O_7$. Needles (from alcohol), nearly insol. water (Schiff, *Z.* [2] 5, 51).

Benzoyl derivative $C_{20}H_{22}O_8$ *i.e.* $C_{13}H_{17}BzO_7$. *Populin.* [180°]. S. ·05 at 9° (Piria); ·04 at 15°; ·24 at 100° (Schiff); S. (alcohol) 1 at 16°. Occurs in the bark and leaves of the aspen (*Populus tremula*) (Braconnot, *A. Ch.* [2] 44, 296; Piria, *A. Ch.* [3] 34, 278; 44, 366; *A.* 81, 245). Formed by heating salicin with Bz_2O (Schiff, *A.* 154, 5). Prepared by boiling the leaves of the aspen with water, ppg. with lead subacetate, removing lead from the filtrate by H_2S, and evaporating to crystallisation. Light silky needles (containing 2aq). Tastes sweet. Lævorotatory (Biot a. Pasteur, *C. R.* 34, 607). Sl. sol. water and alcohol, nearly insol. ether. $K_2Cr_2O_7$ and H_2SO_4 form salicylic aldehyde. HNO_3 (S.G. 1·3) forms benzoyl-helicin. Conc. H_2SO_4 forms a deep-red solution, whence water ppts. a red powder ('rutilin'). Boiling dilute acids split it up into glucose, benzoic acid, and saliretin. Alcoholic NH_3 at 100° forms benzamide, benzoic ether, and salicin. Populin is not hydrolysed by emulsin.

Di-benzoyl derivative $C_{13}H_{16}Bz_2O_7$. Formed, together with the mono- and tetra-benzoyl derivatives, by heating salicin with Bz_2O (Schiff). Flocculent mass, nearly insol. water, sl. sol. ether.

Tetra-benzoyl derivative $C_{13}H_{14}Bz_4O_7$. Amorphous resin, not coloured by cold H_2SO_4.

Chloro-salicin $C_{13}H_{17}ClO_7$. Formed by passing Cl_2 into water in which salicin is suspended (Piria, *A. Ch.* [3] 14, 275). Long silky needles (containing 2aq), sol. water and alcohol, insol. ether. Tastes bitter. Resolved by emulsin into glucose and chloro-saligenin. Yields a tetra-acetyl derivative, crystallising from alcohol in prisms.

Di-chloro-salicin $C_{13}H_{16}Cl_2O_7$. Formed by the action of Cl on chloro-salicin. Silky needles (containing aq), nearly insol. cold water, m. sol. alcohol. Gives no colour with $FeCl_3$ or H_2SO_4. Split up by emulsin into glucose and di-chloro-saligenin.

Tri-chloro-salicin $C_{13}H_{15}Cl_3O_7$. Formed by chlorinating the preceding body in presence of water and $CaCO_3$. Yellowish needles (containing aq) (from dilute alcohol), almost insol. cold water.

Bromo-salicin $C_{13}H_{17}BrO_7$. [160°]. Formed by slowly adding Br to salicin (1 pt.) in water (20 pts.) (O. Schmidt, *Z.* [2] 1, 320). Four-sided prisms, v. sol. water and alcohol. Split up by emulsin into glucose and bromosaligenin.

SALICYL. The radicle *o*-oxy-benzoyl [1:2]$C_6H_4(OH)$.CO. The same name is sometimes applied to the radicle *o*-carboxyl-phenyl [1:2]$CO_2H.C_6H_4$ and, rarely, to *o*-oxy-benzyl $C_6H_4(OH).CH_2$.

SALICYLAMIC ACID. An old name for *o*-Amido-benzoic acid.

SALICYLAMIDE. The amide of *o*-Oxy-benzoic acid.

SALICYLAMINE. A name for *o*-Oxy-benzyl-amine.

SALICYL-GLYCIDIC ACID *v.* Oxy-phenyl-glycidic acid.

SALICYL-GLYCOLLIC ACID is *o*-Carboxy-phenoxy-acetic acid.

SALICYLIC ACID *v.* *o*-Oxy-benzoic acid.

Homosalicylic acid *v.* Oxy-toluic acid.

SALICYLIC ALDEHYDE *v.* *o*-Oxy-benzoic aldehyde.

SALICYL-LACTIC ACID *v.* Di-oxy-phenyl-propionic acid.

SALICYL-PHENOL *v.* Di-oxy-benzophenone.

SALICYL-RESORCIN *v.* Tri-oxy-benzophenone.

SALICYL-SULPHURIC ACID *v.* Carboxy-phenyl sulphuric acid.

SALIGENIN *v.* *o*-Oxy-benzyl alcohol.

SALIGENOL. Another name for *o*-Oxy-benzyl alcohol.

SALIRETIN *v.* *o*-Oxy-benzyl alcohol.

SALOL *v.* *Phenyl ether* of *o*-Oxy-benzoic acid.

SALT-FORMING OXIDES. Oxides which form salts, either by reacting with acids (or acidic oxides)—in which case the oxides are basic—or by reacting with basic oxides or hydroxides—in which case the oxides are acidic. For a table showing the compositions and general characters of the characteristic highest salt-forming oxides of each group of elements, *v.* vol. iii. p. 661. M. M. P. M.

SALTPETRE. A common name for potassium nitrate; *v.* vol. iii. p. 514.

SALTS. The earliest use of the word *salt* seems to have been to designate the solid obtained by evaporating sea-water. The term was afterwards applied to solids which more or less resembled sea-salt, especially to those solid bodies which were easily soluble in water. The study of the compositions of salt-like substances led to the view that they were made up of two parts, one of which was electro-positive with regard to the other. When the compositions of acids had been generalised in the statement that acids are compounds of hydrogen with non-metallic, or negative, elements, the relation of salts to acids was indicated by calling salts metallic derivatives of acids. This conception of the composition of salts included the older view, inasmuch as the metallic derivative of an acid is necessarily a compound of a positive metal with a less positive non-metal, or with a (less positive) group of elements, which non-metal, or group of elements, was combined with hydrogen in the parent acid.

The most general conception of the composition of salts is that which formulates them as M_xR_y, where M is the positive, or basic, or basylous part, and R is the negative, or acidic, or chlorous part of the salt. Both M and R may be either simple or complex. Common salt, NaCl, is the type of all salts as regards composition; the positive radicle, Na, may be replaced by other metals, or by groups of elements which are positive with regard to the other part of the compound; so the negative radicle Cl may be replaced by other non-metals, or by groups of elements which are negative with regard to the other part of the compound.

When an aqueous solution of a salt is electrolysed, the positive radicle is separated at the negative electrode, and the negative radicle at the positive electrode (secondary reactions may occur). An element may form part of the positive radicle of a salt, and the same element may form part of the negative radicle of another salt. Thus in the electrolysis of a ferric salt the iron travels to the cathode, but in the electrolysis of $K_4Fe(CN)_6$ the iron travels, with the cyanogen, to the anode. In the electrolysis of $PtCl_4$ the Pt is separated at the negative electrode, but in the electrolysis of Na_2PtCl_6 the Pt is separated, with the Cl, at the positive electrode. We must then regard the radicles of, say, $FeCl_3$, as Fe and 3Cl, the radicles of $PtCl_4$ as Pt and 4Cl, and the radicles of NaCl as Na and Cl; but we must look on the radicles of $K_4Fe(CN)_6$ as 4K and $Fe(CN)_6$, and the radicles of Na_2PtCl_6, not as 2Na, Pt, and 6Cl, but as 2Na and $PtCl_6$. Again, neither the salt $K_4Fe(CN)_6$, nor the salt Na_2PtCl_6, in aqueous solution, gives the ordinary reactions of iron or platinum; but if these salts were composed of the radicles 4K, Fe, and 6CN, and 2Na, Pt, and 6Cl respectively, we should expect them to show the same qualitative reactions as solutions of $FeCl_3$ and $PtCl_4$. In contrast with these salts is the compound formed by evaporating a mixture of K_2SO_4Aq and $CuSO_4Aq$. The salt thus produced, $K_2SO_4.CuSO_4.6H_2O$, when dissolved in water, gives the ordinary reactions of sulphates, of K compounds, and of Cu compounds; moreover, on electrolysis the K and Cu appear at the cathode, and the group SO_4 is set free at the anode (where it reacts with H_2O to give H_2SO_4 and O).

But all these salts—NaCl, $PtCl_4$, $FeCl_3$, $K_4Fe(CN)_6$, Na_2PtCl_6, and $CuSO_4.K_2SO_4$—are represented, as regards composition, by the general formula M_xR_y. This formula satisfactorily expresses the composition of all salts; but it says nothing about the properties of these compounds. When solutions of two salts are mixed, a more or less complete interchange of positive radicles generally takes place. This capability of reacting as if they were composed of two parts—or, one may say, of reacting in a binary way—is characteristic of salts. Salts in solution are most probably dissociated into two parts, each of which carries an electric charge. Even if the whole of the salt is not dissociated, the portion which readily takes part in chemical changes is most probably dissociated binarily (*cf.* ELECTRICAL METHODS, p. 184).

Salts, then, may be regarded as compounds of the form M_xR_y, which readily exchange M and R with other compounds of similar composition, and which in aqueous solutions are wholly or partially separated into their positive and negative radicles, each radicle carrying with it an electric charge.

Salts are often classified as *normal, acid, basic*, and *double salts*.

An acid salt is one whose negative radicle contains hydrogen that can be eliminated by causing the salt to react with an alkali or basic oxide, while a normal salt contains no replaceable hydrogen. As an acid is described as a compound containing hydrogen, all or part of which is replaceable by metal when the acid interacts with a metal or a basic oxide, it is evident that an acid salt comes under the description of an acid, and, strictly speaking, is an acid. According to the meaning already given to the term 'salt,' the class of salts includes acids. It is, however, convenient to give a special name to the compounds of hydrogen with negative radicles. A basic salt contains a positive radicle or radicles which can be replaced by a negative radicle with formation of a normal salt. This positive radicle is sometimes the group OH, sometimes it is a group M_xO_y, where M is the metal of the salt. Thus $Bi(OH)_2NO_3$ and $Pb(PbO)NO_3$ are basic salts. When treated with nitric acid the former gives the normal salt $Bi(NO_3)_3$, and the latter the normal salt $Pb(NO_3)_2$. The basic salt is an intermediate stage between the base and the normal salt, just as the acid salt is an intermediate stage between the acid and the normal salt.

Basic salts are formed by fairly weak bases; the very strong bases, Na_2O, K_2O, CaO, &c., do not form basic salts.

Normal salts frequently combine with other normal salts to form double salts. Generally speaking, one of the components of a double salt is a salt of a strong base which forms acid salts but not basic salts, and the other component is a salt of a weaker base which readily forms basic salts but does not form acid salts. That component which is itself the salt of a strong base—*e.g.* K_2SO_4, NaCl, &c.—may be regarded as the more acidic or negative radicle of the double salt, while the component which is itself the salt of a weaker base—*e.g.* $Al_2(SO_4)_3$, $Zn_3(PO_4)_2$, &c.—may be regarded as the more basic or positive radicle of the double salt. The double salt belongs to the type M_xR_y; both M and R are themselves salts. And just as many normal salts are formed by the direct union of their radicles—*e.g.* NaCl by combining Na and

Cl, $BaSO_4$ by combining BaO and SO_3—so double salts are formed by the union of a more positive with a less positive radicle, which is, in such cases, itself a salt.

The reactions of some double salts indicate that these salts are to be regarded as composed of the two simple salts which were brought together when the double salts were formed; the salt $MgSO_4.K_2SO_4.6aq$, for instance, gives, in solution, the reaction of sulphates, of Mg, and of K, and on electrolysis the Mg and K go to the negative electrode. On the other hand, the reactions of some double salts indicate that these salts are not to be regarded as composed of the simple salts by the union of which the double salts were formed; the salt $Cr_2(C_2O_4)_3.K_2C_2O_4$, for instance, does not give the reactions of oxalates, nor the reactions of Cr: this salt must be looked on as the potassium salt of the acid $H_2Cr_2(C_2O_4)_4$. If the salt $(NH_4)_2Cr_2(C_2O_4)_4.2H_2O$ is treated with NH_3Aq, a new salt is formed having the composition $Cr_2(C_2O_4)_3.(NH_4)_2C_2O_4.4NH_3.xH_2O$, and the reactions of this salt show that it is an oxalate, and therefore that it has a different constitution from that of the salt $(NH_4)_2Cr_2(C_2O_4)_4$ from which it is obtained.

The salts of the haloid acids combine to form many double salts, *e.g.* $PbI_2.KI$, $BiCl_3.3KCl$, $AuCl_3.KCl$, &c. Most of these double haloids are generally regarded as double salts in the usual acceptation of the term; but several of them do not give the ordinary reactions of the less positive metal they contain, nor the reactions of the halogen which enters into their composition. For instance, $PtCl_4.2NaClAq$ reacts with two equivalents of $AgNO_3$ to give $PtCl_4.2AgCl$; if $PtCl_4.2NaCl$ were a double salt, reacting in solution as if it were composed of the two radicles $PtCl_4$ and NaCl, it would interact with six equivalents of $AgNO_3$, and the products would be $Pt(NO_3)_4$, $NaNO_3$, and AgCl. It is evident, then, that the Na-Pt chloride is the Na salt of the acid H_2PtCl_6, and that the constitution of this salt is similar to that of the ordinary simple salts.

Remsen (*Am.* 11, No. 5 [1889]) proposes to regard all the so-called double haloids as simple salts similar to ordinary oxysalts. It seems to me that the constitutions of these salts cannot be determined by an examination of their composition only, but that the reactions of each salt must be examined. Some of the double haloids are undoubtedly simple salts, as some of the double oxysalts are certainly simple salts of metal-containing acids; but as some oxysalts containing two metals react so as to show that they are composed of two radicles, each of which is a simple salt, so some of the double haloids also give the ordinary reactions of both the metals, and also of the acidic radicle, which they contain, and must therefore be regarded as true double salts. M. M. P. M.

SALVIOL $C_{10}H_{18}O$. (200°). S.G. $\underline{15}$ ·938. $\mu_D = 1·462$ at 20°. R_∞ 74·2. (M. M. P. Muir, *C. J.* 33, 292; 37, 683). A constituent of oil of SAGE (*q.v.*). It is a dextrorotatory liquid. On distillation some of it splits up into H_2O and $C_{10}H_{16}$.

Reactions.—1. *Chromic acid* mixture or dilute nitric acid produces acetic and oxalic acids and camphor [174°].—2. P_2O_5 produces polymerides of $C_{10}H_{16}$, a terpene (171°), an aromatic hydrocarbon (c. 130°), and a paraffin-like hydrocarbon (170°-180°). Cymene is not formed. Hence salviol is not $C_{10}H_{16}O$. However, according to Semmler (*B.* 25, 3350), salviol is identical with tanacetone.

Constitution.—Refractive index appears to indicate absence of C:C groups.

SALYLIC ACID. A name given by Kolbe to a supposed isomeride of benzoic acid got from salicylic acid by successive treatment with PCl_5 and sodium-amalgam. It is identical with benzoic acid (Reichenbach a. Beilstein, *A.* 132, 309). The name is also applied by Städeler (*A. Suppl.* 7, 159) to two acids: (α) $C_{11}H_{11}O_5$ [101°] and (β) $C_{21}H_{22}O_8$ [95°], obtained by allowing salicylic aldehyde to stand for 12 years under water. The (α)- acid forms small four-sided prisms, gives no colour with $FeCl_3$, and yields Ag_2A''. The (β)- acid forms aggregates of needles, gives an intense violet colour with $FeCl_3$, and yields Ag_3A'''. Both acids are v. sol. alcohol and ether.

SAMARIUM. This name was given by Lecoq de Boisbaudran (*C. R.* 88, 322; 89, 212) to the metal of an earth which he separated from what was then known as didymia, occurring in *samarskite*. Delafontaine (*C. R.* 89, 632) obtained from didymia an earth which he called *decipia*, and when this had been removed by ppn. as sulphate, the new earth, samaria, remained in solution, and was obtained by fractionally ppg. by NH_3Aq. Cleve (*C. J.* 43, 362) separated what he regarded as pure samaria from *orthite*; he prepared and described several salts of the new element. Cleve found the at. wt. of Sm to be 150, supposing the oxide to be Sm_2O_3; this number was confirmed by Bettendorff (*A.* 263, 164). It is still very doubtful whether samaria is a homogeneous substance; according to Crookes, it contains at least four different bodies (*v.* METALS, RARE, vol. iii. p. 244). Because of the great uncertainty attaching to the homogeneous nature of the so-called samaria it does not seem desirable to give an account of the bodies which have been described as compounds of Sm. The student is referred to the memoirs cited above, and also to the following:—L. de Boisbaudran, *C. R.* 114, 575; 116, 611 (spectrum and compounds of samaria); Marignac, *Ar. Sc.* [3] 3, 413 (spectrum, and compounds); Krüss a. Nilson, *B.* 20, 2134; 21, 2310 (spectrum); *v.* also, for spectrum, *B. A.* 1884. 438. The compounds of the supposed element are described by Cleve (*l.c.*, and also *Bl.* [2] 43, 162) (*cf.* also EARTHS, vol. ii. p. 422). M. M. P. M.

SANDAL WOOD. A dye wood furnished by *Pterocarpus santalinus*, which grows in tropical Asia. It dyes mordanted cotton red. It contains santalin (Meier, *A.* 72, 320). Yellow sandal wood (from *Santalum album*), yields by steam-distillation an oil containing santalol $C_{15}H_{26}O$, and santalal $C_{15}H_{24}O$ (Chapoteaut, *Bl.* [2] 37, 303). After treatment with Na the oil yields a terpene $C_{10}H_{16}$, S.G. ·919, $\mu_A = 1·487$ (Gladstone, *C. J.* [2] 10, 6). The crude oil heated in sealed tubes at 310° forms $C_{40}H_{62}O_3$ (c. 340°), $C_{40}H_{60}O_2$ (350°) and $C_{20}H_{30}O$ (240°) whence P_2O_5 forms $C_{10}H_{14}$ (c. 177°).

Santalol (310°) is converted by P_2O_5 into water and $C_{15}H_{24}$ (260°). HOAc at 150° forms the acetyl derivative $C_{15}H_{25}OAc$ (298°), and a compound $C_{30}H_{46}O$ (283°).

Santalal (300°) is converted by P_2O_5 into $C_{15}H_{22}$ (248°).

Sandal wood oil from *Santalum Preissianum* contains a crystalline solid [105°] (*Ph.* [3] 22, 828).

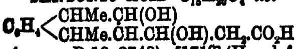
SANDARACH. A gum resin which exudes from *Thuja articulata* growing in Barbary, and from various species of *Callitris* growing in Australia and New Zealand (Johnston, *J. pr.* 17, 157; Maiden, *Ph.* [3] 20, 562). Transparent yellowish mass with vitreous fracture, resembling pine-resin in taste and smell. Sol. alcohol. Completely sol. ether. Its alcoholic solution is ppd. by $Pb(OAc)_2$. It appears to contain several resins (*e.g.* $C_{40}H_{62}O_5$, $C_{40}H_{62}O_6$, and $C_{40}H_{60}O_6$) differing in solubility in alcohol.

SANGUINARINE $C_{17}H_{15}NO_4$ (E. Schmidt, *Ar. Ph.* [3] 26, 622). Prepared from the root of *Sanguinaria canadensis* (Dana, *Annals of the Lyceum of New York*, 2, 245; Probst, *A.* 29, 120; 31, 241; Schiel, *A.* 43, 233; *Am. S.* [2] 10, 220; Naschold, *J. pr.* 106, 385). According to Probst and Schiel it is identical with chelerythrine, but Naschold and Schmidt assign the formula $C_{17}H_{15}NO_4$ to sanguinarine and $C_{19}H_{17}NO_4$ to chelerythrine. Prepared by exhausting the root with ether and ppg. the hydrochloride by HCl. Pearly grains, insol. water, sol. alcohol and ether. Poisonous.—Salts: B'HCl aq.—$B'_2H_2PtCl_6$ (dried at 100°).—$B'_2H_2PtCy_6$. According to König (*C. C.* 1891, i. 321) sanguinarine has the formula $C_{20}H_{15}NO_4$, crystallises with ½aq, melts at 211°, and forms the red salts B'HCl 5aq, $B'HNO_3$ aq, $B'HAuCl_4$, and $B'_2H_2PtCl_6$.

SANTAL $C_8H_6O_3$. Obtained from sandal wood by extracting with very dilute KOH, ppg. with HCl, and extracting the pp. with ether (Weidel, *Z.* [2] 6, 83). It is accompanied by a scarlet crystalline powder $C_{14}H_{12}O_4$? Santal crystallises from alcohol in colourless iridescent four-sided laminæ (containing 1½aq), insol. water, sl. sol. cold alcohol, sol. KOHAq, sl. sol. NH_3Aq. $FeCl_3$ colours its alcoholic solution dark red. Potash-fusion yields protocatechuic acid.

SANTALIN $C_{15}H_{14}O_5$ (Meier, *A.* 72, 320); $C_{15}H_{16}O_5$ (Wegermann a. Häffely, *A.* 74, 226); $C_{17}H_{16}O_6$ (Franchimont, *B.* 12, 14). [105°]. The colouring matter of sandal wood and of coliatur wood. Extracted by ether or alcohol, and purified by ppg. its alcoholic solution with $Pb(OAc)_2$, and decomposing the pp. by dilute H_2SO_4. Minute red prisms (M.) or amorphous (F.), without taste or smell, insol. water. Its alcoholic solution is blood-red. Sol. alkalis, forming violet solutions in which $BaCl_2$ ppts. $Ba(C_{15}H_{13}O_5)_2$ as a dark-violet amorphous pp. $Pb(OAc)_2$ added to its alcoholic solution ppts. $PbC_{15}H_{14}O_6$ (dried at 100°). On heating with HCl, santalin gives off MeCl (1 mol.). Gives resorcin and HOAc on fusion with potash. $KMnO_4$ gives off an odour of vanilla.

SANTONIC ACID $C_{15}H_{20}O_4$ *i.e.*



$C_6H_4<\begin{matrix}CHMe.CH(OH)\\CHMe.CH.CH(OH).CH_2.CO_2H\end{matrix}$ (?) (Cannizzaro, *B.* 18, 2748). [171°] (Hvoslef, *B.* 6, 1471). S. ·56 at 17°. $[\alpha]_D = -74°$ at 20° in chloroform (Nasini, *B.* 13, 2210; *G.* 13, 164). Formed by boiling santonin with baryta-water (Cannizzaro a. Sestini, *G.* 3, 241; Hesse, *B.* 6, 1280). Colourless trimetric plates (Strüver, *G.* 6, 349), m. sol. hot water, v. sol. ether, v. e. sol. alcohol. Acid to litmus. Lævorotatory. HIAq forms $C_{15}H_{24}$ (235°–245°) and $C_{15}H_{25}I$ (144° at 3 mm.) (Cannizzaro a. Amato, *B.* 7, 1104). Boiling HIAq and P form (α)- and (β)-metasantonin. By boiling with HOAc and heating the residue it is converted into santonide and parasantonide. Sodium-amalgam yields hydrosantonic acid. Does not react with hydroxylamine. When its chloroform solution is heated with $POCl_3$ as long as HCl comes off, and a current of damp air passed through the product, there is formed $PO(C_{15}H_{18}O_3Cl)_3$ [98°] (Cannizzaro, *G.* 10, 459)

Salts.—NaA'. Stellate groups of needles.—BaA'_2.—AgA': white pp.

Methyl ether MeA'. (86°). Colourless needles (Cannizzaro, *G.* 6, 335).

Ethyl ether EtA'. [95°]. $[\alpha]_D = -45°$ at 26°. Trimetric crystals.

n-Propyl ether PrA'. (220° at 3 mm.). S.G. $^{20}_{4}$ 1·125. $[\alpha]_D = -40°$ at 20°.

Isobutyl ether CH_2PrA'. [67°]. $[\alpha]_D = -41°$. Needles (Carnelutti a. Nasini, *B.* 13, 2208; *G.* 10, 530).

Allyl ether C_3H_5A'. [55°]. $[\alpha]_D = -40°$.

Acetyl derivative $C_{15}H_{19}AcO_4$. [140°]. Got by boiling the acid for six hours with AcCl (Sestini, *G.* 5, 121). Prisms (from $CHCl_3$). It is accompanied by $C_{19}H_{26}O_7$ [128°].

Chloride $C_{15}H_{19}O_3Cl$. [155°].

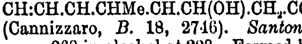
Bromide $C_{15}H_{19}O_3Br$. [145°].

Iodide $C_{15}H_{19}O_3I$. [136°].

Hydrosantonic acid $C_{15}H_{22}O_4$. [170°]. Formed by reducing santonic acid with sodium-amalgam (Cannizzaro, *G.* 6, 341). Colourless trimetric crystals (from ether), less sol. alcohol than santonic acid. Dextrorotatory. Oxidised by Ag_2O to metasantonic acid. HOAc at 150° forms hydrosantonide $C_{15}H_{20}O_3$ [156°], which is reconverted into hydrosantonic acid by alcoholic potash (Cannizzaro a. Valente, *G.* 8, 309). AcCl converts hydrosantonic acid into acetyl-hydrosantonide $C_{15}H_{19}AcO_3$ [204°], which is converted by alcoholic NH_3 at 130° into hydrosantonamide $C_{15}H_{21}O_3.NH_2$ [190°]. BzCl forms benzoyl-hydrosantonide $C_{15}H_{19}BzO_3$ [157°].

Salts.—NaA' 3aq: trimetric crystals.—KA' 2aq: monoclinic crystals.

Santoninic acid $C_{15}H_{20}O_4$ *i.e.*



$\begin{matrix}CH{:}CH.CH.CHMe.CO\\CH{:}CH.CH.CHMe.CH.CH(OH).CH_2.CO_2H\end{matrix}$ (?)

(Cannizzaro, *B.* 18, 2746). *Santonous acid.* $\alpha_j = -26°$ in alcohol at 22°. Formed by heating santonin with KOHAq (Hesse, *B.* 6, 1280). Trimetric tables, sl. sol. cold water, m. sol. ether, v. e. sol. alcohol. Not turned yellow by light. Acid to litmus. Not coloured red by alcoholic potash. At 120° it splits up into water and santonin; dilute H_2SO_4 acts in like manner.

Salts.—NaA' 3½aq. S. 33 in cold water. S. (90 p.c. alcohol) 25 (Lepage, *J.* 1876, 618). Stellate groups of needles. Lævorotatory; $\alpha_j = -18°$ at 22°.—BaA'_2 aq.

Metasantonic acid $C_{15}H_{20}O_4$. [161°]. Formed by heating silver hydrosantonate with water. Got also by distilling santonic acid at 45 mm., by boiling santonide with KOHAq, and by the action of Na_2CO_3Aq on isosantonin. Trimetric crystals (from ether). Lævorotatory. Its K and Na salts are very soluble.—AgA′: pp., m. sol. water.

Methyl ether MeA′. [102°].

Chloride $C_{15}H_{19}O_3Cl$. [139°].

Parasantonic acid $C_{15}H_{20}O_4$. [173°], [α] = −99° in chloroform (Carnelutti a. Nasini *G.* 10, 534). Formed by boiling parasantonide with NaOHAq or HClAq. Trimetric crystals, m. sol. water and ether. Converted by AcCl, Ac_2O, or PCl_5 into parasantonide. Boiling HIAq and P form (α)- and (β)- metasantonin. The parasantonates are mostly v. sol. water.—BaA'_2: slender needles (from water).

Methyl ether Me_2A'. [184°]. $[\alpha]_D = -109°$ in chloroform at 27°.

Ethyl ether EtA′. [173°]. $[\alpha]_D = -100°$ in chloroform at 20°.

n-Propyl ether PrA′. [113°]. $[\alpha]_D = -91°$ at 26°. Colourless prisms.

Allyl ether C_3H_5A'. [149°]. $[\alpha]_D = -92°$. Lævorotatory.

Photosantonic acid $C_{15}H_{22}O_5$ *i.e.*

$$\begin{array}{l}\text{ÇH:CH.ÇH.CHMe.CO}_2\text{H}\\ \text{CH:CH.CH.CHMe.CH}_2\text{.CH(OH).CH}_2\text{.CO}_2\text{H}\end{array}\quad(?).$$

[155°]. $[\alpha]_D = -125°$. Formed, as ethyl ether of the lactonic acid, by exposing a solution of santonin in 65 p.c. alcohol to direct sunlight (Sestini, *Rep. ital. chim. pharm.* 1865). Formed also by exposing an aqueous solution of sodium santonate to sunshine. Prepared by insolation of a 1 p.c. solution of santonin in diluted HOAc for one month (Cannizzaro a. Villavecchia, *B.* 18, 2750, 2859). Trimetric prisms (from alcohol). Gives off H_2O at 100°, forming the lactonic acid $C_{15}H_{20}O_4$, and then melts at 155°. V. sl. sol. water, v. sol. alcohol and ether. Lævorotatory.

Salts.—$(NH_4)_2A''$.6aq. — BaA″ aq: white amorphous pp.—$CaH_2A''_2$ 3aq: silky needles, sl. sol. cold water.—CaA″ *x*aq.—Ag_2A'': white pp.

Methyl ether of the lactonic acid. [57°]. Got by the action of sunshine on a solution of santonin in MeOH. Long prisms (from MeOH).

Ethyl ether of the (α)-lactonic acid $C_{17}H_{24}O_4$. [69°]. (305°). $[\alpha]_D = -118°$ in a 6 p.c. alcoholic solution at 14°. Got by exposing an alcoholic solution of santonin to sunlight (Sestini, *J.* 1876, 622). Formed also from $Ag_2C_{15}H_{20}O_5$ and EtI (V.). Formed also by the action of alcohol and H_2SO_4 on photosantonic acid. Thin tables, almost insol. cold water, v. sol. alcohol and ether. Lævorotatory. NaOH converts it into sodium photosantonate.

Ethyl ether of the (β)-lactonic acid $C_{17}H_{24}O_4$. [155°]. $[\alpha]_D = 77°$ in alcohol at 14°. Formed, together with the preceding, by insolation of a solution of santonin in absolute alcohol. Tables (from ether). Dextrorotatory.

Anhydrophotosantonic acid $C_{15}H_{20}O_4$ *i.e.* $C_{13}H_{18}(CO_2H)_2$. [133°]. $[\alpha]_D = +31{\cdot}9$. Obtained by saponification of its ether, which is formed by passing gaseous HCl into a solution of photosantonic acid in absolute alcohol (Villavecchia, *B.* 18, 2862). Crystalline solid. V. sol. alcohol and ether.—BaA″: white amorphous solid, v. e. sol. water.

Di-ethyl ether Et_2A'': (180°–185°). $[\alpha]_D = +20{\cdot}4°$. Colourless liquid.

Isophotosantonic acid $C_{15}H_{22}O_5$ *i.e.*

$$\begin{array}{l}\text{ÇH:CH.ÇH.CHMe.Ç(OH)}_2\\ \text{CH:CH.CH.CHMe.CH.CH(OH).CH}_2\text{.CO}_2\text{H}\end{array}\,(?)$$

$[\alpha]_D = 124°$ in a 3 p.c. alcoholic solution at 11°. Formed, together with photosantonic acid, by exposing a solution of santonin (1 kilo.) dissolved in HOAc (52 litres of S.G. 1·054) for several months to sunshine (Cannizzaro a. Fabris, *B.* 19, 2260). Thick trimetric crystals (from alcohol), sl. sol. water, m. sol. ether, v. sol. alcohol. Dextrorotatory. At 100° it gives an anhydride $C_{15}H_{20}O_4$. Sol. alkalis and hot Na_2CO_3Aq, forming orange-red solutions.—BaA'_2 aq: white amorphous powder, v. e. sol. alcohol and water.

Acetyl derivative $C_{15}H_{21}AcO_5$. [183°]. $[\alpha]_D = 59°$. Transparent needles. Dextrorotatory.

Di-acetyl derivative ×$C_{15}H_{20}Ac_2O_5$. [c. 166°]. Crystals, v. sl. sol. alcohol and ether. Converted into $C_{15}H_{21}AcO_5$ by heating with absolute alcohol at 120°.

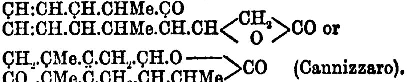
Pyrophotosantonic acid $C_{14}H_{20}O_2$. [94·5°]. Formed by heating photosantonic acid in a current of CO_2 or H_2 (Sestini a. Danesi, *G.* 12, 83). Got also by heating photosantonic acid with HI (Cannizzaro a. Fabris, *B.* 19, 2260). Crystals, sol. alcohol and ether.—BaA'_2. Forms, on distillation, $C_{13}H_{20}$ (222°).

SANTONIDE $C_{15}H_{18}O_3$. [127·5°]. $[\alpha]_D = 754°$ in chloroform at 20°; 666° in alcohol at 20°. S.V.S. 206. Formed by evaporating a solution of santonic acid in HOAc and heating the residue at 180° (Cannizzaro a. Valente; Carnelutti a. Nasini, *G.* 10, 528; 13, 149). Trimetric crystals. Dextrorotatory. M. sol. chloroform, v. sl. sol. alcohol. Not attacked by PCl_5. Boiling KOHAq forms metasantonic acid.

Parasantonide $C_{15}H_{18}O_3$. [110°]. S.G. $\frac{20}{4}$ 1·202. $[\alpha]_D = 897°$ at 26°. S.V.S. 206. Formed by boiling santonic acid with HOAc, evaporating, and heating the residue at 260° (Cannizzaro, *G.* 8, 309; 10, 528). Trimetric crystals, v. sl. sol. alcohol, m. sol. Ac_2O. Not attacked by Ac_2O or PCl_5. Boiling KOHAq converts it into parasantonic acid.

Metasantonide. [138°]. $[\alpha]_D = -223°$ at 26°. S.V.S. 236. Prepared by heating santonin with conc. H_2SO_4 for some hours at 100° and ppg. by water (Cannizzaro a. Valente, *Rend. Accad. Lincei*, ii.; *G.* 10, 42). Crystals (from ether). Converted by Na_2CO_3Aq into metasantonic acid.

SANTONIN $C_{15}H_{18}O_3$ *i.e.*



$$\begin{array}{l}\text{ÇH:CH.ÇH.CHMe.ÇO}\\ \text{CH:CH.CH.CHMe.CH.CH}\left<\begin{array}{c}\text{CH}_2\\ \text{O}\end{array}\right>\text{CO}\end{array}\ \text{or}$$

$$\left.\begin{array}{l}\text{ÇH}_2\text{.ÇMe.Ç.CH}_2\text{.ÇH.O}\\ \text{CO .CMe.C.CH}_2\text{.CH.CHMe}\end{array}\right>\text{CO}\quad\text{(Cannizzaro).}$$

Mol. w. 246. [170°]. S.G. $\frac{22}{}$ 1·247. $[\alpha]_D = -174°$ in alcohol of 90 v. p.c. (Hesse, *A.* 176, 125); = −172° in chloroform at 20°. S. ·02 at 17·5°; ·4 at 100°. S. (alcohol) 2·3 at 22·5°; 8 at 50°; 37 at 80°. S. (ether) 2·4 at 40°. S. (chloroform) 23 (Schlimpert, *N. Br. Arch.* 100, 151). Occurs in wormseed (semen contra, semen cinæ, or semen santonici), the undeveloped flower heads of *Artemisia Vahliana* and other species of *Artemisia* (Kahler, *Brandes Archiv*, 34, 318; 35, 216; Alms, *ibid.* 34, 319; 39, 190; H. Trommsdorff, *A.* 11, 190; Heldt, *A.* 63, 10, 40).

Preparation.—From *Artemisia maritima* (Linn.) which contains 2 p.c. The seeds (5 pts.) are treated with lime (1 pt.) and water, and extracted with alcohol. The extract is freed from alcohol by evaporation and neutralised with HCl, when santonin crystallises out. In this process a lime- compound $(C_{15}H_{19}O_4)_2Ca$, is first formed, and afterwards decomposed by HCl, which forms santonic acid, $C_{15}H_{20}O_4$, whence santonin is formed by splitting off H_2O (Busch, *J. pr.* [2] 35, 322).

Properties.—Flattened hexagonal prisms, which turn yellow in light. May be sublimed. Lævorotatory, the specific rotation being but little affected by temperature or concentration of the solution (Hesse; Nasini, *G.* 13, 139). Nearly insol. cold water, v. sol. hot alcohol and ether. Poisonous, exerting an anthelmintic action, and producing temporary colour-blindness (Lavater, *Pharm. Viertelj.* 2, 110; Wells, *J. Ph.* [3] 15, 111; Martini, *C. R.* 47, 259; 50, 545). Reacts with hydroxylamine, forming an oxim (Cannizzaro, *B.* 18, 2746); santonin is best administered as oxim (Coppola, *C. C.* 1887, 1206, 1301). Not attacked by aqueous $KMnO_4$. Resinified by boiling conc. HClAq. KOH turns santonin crimson (especially in presence of alcohol) and forms $C_{15}H_{19}KO_4$. AcCl has no action. Conc. H_2SO_4 containing $FeCl_3$ gives a violet colour (Lindo, *C. N.* 36, 222; Knapp, *D. P. J.* 268, 42).

Reactions.—1. By treatment with 1 mol. of PCl_5 it gives a compound $C_{15}H_{17}ClO_2$ [125° uncor.]. With 2 mols. of PCl_5 it gives a compound $C_{15}H_{16}Cl_2O$, [182° uncor.] (Pawlewski, *B.* 18, 2900). According to Klein (*B.* 26, 982) the compound is $C_{15}H_{15}Cl_3O_2$.—2. Reduced by HI and P to santonous acid $C_{15}H_{20}O_3$.—3. HNO_3 (S.G. 1·123) at 95° forms CO_2, succinic, oxalic, and acetic acids, and HCy (Wagner, *B.* 20, 1662).—4. Boiling *baryta-water* forms santonic acid.—5. Hot KOHAq forms santoninic acid.—6. *Potash-fusion* forms formic and propionic acids (Banfi a. Chiozza, *A.* 91, 112).—7. An alcoholic solution exposed for some months to sunlight forms the ethyl ether of the lactonic acid of photosantonic acid (*v. supra*).—8. A solution in HOAc exposed to sunshine yields photo- and isophoto- santonic acids.—9. Forms santonol on distillation with zinc-dust. Distillation over red-hot zinc-dust gives di-methyl-naphthalene (Cannizzaro, *G.* 12, 415).—10. Cold conc. HClAq forms an isomeride $C_{15}H_{18}O_3$, [260°], sl. sol. hot alcohol, insol. water (Andreocci, *B.* 26, 1373). $[\alpha]_D = +112°$. This body is not acted upon by hydroxylamine or phenyl-hydrazine, but yields an acetyl derivative $C_{15}H_{17}AcO_3$ [156°]. Like santonin it is insol. Na_2CO_3Aq, but sol. NaOHAq. It is reduced by zinc-dust and HOAc to $C_{15}H_{20}O_3$ [175°] $[\alpha]_D = -53·3°$ an acid isomeric with santonous acid, which when fused with potash yields propionic acid and di-methyl-(β)-naphthol.—11. Br in glacial acetic acid forms $C_{15}H_{18}O_3.HOAc,Br_2$. Crystals (from alcohol), decomposing above 60°. On boiling with alcohol and aniline it yields bromo-santonin $C_{15}H_{17}BrO_3$ [151°]. On boiling with KOHAq the acetate bromide yields santonin (Klein, *B.* 25, 3317).

Oxim $C_{15}H_{18}O_2(NOH)aq$. [209°] (Klein, *B.* 26, 411; *cf.* Gucci, *G.* 19, 367). Needles (from dilute alcohol). Ac_2O yields $C_{15}H_{18}O_2(NOAc)$ [166°] or [170°] (K.); [203°] (G.). The oxim prepared by alkaline hydroxylamine gives with HCl and $FeCl_3$ a violet-red colour [*syn*-oximic acid].

Benzyl ether of the oxim [152°]. HIAq forms benzyl iodide.

Phenyl-hydrazide $C_{15}H_{18}O_2(N_2HPh)$. [220°]. Pale-yellow needles (from alcohol), not decomposed by cold acids (Cristaldi, *G.* 17, 526; Grassi, *C. C.* 1887, 1163).

Chlorosantonin $C_{15}H_{17}ClO_3$. Formed from santonin and chlorine-water (Heldt, *A.* 63, 34; Sestini, *Bl.* 5, 202). Crystalline. Turns yellow in light.

Di-chloro-santonin $C_{15}H_{16}Cl_2O_3$. Formed by passing Cl for a long time through water containing santonin in suspension (Sestini). Groups of small plates (from alcohol). Coloured orange-red by alcoholic potash.

Tri-chloro-santonin $C_{15}H_{15}Cl_3O_3$. [213°]. Monoclinic prisms, not coloured by sunshine, m. sol. alcohol and ether.

(α)-Metasantonin $C_{15}H_{18}O_3$. [161°]. (239°). S.V.S. 205. $[\alpha]_D = 124°$ in chloroform at 20°. Formed, together with (β)-metasantonin, by boiling santonic acid or parasantonide with HIAq and P (Cannizzaro, *G.* 4, 446, 452; 8, 318; 10, 461). Trimetric hemihedral plates (from ether). Dextrorotatory. Not affected by light. Yields $C_{15}H_{17}BrO_3$ [212°] and $C_{15}H_{16}Br_2O_3$ [184°].

(β)-Metasantonin $C_{15}H_{18}O_3$. [136°]. S.V.S. 211. $[\alpha]_D = 124°$. Formed as above. Monoclinic crystals. Yields $C_{15}H_{17}BrO_3$ [114°] and $C_{15}H_{16}Br_2O_3$ [186°].

Photosantonin. A name for the ethyl ether of the (α)-lactonic acid of photosantonic acid (*v. supra*).

SANTONOUS ACID $C_{15}H_{20}O_3$ *i.e.* $C_{10}H_8Me_2(OH).C_2H_4.CO_2H$? [179°]. $[\alpha]_D = 74°$ in alcohol at 20°. Formed by boiling santonin with HIAq and P (Cannizzaro a. Carnelutti, *B.* 12, 1574; *G.* 12, 393; 13, 385). White needles, v. e. sol. alcohol and ether, sl. sol. cold water, sol. Na_2CO_3Aq. May be distilled *in vacuo.* Distilled over powdered zinc in a current of hydrogen it yields di-methyl-naphthalene, di-methyl-naphthol, propylene, and a little xylene. On heating with $Ba(OH)_2$ above 360° it yields CO_2, CH_4, and di-methyl-naphthol $C_{12}H_{11}OH$ [135°], which yields $C_{12}H_{11}OMe$ [68°]. Converted by heat into the anhydride of isosantonous acid, and, finally, into di-methyl-naphthol dihydride and propionic acid.

Salts.—NaA′. Needles, ppd. by adding ether to its alcoholic solution. V. sol. water.—BaA′₂.—*AgA′: white pp., quickly turning black.

Methyl ether MeA′. [82°].

Ethyl ether EtA′. [117°]. $[\alpha]_D = 78°$ in chloroform or 67° in HOAc at 20°. White crystals, sol. alcohol and ether. Dextrorotatory. Converted by BzCl into $C_{15}H_{18}BzEtO_3$ [78°]. Na added to its ethereal solution ppts. $C_{15}H_{18}NaEtO_3$, whence EtI produces $C_{15}H_{18}Et_2O_3$ [32°], which on saponification yields ethyl-santonous acid $C_{15}H_{19}EtO_3$ [116°], $[\alpha]_D = +75°$ in alcohol.

Isosantonous acid $C_{15}H_{20}O_3$. [155°]. Formed by heating santonous acid, dissolving the resulting anhydride in NaOHAq, and ppg. with

HClAq. Got also by heating santonous acid (1 pt.) with $Ba(OH)_2$ (3 pts.) in a bath of molten lead (Cannizzaro a. Carnelutti, *B.* 12, 1574; *G.* 12, 400). Small plates, sl. sol. water, sol. alcohol and ether. Inactive to light. May be distilled *in vacuo.*

Ethyl ether EtA'. [125°]. Crystalline. BzCl at 100° yields $C_{15}H_{18}BzEtO_3$ [91°]. Na added to its ethereal solutions gives no pp., but on adding alcohol $C_{15}H_{18}NaEtO_3$ is thrown down as an amorphous powder, readily decomposed by water. The Na derivative is converted by EtI into $C_{15}H_{18}Et_2O_3$ [54°], whence alcoholic potash produces $C_{15}H_{19}EtO_3$ [143°], v. sol. alcohol and ether.

SAPONIFICATION. The conversion of the natural fats into soap (and glycerin) by boiling with alkalis. In a more general sense it is used to denote the resolution of compound ethers into acids and alcohols. In the widest sense it is used to denote the production of an acid from a neutral substance by hydrolysis.

SAPONIN $C_{32}H_{54}O_{18}$ (Rochleder, *Z.* [2] 3, 632); $C_{19}H_{30}O_{10}$ (Stütz, *A.* 218, 231); $C_{32}H_{52}O_{17}$ (Hesse, *A.* 261, 373). *Struthiin. Githagin. Polygalin. Polygalic acid. Senegin.* A glucoside occurring in the common soapwort (*Saponaria officinalis*) (Schrade, *N. Journ. d. Chem.* 8, 548), in the Oriental soapwort (*Gypsophila Struthium*) (Bley, *A.* 4, 283; Bussy, *A.* 7, 168), in quillaja bark (O. Henry a. Boutron-Charland, *J. Ph.* 4, 249), in the corncockle (*Agrostemma Githago*) (Malapert, *J. Ph.* [3] 10, 339; Scharling, *A.* 74, 351; Christophsohn, *Ar. Ph.* [3] 6, 432, 461), in the root of *Polygala Senega* (Bolley, *A.* 90, 211; 91, 117), and in many other plants. White amorphous powder, insol. alcohol and ether, v. e. sol. water. The dilute aqueous solution froths like soap when shaken; the lather is prevented by addition of alcohol. Impure saponin produces sneezing. Saponin begins to turn black at 145° (Blyth), but does not melt or sublime when heated. Baryta forms amorphous $(C_{19}H_{30}O_{10})_2Ba(OH)_2$. A solution of saponin is ppd. by lead acetate. Decomposed by *boiling dilute acids* into sapogenin and sugar $C_6H_{12}O_6$ ($[\alpha]_D = 52°$ at 25°) (Rochleder a. Schwarz, *Sitz. W.* 11, 339; Overbeck, *N. Br. Arch.* 77, 135; Schiaparelli; *cf.* Crawford, *Pharm. Viertelj.* 6, 361; Flückiger, *Ph.* [3] 8, 488).

Acetyl derivatives $C_{19}H_{26}Ac_4O_{10}$. [161°].—$C_{19}H_{25}Ac_5O_{10}$. [99°].—$C_{19}H_{25}Ac_7O_{11}$. [137°].—$C_{19}H_{25}Ac_9O_{12}$. [84°] (Stütz).—$C_{32}H_{45}Ac_7O_{17}$.—$C_{32}H_{44}Ac_8O_{17}$. — $C_{32}H_{40}Ac_{12}O_{17}$. — $C_{32}H_{40}Ac_{15}O_{20}$ (Hesse).

Butyryl derivative $C_{19}H_{26}(C_4H_7O)_4O_{10}$ (Stütz); $C_{32}H_{43}(C_4H_7O)_7O_{17}$ (Hesse). [68°–72°]. According to Schiaparelli (*G.* 13, 422; *Ph.* [3] 14, 801), saponin obtained from soapwort has the formula $C_{32}H_{54}O_{18}$, is lævorotatory, $[\alpha]_D = -8$ at 20°, yields amorphous $Ba_2H_2(C_{32}H_{52}O_{18})_3$, and is split up by boiling dilute H_2SO_4 into glucose and saponetin $C_{40}H_{66}O_{15}$.

SAPOGENIN $C_{14}H_{22}O_2$. Formed by hydrolysis of saponin. Concentric groups of needles (from alcohol), sol. ether, insol. water. From solution in dilute potash it is ppd. by conc. KOHAq as flocculent potassium-saponin. Potash-fusion gives acetic and butyric acids and a crystalline compound [128°].

Oxysapogenin $C_{14}H_{22}O_3$ is obtained by the action of HClAq on a glucoside present in the alcoholic extract of *Herniaria* (Barth a. Herzig, *M.* 10, 172).

SAPPANIN $C_{12}H_{10}O_4$. Formed, together with resorcin and a little pyrocatechin, by fusing extract of sapan wood with NaOH (Schreder, *B.* 5, 572). Crystallises from water in plates (containing 2aq), nearly insol. cold water, v. sol. alcohol and ether, insol. $CHCl_3$. Neutral in reaction. $FeCl_3$ colours its aqueous solution red. NaOCl gives a grass-green colour. May be distilled. $Pb(OAc)_2$ gives a yellowish pp. Reduces hot Fehling's solution and ammoniacal $AgNO_3$. HNO_3 forms tri-nitro-resorcin (styphnic acid). Yields diphenyl on distillation with red-hot zinc-dust. AcCl gives $C_{12}H_6Ac_4O_4$, crystallising from alcohol in prisms. Br and HOAc give $C_{12}H_5Br_5O_4$, crystallising from dilute alcohol in needles.

SAPRINE $C_5H_{16}N_2$. [From σαπρός, putrid.] An alkaloid in putrefying flesh (Gautier, *Bl.* [2] 48, 13), *v.* PTOMAÏNES.

SARCINE *v.* HYPOXANTHINE.

SARCOLACTIC ACID *v.* LACTIC ACID.

SARCOLEMMA *v.* MUSCLE.

SARCOSINE *v.* METHYL-AMIDO-ACETIC ACID.

SARCOSINIC ACID $C_3H_7NO_2$. [195°]. Occurs in a variety of shellac known as Sonora gum (Hertz, *J.* 1876, 912). White silky scales, v. sol. water, insol. alcohol and ether. Cannot be sublimed. Converted by nitrous acid into lactic acid. Forms salts with acids and bases. It is a weaker acid than alanine.

SARCOSINURIC ACID *v.* vol. iii. p. 260.

SARSAPARILLA *v.* PARILLIN.

SASSAFRAS OIL. Obtained by steam-distillation from the bark and wood of the root of *Laurus sassafras* of North America. Contains saffrole (*q. v.*) and a terpene $C_{10}H_{16}$ (156°). S.G. $\underline{0}$ ·835.

SATIVIC ACID *v.* TETRA-OXY-STEARIC ACID.

SATURATION, CAPACITY OF. When a base is added to an acid, a point is reached whereat the properties of the base are neutralised by those of the acid, and the properties of the acid are neutralised by those of the base. The compound that is produced—a salt—has neither the properties of the acid nor the properties of the base. The capacity of saturation of an acid is measured by the quantity of a base, taken in formula-weights, which must be added to the quantity of the acid expressed by its formula in order to form a normal salt. The capacity of saturation of a base is measured by the number of formula-weights of an acid which must be added to a formula-weight of the base in order to form a normal salt. The study of the capacities of saturation of acids and bases leads to the classification of acids as monobasic, dibasic, tribasic, &c., and of bases as mono-acid, di-acid, tri-acid, &c. (*v.* ACIDS, vol. i. p. 49; and ACIDS, BASICITY OF, vol. i. p. 51). The notion of equivalency also arises from the study of the capacities of saturation of acids and bases (*v.* vol. ii. p. 446).

When chlorine combines with potassium, one atom of the metal is saturated by one atom of the halogen; but three atoms of chlorine are required to saturate a single atom of bismuth or antimony. The notion of a definite capacity of saturation has been extended from the acids and

bases to the atoms of the elements. The development of this conception leads to the hypotheses of valency and atom-linking (v. CLASSIFICATION, vol. ii. pp. 213–215; EQUIVALENCY, vol. ii. p. 446; and FORMULÆ, vol. ii. p. 572). M. M. P. M.

SAVINE OIL. *Oleum Sabinæ.* The essential oil from *Juniperus Sabina* contains a sesquiterpene $C_{15}H_{24}$, which has a crystalline hydrochloride $C_{15}H_{24}2HCl$ [118°] (Wallach, *A.* 238, 82).

SAVORY. Essence of savory (from *Satureja montana*) contains 40 p.c. carvacrol (232°) and two terpenes (174°) and (183°) (Haller, *C. R.* 94, 132). The oil from *Satureja hortensis* contains 20 p.c. cymene, 50 p.c. carvacrol, a terpene (179°). S.G. $\frac{15}{}$ ·855, and a very small quantity of a phenol which differs from carvacrol in not being extracted by ether from its dilute alkaline solution, and yields a phosphate [69°] (Jahns, *B.* 15, 816).

SCAMMONY. A purgative gum-resin composed of the dried milky juice of *Convolvulus scammonia* and of other species of *Convolvulus*. It is purified by boiling with alcohol, neutralising the alkaline filtrate by dilute H_2SO_4, filtering, and evaporating (Perret, *Bl.* [2] 28, 522). It contains jalapin (*q. v.*).

SCANDIUM. Sc. At. w. 44. Mol. w. unknown. The oxide of a new element was isolated in 1879 by Nilson (*B.* 12, 554) from *euxenite* and *gadolinite*; the same oxide was obtained, about the same time, by Cleve, also from Scandinavian minerals (*Bl.* [2] 31, 486 [1879]). The name *scandium* was given to the metal of the new earth by Nilson to denote the locality of the minerals from which the oxide had been obtained. In his first memoir Nilson represented scandia as ScO_2, and determined the at. w. of Sc to be c. 170; in his second memoir (*B.* 13, 1439) he adopted Cleve's correction, and formulated the oxide as Sc_2O_3, and gave the at. w. of the metal as 44. The element scandium has not yet been isolated.

Occurrence.—Sc_2O_3 is found, along with yttria, ytterbia, &c., in very small quantities in a few rare minerals—*gadolinite*, *keilhauite*, *yttrotitanite*, and *euxenite*. From 4 kilos. *gadolinite* Cleve obtained ·8 g. Sc_2O_3, and 1·2 g. Sc_2O_3 from 3 kilos. *yttrotitanite*.

Preparation.—The metal has not been isolated (*v.* SCANDIUM OXIDE, *infra*).

Detection.—Sc salts give a very brilliant emission-spectrum, rich in rays. Thalén (*B.* 12, 555) gives the wave-lengths of the most characteristic lines as 6304, 6079, 6037 in the orange; 5526 in the yellow (very marked); 5031 in the green; 4415, 4400, 4374, 4325, 4326, 4314, and 4249 in the indigo (*v.* also *B. A.* 1884. 440).

Chemical relations.—Ten years before Nilson discovered Sc, Mendeléeff asserted that an element would be found in the group of which boron is the first member, and that this element would resemble B and Al. To this unknown element Mendeléeff gave the name *ekaboron*, and he stated the properties of the element and its compounds in detail. The properties of the compounds of scandium correspond with great closeness with those of Mendeléeff's ekaboron (*v.* tables in vol. i. p. 352; *cf.* vol. iii. p. 815). The properties of ekaboron were arrived at by comparing the properties of pairs of elements related to one another, as regards positions in the periodic arrangement, similarly to ekaboron and its atom-analogues. The relations expressed by the following scheme were specially studied by Mendeléeff:

Eb:Al = Ca:Mg = Ti:Si = V:P = Cr:S:
Eb:B = Ca:Be = Ti:C = V:N = Cr:O = Mn:F.

These statements mean, the relations between the properties of Eb and Al are similar to the relations between the properties of Ca and Mg, &c. For a brief working out of similar relations in the case of eka-aluminium *v.* GALLIUM (vol. ii. pp. 598–9). Scandium is the second even-series member of Group III. It follows B, and is followed by Y, La, and Yb in the even series of this group. Sc resembles Al in many respects, but the difference between these elements is shown, among other ways, in the fact that the double sulphate of Sc and K—$Sc_2(SO_4)_3.3K_2SO_4$—is not an alum (*v.* EARTHS, METALS OF THE; vol. ii. p. 424).

Scandium, chloride of, $ScCl_3$(?). White hygroscopic needles separate on evaporating a solution of the oxide in HClAq to a syrup; HCl is given off on heating, and an oxychloride remains as a white powder (Cleve, *l.c.*).

Scandium, oxide of, Sc_2O_3. (*Scandia.*) Prepared by ppg. solutions of Sc salts by NH_3Aq, washing the white, gelatinous, very bulky pp. of hydrated oxide, drying at 100°, and then heating strongly; also obtained by heating to redness Sc nitrate, sulphate, or oxalate. A white, light powder, resembling MgO; sol. in hot conc. H_2SO_4Aq or HNO_3Aq. S.G. 3·864 (Nilson a. Pettersson, *B.* 13, 1461). S.H. from 0° to 100° = ·153 (N. a. P.).

Scandia is best obtained from ***euxenite***. The finely-powdered mineral is fused with $KHSO_4$, the product is dissolved in cold water, and ppd. by NH_3Aq, the pp. is dissolved in HNO_3Aq, the solution is boiled for some time, filtered from any pp. which forms, and ppd. by oxalic acid; the ppd. oxalates are dried, heated strongly, washed with hot water to remove the K_2CO_3, dissolved in HNO_3Aq, and the solution is evaporated to dryness and the residue heated till it melts; the fused nitrates are treated with water, when a pp. forms, consisting of oxide of Th with small quantities of oxides of Ce, U, and Fe; the filtered solution is evaporated to dryness, the nitrates are partly decomposed by heating, and then treated with water; the residue, which contains a basic nitrate of Sc, is evaporated with HNO_3Aq, and the residue is again heated for some time, treated with water, and the insoluble evaporated with HNO_3Aq, and so on. This process separates didymia, yttria, and terbia, the nitrates of which earths are not so readily decomposed by heat to basic nitrates as Sc nitrate is. By repeating this process 68 times Nilson (*B.* 13, 1442) obtained a nitrate solution which showed no absorption bands, and contained only salts of Sc and Yb. The solution of Sc and Yb nitrates is evaporated with conc. H_2SO_4, saturated K_2SO_4Aq is added, the salt $Sc_2(SO_4)_3.3K_2SO_4$ which separates (Yb sulphate remains in solution) is dissolved in water, and ppd. by NH_3Aq; the ppd. $Sc_2O_3.xH_2O$ is washed and dissolved in HNO_3Aq, and Sc oxalate is ppd. by oxalic acid; the ppd. oxalate is washed,

Barium selenate $BaSeO_4$. A white salt, obtained by decomposing an alkali selenate by $BaCl_2Aq$, filtering, and washing. Insol. water and HNO_3Aq; boiled with HClAq gives $BaSeO_3$, which dissolves. S.G. 4·67 at 22° (Schafarik, *J.* 1863. 15; Michel, *C. R.* 106, 878).

Beryllium selenate $BeSeO_4.4aq$. Rhombic crystals (Topsöe, *W. A. B.* 66, 5).

Cadmium selenate $CdSeO_4.2aq$. By dissolving $CdO.xH_2O$ in H_2SeO_4Aq, and crystallising; lustrous, rhombic plates; S.G. 3·632 (von Hauer, *J. pr.* 80, 214). Forms *double salts* with NH_4 and K (Topsöe, *l.c.*; von H., *l.c.*; von Gerichten, *B.* 6, 162).

Calcium selenate $CaSeO_4.2aq$. Resembles $CaSO_4$; obtained by ppg. K_2SeO_4Aq by $Ca(NO_3)_2Aq$, dissolving in cold water, and ppg. by heating (von Hauer, *l.c.*). Also formed by fusing $CaCl_2$ with K_2SeO_4 and NaCl (Michel, *C. R.* 106, 878).

Chromium selenate. Not isolated. *Double salts*, which are *alums*, are known, of the composition $Cr_2(SeO_4)_3.M_2SeO_4.24aq$ (Wohlwill, *A.* 114, 162; Fabre, *C. R.* 105, 114; Pettersson, *B.* 6, 1466). Alums are also known of the composition $Cr_2(SeO_4)_3.M_2SO_4.24aq$ (von G., *l.c.*).

Cobalt selenate $CoSeO_4.7aq$. Hydrated salts have been obtained with 6aq and 5aq (*v.* Mitscherlich, *P.* 11, 327; Topsöe, *W. A. B.* 66, 5). Forms *double salts* with K_2SeO_4, and $(NH_4)_2SeO_4$ (T., *l.c.*; von G., *l.c.*; von H., *l.c.*).

Copper selenate $CuSeO_4.5aq$. Blue, transparent, lustrous crystals, isomorphous with the sulphate. By dissolving CuO_2H_2 in H_2SeO_4Aq (Mitscherlich, *P.* 11, 330). Forms *double salts* with selenates of NH_4, K (Topsöe, *l.c.*; von G., *l.c.*); also with Mg and Zn selenates (Wohlwill, *l.c.*).

Didymium selenate $Di_2(SeO_4)_3$ (Cleve, *Bl.* [2] 43, 362). Also with 5aq (C., *l.c.*); and with 6aq (Frerichs a. Smith, *A.* 191, 350). Forms *double salts* with NH_4 and K selenates (C., *l.c.*).

Iron selenate $FeSeO_4.7aq$ (*Ferrous selenate*). By evaporating, in H, a solution of Fe, or $FeCO_3$, in H_2SeO_4Aq; resembles $FeSO_4.7aq$ (Topsöe, *l.c.*). Obtained by Wohlwill (*A.* 114, 189) with 5aq. Forms a *double salt* with K_2SeO_4 (von G., *l.c.*).

Lanthanum selenate $La_2(SeO_4)_3.12aq$ (F. a. S., *l.c.*).

Lead selenate $PbSeO_4$. A white powder; by ppg. K_2SeO_4Aq by $Pb(NO_3)_2Aq$ (Schafarik, *J.* 1863. 15).

Magnesium selenate $MgSeO_4.6aq$. White, monoclinic crystals; isomorphous with the sulphate; S.G. 1·928 (Topsöe, *l.c.*). Forms *double salts* with NH_4 and K selenates (T., *l.c.*; von G., *l.c.*).

Nickel selenate $NiSeO_4.aq$. By evaporating solution of $NiCO_3$ in H_2SeO_4Aq (Mitscherlich, *l.c.*; Wohlwill, *l.c.*). Forms *double salts* with selenates of NH_4 and K (von G., *l.c.*; von Hauer, *J. pr.* 80, 214).

Mercury selenates. 1. *Mercuric selenate*, $HgSeO_4$. By digesting HgO with H_2SeO_4Aq, or by adding excess of H_2SeO_4Aq to mercuric acetate, and evaporating; a yellowish-white solid. Decomposed by water, giving a *basic salt* $HgSeO_4.2HgO$ (Cameron a. Davy, *Trans. I.* 28, 187). 2. *Mercurous selenate*, Hg_2SeO_4; by ppg. $HgNO_3Aq$ by K_2SeO_4Aq (C. a. D., *l c.*). With NH_3Aq forms $(NHg_2)_2SeO_4.2aq$.

Potassium selenates. The *normal salt*, K_2SeO_4, is obtained by fusing Se, K_2SeO_3, or native lead selenide, with KNO_3, dissolving in hot water, allowing to cool partly, pouring off from excess of KNO_3 which separates, and collecting the crystals which separate from the mother-liquor. Equally sol. hot and cold water (Mitscherlich, *P.* 9, 623; 11, 327). Closely resembles K_2SO_4. The *acid salt* $KHSeO_4$ is obtained like, and closely resembles, $KHSO_4$ (M., *l.c.*). K_2SeO_4 forms many *double salts*; with MSO_4, M = Cd, Co, Cu, Fe, Mn, Hg, and Zn (von Gerichten, *B.* 6, 162); with $Al_2(SeO_4)_3$ and $Cr_2(SeO_4)_3$, the compounds being *alums* (von G., *l.c.*; Pettersson, *B.* 9,1559, 1676; Schröder, *J. pr.* [2] 22, 432; Fabre, *C. R.* 105, 114).

Silver selenate Ag_2SeO_4. Similar to, and isomorphous with, Ag_2SO_4 (Mitscherlich, *l.c.*).

Sodium selenate Na_2SeO_4. Prepared like K_2SeO_4; separates with 10aq when crystallised below 40° (M., *l.c.*).

Strontium selenate $SrSeO_4$. Obtained by fusing $SrCl_2$ with NaCl and an alkali selenate; S.G. 4·23. Exactly resembles *celestine* in crystallographic and optical properties (Michel, *C. R.* 106, 878).

Thallium selenate Tl_2SeO_4. By dissolving Tl_2CO_3 in H_2SeO_4Aq, and evaporating. Forms white, prismatic needles, isomorphous with K_2SeO_4; sl. sol. cold water; insol. alcohol or ether (Kuhlmann, *Bl.* 1864 [1] 330; Oettinger, *Zeit. Chem. Pharm.* 1864. 440). Forms *double salts*, which are *alums*, with $Al_2(SeO_4)_3$ and with $Cr_2(SeO_4)_3$ (Fabre, *C. R.* 105, 114).

Zinc selenate $ZnSeO_4.7aq$. Various hydrates are known (*v.* Mitscherlich, *P.* 11, 326; 12, 144; Topsöe, *l.c.*). Forms a *double salt* with Tl_2SeO_4 (Werther, *Bl.* 1865 [1] 60); also with K_2SO_4 (von Gerichten, *B.* 6, 162).

THIOSELENATES $M^{I}_2SeSO_3$. (*Selenothiosulphates. Selenosulphates.*) Solutions of the normal alkali sulphites dissolve Se, forming these salts. The acid has not been isolated. The salts correspond with the thiosulphates, S being replaced by Se.

Potassium thioselenate $K_2SeSO_3.aq$. Formed by mixing K_2SeAq with SO_2Aq (Cloëz, *Bl.* 3, 112; [2] 4, 419). Better prepared by digesting K_2SO_3Aq with excess of Se, filtering the cold liquid from Se, and concentrating without heat; crystals of K_2SO_4 mixed with $K_2SeS_2O_6$ (*v. infra*) separate, and K_2SeSO_3 crystallises from the mother-liquor (Cloëz, *l.c.*; Rathke, *J. pr.* 95, 1). White, lustrous, six-sided tablets; deliquescent in moist air; effloresce over H_2SO_4. Decomposed rather easily by heat, giving K polyselenides; cold water separates Se, and forms $K_2SeS_2O_6$ (*v. infra*); acids evolve SO_2 and separate Se; $BaCl_2Aq$ ppts. $BaSO_3$ and Se from an aqueous solution of the salt; an ammoniacal solution of Ag_2O forms Ag_2Se and K_2SO_4Aq on heating.

DITHIO-TRISELENATES $M^{I}_2SeS_2O_6$. (*Selenotrithionates.*) These salts may be regarded as derived from trithionates ($M^{I}_2S_3O_6$) by replacing S by Se; as the salts $M_2S_3O_6$ are called trithionates, so the salts $M^{I}_2Se_3O_6$ might be called triselenates if they were isolated, and the salts $M^{I}_2S_2SeO_6$ may be called dithio-triselenates.

Potassium dithio-triselenate $K_2SeS_2O_6$. This salt is formed in the preparation of potassium thioselenate (*v. supra*); if $KHSO_3$ is present in the K_2SO_3 used considerable quantities of $K_2SeS_2O_6$ are produced (Rathke, *J. pr.* 95, 1). It is also obtained by mixing K_2SeSO_3 with excess of K_2SO_3 and conc. H_2SeO_3Aq. Forms lustrous, greenish-yellow, monoclinic prisms, isomorphous with $K_2S_3O_6$; stable in air; sol. water without change (Rathke, *J. pr.* [2] 1, 33). Acids evolve SO_2 and ppt. Se, on warming; ammoniacal solution of Ag_2O ppts. Ag_2Se, forming also K_2SO_4Aq and H_2SO_4Aq.

Dithio-triselenic acid, $H_2SeS_2O_6$, is said to be present in the solution obtained by the action of excess of SO_2 on SeO_2Aq (Schulze, *J. pr.* [2] 32, 390). M. M. P. M.

SELENHYDRIC ACID H_2Se; *v.* HYDROGEN SELENIDE, vol. ii. p. 724.

SELENIC ACID H_2SeO_4. Mol. w. not determined. S.G. 2·9508 at 15°; S.G. of superfused acid, 2·6083 at 15° (Cameron a. Macallan, *Pr.* 46, 13). Melts at 58°; the molten acid may be cooled below 5° without solidifying (C. a. M., *l.c.*). H.F. $[Se,O^3,Aq]=76,660$; $[SeO^2Aq,O]=20,500$ (*Th.* 2, 279).

Formation.—1. By passing Cl into H_2SeO_3Aq, and evaporating.—2. By fusing Se or SeO_2 with KNO_3, ppg. $BaSeO_4$ from solution of the fused mass, decomposing by K_2CO_3, filtering from $BaCO_3$, neutralising any K_2CO_3 present by HNO_3Aq, ppg. $PbSeO_4$, and decomposing this salt by H_2S (von Gerichten, *A.* 168, 214).—3. By heating Se with HNO_3Aq, boiling with HClAq (to reduce any H_2SeO_4 to H_2SeO_3), ppg. traces of H_2SO_4 by adding a little $Ba(NO_3)_2$Aq, filtering from $BaSO_4$, neutralising by Na_2CO_3, evaporating to dryness, heating to dull redness, boiling with HNO_3Aq, ppg. $PbSeO_4$ by addition of $Pb(NO_3)_2$Aq, and decomposing by H_2S (Fabian, *A. Suppl.* 1, 241). — 4. By fusing SeO_2 with excess of KNO_3, boiling with HNO_3Aq, ppg. $CaSeO_4$ by addition of $Ca(NO_3)_2$Aq, decomposing the $CaSeO_4$ by addition of CdC_2O_4, and decomposing the $CdSeO_4$ so obtained by H_2S (von Hauer, *J. pr.* 80, 214).—5. By adding $AgNO_3$ or Ag_2CO_3 to a solution of pure SeO_2 in water, digesting the ppd. Ag_2SeO_3 with water and a slight excess of Br, filtering from AgBr, and evaporating the filtrate, which contains H_2SeO_4 (Thomsen, *B.* 2, 598). — 6. By oxidising H_2SeO_3Aq by K_2CrO_4Aq, PbO_2, or MnO_2 (Wohlwill, *A.* 114, 169, 176).

Preparation.—SeO_2 is heated till sublimation begins; it is then dissolved in water, and BaOAq is added so long as a few drops, when filtered, continue to give a pp. with BaOAq; the filtered liquid is now free from H_2SO_4 and H_2SeO_4, it is evaporated to dryness, and the residual SeO_2 is heated till it sublimes (Thomsen, *B.* 2, 598). The pure SeO_2 thus obtained is dissolved in water, excess of $AgNO_3$Aq is added, the ppd. Ag_2SeO_3 is washed with water and shaken with water and Br—at first Br is added, and then BrAq till the liquid shows a faint orange colour; the liquid filtered from AgBr contains only H_2SeO_4, it is evaporated and treated as described hereafter (T., *l.c.*). Another method consists in neutralising the solution of pure SeO_2 by K_2CO_3, evaporating to dryness, fusing with a little KNO_3 for some time, dissolving in water, slightly acidifying with HNO_3Aq, boiling for some time to decompose any nitrite present, allowing to cool, adding $Pb(NO_3)_2$Aq, washing the ppd. $PbSeO_4$, suspending this salt in water, and decomposing it by a *rapid* stream of H_2S; the filtered liquid is then evaporated (von Gerichten, *A.* 168, 214).

The solution of H_2SeO_4 is concentrated by evaporation in an open dish on a water-bath so long as water passes off; an acid containing c. 83–84 p.c. H_2SeO_4 is thus obtained; this acid is placed in a small flask connected with a short wide tube containing solid KOH, which is connected with a large U tube also containing solid KOH; the U tube is connected with the receiver of an air-pump, or with a vessel in connection with a good water-pump. The air is pumped out of the apparatus, and when a good vacuum is obtained the small flask is heated to 100° so long as acid distils over (this is known by the KOH effervescing slightly, as ordinary KOH contains K_2CO_3); the temperature is then raised to 180° (an oil-bath being used to heat the flask), and heating at this temperature is continued so long as acid distils off; as soon as the potash ceases to be acted on the heating is stopped and the flask is at once cooled; a very good vacuum must be maintained throughout the process. H_2SeO_4 crystallises as the flask is cooled. A small quantity of H_2SeO_4Aq should be evaporated thus at a time (Cameron a. Macallan, *Pr.* 46, 13).

Properties.—A white crystalline solid, crystallising in long hexagonal prisms, and melting at 58° to a colourless oily liquid. The liquid acid may be cooled below 5° without solidifying if it is not stirred; a crystal of H_2SeO_4 dropped into the liquid causes it to solidify at once, the temperature rising to 58°. The liquid acid is specifically lighter than the solid (*v.* data at beginning of article) (C. a. M., *l.c.*). H_2SeO_4 is very hygroscopic; it mixes with water, with production of heat.

The following table is taken from Cameron and Macallan (*l.c.*):—

P.c. H_2SeO_4	S.G. H_2SeO_4Aq at 15°	P.c. H_2SeO_4	S.G. H_2SeO_4Aq at 15°
99·73	2·6083	90	2·3848
99·5	2·6051	89	2·3568
99·0	2·5975	88	2·3291
98·5	2·5863	87	2·3061
98·0	2·5767	86	2·2795
97·5	2·5695	85	2·2558
97	2·5601	84	2·2258
96	2·5388	83	2·1946
95	2·5163	82	2·1757
94	2·4925	81	2·1479
93	2·4596	80	2·1216
92	2·4322	79	2·0922
91	2·4081	73·5	1·9675

Reactions.—1. With *water* much heat is produced, and hydrates are probably formed (*v. infra*, *Hydrates of selenic acid*). H_2SeO_4 acts as a dehydrating agent, similarly to H_2SO_4 (C. a. M., *l.c.*).—2. *Heated in vacuo* begins to decompose into O, H_2O, and SeO_2 at c. 200°; the water formed dilutes the remaining acid, which then distils over. When dilute H_2SeO_4Aq is *heated at ordinary pressure* water distils off till temperature rises to 205°, when the acid has the

composition $H_2SeO_4.H_2O$; traces of H_2SeO_4 then distil over; at 260° white fumes of H_2SeO_4 come off. When H_2SeO_4 is strongly heated at the ordinary pressure, some of it is decomposed to SeO_2, O, and H_2O; the remaining acid is diluted by the water till a dilute acid distils off (C. a. M., *l.c.*).—3. Dilute H_2SeO_4Aq dissolves many *metals*, with evolution of H; warm conc. acid dissolves *copper* and *gold*, with partial reduction to H_2SeO_3.—4. Digestion with *hydrochloric acid* reduces H_2SeO_4Aq to H_2SeO_3Aq, with evolution of Cl; the acid is *not* reduced by *sulphur dioxide* nor by *sulphuretted hydrogen*.—5. *Sulphur* reacts with liquid H_2SeO_4 at c. 60°, forming a deep-blue, very unstable substance (? $SeSO_3$) which decomposes to SO_2 and H_2SeO_3 (C. a. M., *l.c.*).—6. *Selenion* dissolves in H_2SeO_4, giving a green unstable substance—? Se_2O_3 (C. a. M., *l.c.*).—7. *Tellurium* dissolves in H_2SeO_4, forming a reddish body, probably $TeSeO_3$ (C. a. M.).—8. Heated with *phosphoric anhydride*, SeO_2 is given off; but at a lower temperature crystals were obtained which C. a. M. think were SeO_3.

HYDRATES OF SELENIC ACID. The *monohydrate* $H_2SeO_4.H_2O$ was obtained by C. a. M. (*l.c.*) by diluting H_2SeO_4 to 88·96 p.c., freezing at −23°, melting and re-crystallising by freezing several times. This hydrate forms long needles, melting at 25°, and remaining liquid even 50° below its melting-point; Pickering (*priv. comm.*) gives melting-point as 16·6°. S.G. of solid hydrate = 2·6273 at 15°; S.G. of superfused hydrate = 2·3557 at 15°. C. a. M. did not succeed in obtaining other hydrates as solids. For salts of H_2SeO_4 *v.* SELENATES, p. 433.

M. M. P. M.

SELENIDES. Se combines with most metals when heated with them. Se also combines with many non-metals, *e.g.* with B, Br, Cl, F, H, I, O, P, and S. Many metallic selenides are formed by heating the elements together (Uelsmann, *A.* 116, 122; Schneider, *A.* 97, 192; Little, *A.* 112, 211); also by the interaction of Se and metallic salts (Schneider, *P.* 127, 642; Potilitzin, *B.* 12, 697); sometimes by the interaction of Se and metallic sulphides at high temperatures (P., *l.c.*). For thermal data regarding the formation of many metallic selenides *v.* Fabre (*C. R.* 102, 1469; 103, 269, 345). Selenides of the alkali metals are sol. water; they are formed by saturating the hydroxides in water by H_2Se (Fabre, *C. R.* 102, 613), by reducing the selenites by C (Wöhler a. Dean, *A.* 97, 1), by reducing selenates by H at 200° (Fabre, *C. R.* 102, 1469), and by heating the elements together (Uelsmann, *A.* 116, 122). The selenides of metals other than the alkali metals are insol. water.

M. M. P. M.

SELENION. Se. (*Selenium.*) At. w. 78·8. Mol. w. 157·6 (*v. infra*). M.P. 217° for crystalline variety (Hittorf, *P.* 84, 214; Draper a. Moss, *C. R.* 33, 1; *v. Action of heat on selenion*). Boils at 676°–683° (Carnelley a. Williams, *C. J.* 35, 563). S.G. c. 4·7 crystalline; c. 4·3 amorphous (for more details *v.* description of varieties of Se, *infra*). V.D. 111 at 860°, 92 at 1040°, 82 at 1420° (Deville a. Troost, *C. R.* 49, 239; 56, 891). S.H. crystalline −20° to +7° = ·0732, crystalline 20° to 98° = ·0762, amorphous −27° to +8° = ·0746, amorphous 19° to 87° = ·1036 (Regnault, *A. Ch.* [3] 46, 257). C.E. vitreous at 40° = ·0000368 (Fizeau, *C. R.* 68, 1125; *cf.* Spring, *B.* 14, 2580). For E.C. *v. infra.* $\mu_A = 2{\cdot}654$, $\mu_a = 2{\cdot}692$, $\mu_D = 2{\cdot}98$ (*v.* Sirks, *P.* 143, 429). For emission and absorption spectra *v. B. A.* 1884. 440. H.C. $[Se,O^2] = 57{,}080$; $[Se,O^2,Aq] = 56{,}160$; $[Se,O^3,Aq] = 76{,}660$ (*Th.* 2, 274).

Historical.—In 1817 Berzelius (*S.* 23, 309) obtained a new element from the crystals formed in the leaden chamber of a sulphuric acid works at Gripsholm in Sweden; as the new element was found to resemble tellurium (discovered in 1798 by Klapstock), Berzelius gave it the name selenion (σελήνη = the moon). As Se is distinctly a non-metallic element, and as the termination *um* is characteristic of the names of metals, it seems altogether improper to use the name selenium rather than selenion.

Occurrence.—In small quantities uncombined with other elements; in combination with various metals, such as Bi, Cu, Pb, Hg, Ag, generally along with sulphur. Most selenion-containing metallic sulphides are very poor in Se; but certain selenides from the Argentine Republic contain from 29 to 48·5 p.c. Se, combined with Cu, Pb, and Ag. Minerals containing Se are fairly widely distributed, but occur only in small quantities (Stromeyer, *S.* 43, 452; MacIvor, *C. N.* 56, 251; Nordström, *B.* 12, 1723; Pisani, *C. R.* 88, 391; Hensler a. Klinger, *B.* 18, 2556; Stelzner, *J.* 1874. 1234). When sulphides which contain Se are roasted, the Se condenses in the flues. The deposits that form in sulphuric acid chambers often contain Se; and many specimens of the acid also contain this element. Commercial HClAq sometimes contains Se, derived from the H_2SO_4 used in making the HClAq (Kemper, *J.* 1860. 84; Nilson, *B.* 7, 1719; Lamy, *C. R.* 74, 1285; Scheurer-Kestner, *C. R.* 74, 1286; Personne, *C. R.* 74, 1199; Drinkwater, *An.* 8, 63).

Formation.—1. By passing SO_2 into H_2SeO_3Aq; $H_2SeO_3Aq + 2SO_2 + H_2O = 2H_2SO_4 + Se$.—2. By allowing the solution of an alkali selenide to stand in air (Böttger, *J. pr.* 71, 512).—3. By adding acid to solution of a thio-selenate (Böttger, *J. pr.* 94, 439), or to KCNSeAq (Oppenheim, *J. pr.* 71, 266).—4. By the action of such metals as Zn or Fe on H_2SeO_3Aq made strongly acid by HCl or H_2SO_4. 5. By heating $(NH_4)_2SeO_3$ or $(NH_4)_2SeO_4$.

Preparation.—1. *From the flue-dust formed in roasting sulphides containing Se.* The flue-dust is washed with water, dried, and distilled; this method is applicable to dusts rich in Se. Dusts poorer in Se are washed, the heavier particles are lixiviated with dilute HClAq and then with water, dried, fused with pearlash and soda, and washed with water; the solution of alkali selenide thus obtained is allowed to stand in the air, and the Se which ppts. is washed, dried, and distilled (Böttger, *J. pr.* 71, 512). Or the washed dust is made into a thin paste with equal volumes of H_2SO_4 and H_2O, heated to boiling, with addition from time to time of a little HNO_3 or $KClO_3$, till the red colour of the liquid is destroyed, conc. HClAq is added equal to half the volume of the liquid, and the whole is evaporated to one-fourth its bulk, whereby Cl is evolved and H_2SeO_4 is reduced to H_2SeO_3; SO_2 is passed into this solution, the ppd. Se is washed, dried, and distilled (Wöhler, *G. A.* 69, 264).—2. *From the deposit in the leaden chambers of sulphuric acid works.* The washed deposit is boiled with conc. Na_2SO_3Aq till it is black (from formation of PbS), and the liquid, which contains Na_2SeO_3, is filtered into dil. HClAq, whereby Se is ppd. This process is repeated several times (Böttger, *J. pr.* 94, 439). Or the washed deposit is digested at 80°-100° with fairly conc. KCNAq until the red colour of the liquid has changed to grey, the liquid is filtered, the residue washed with boiling water till HClAq ceases to produce a reddish opalescence in the washings, and excess of HClAq is added to the filtrate and washings, whereby Se is ppd. (KCNAq + Se = KCNSeAq; KCNSeAq + HClAq = KClAq + HCNAq + Se). The ppd. Se is dissolved in HNO_3Aq, the solution is evaporated (slowly, to prevent loss of SeO_2) to dryness, the SeO_2 is sublimed in a tube of hard glass in a stream of dry dust-free air, the sublimate is dissolved in water, HClAq is added, and Se is ppd. by SO_2 (Oppenheim, *J. pr.* 71, 266).

Se, as prepared by reducing cold H_2SeO_3Aq, is a red amorphous powder; an amorphous vitreous variety is obtained by melting ppd. Se and cooling very rapidly by pouring on to a porcelain plate (Hittorf, *P.* 84, 214; Rammelsberg, *P.* 152, 151; Regnault, *A. Ch.* [3] 46, 257); a black crystalline variety of Se is prepared by allowing conc. K_2SeAq or Na_2SeAq to stand in air until a crust forms on the surface (H., *l.c.*; R., *l.c.*), also by crystallising any form of Se from Se_2Cl_2 (Rathke, *A.* 152, 181); a red crystalline variety is prepared by slowly and repeatedly heating a solution of Se in CS_2 in a sealed tube to somewhat under 100°, and allowing to cool (R., *l.c.*; Rathke, *A.* 152, 181), also by subliming amorphous Se (Bornträger, *D. P. J.* 242, 55); a grey metal-like variety is prepared by very slowly heating amorphous or red crystalline Se to 96°-97° (H., *l.c.*; R., *l.c.*; Fabre, *C. R.* 103, 53). According to Schutze (*J. pr.* [2] 32, 390) a colloidal soluble form of Se is obtained by reducing H_2SeO_3Aq by SO_2; no acid must be present. The colloidal Se remains in solution, colouring the liquid dark red. The solution is not changed by boiling but on adding an acid or a salt Se is ppd. in red flocks.

Properties.—Se exists in several, probably in five, forms.

I. *Amorphous selenion*; *sol. in* CS_2.—(i.) *Red-powdery amorphous Se* forms sealing-wax-red flocks, or when dried at a low temperature a dark-red powder; when formed by reduction of hot H_2SeO_3Aq it appears as a black powder (Hittorf, *P.* 84, 214). S.G. at 20° = 4·3 (Rammelsberg, *P.* 152, 151; Schaffgotsch, *P.* 90, 66); 4·2 (Rathke, *A.* 152, 131). This variety is a non-conductor of electricity (Hittorf, *l.c.*). It is sol. CS_2; S. at b.p. of CS_2(46·6°) = ·1, at 0° = ·016 (Mitscherlich, *J.* 1855. 314); according to Rammelsberg (*l.c.*) the solubility in CS_2 varies much. For S.H. *v.* beginning of this article. Petersen (*Z. P. C.* 8, 601) gives H.C. of this variety $[Se,O^2]$ = 57,250, and at. vol. 18·4; the change from this form to any other form of Se is attended with contraction and the production of a small quantity of heat. For action of heat *v. infra.*

(ii.) *Amorphous vitreous Se* forms a black lustrous solid, appearing red in thin layers. S.G. 4·282 at 20° (Schaffgotsch, *J. pr.* 43, 308; 60, 312). Sol. in CS_2. No fixed melting-point; when heated it softens at 60°, and becomes gradually less viscous till at 250° it is quite liquid; if this liquid is rapidly cooled, the vitreous variety is re-formed (Hittorf, *l.c.*; Draper a. Moss, *C. N.* 33, 1). Heated very slowly to 96°-97° this variety changes to metallic Se, with production of heat (R., *l.c.*; Regnault, *A. Ch.* [3] 46, 257; Fabre, *C. R.* 103, 53).

II. *Crystalline selenion*; *insol. in* CS_2.—(i.) *Black crystalline Se.* Small, microscopic, glittering leaflets. S.G. 4·8 (R., *l.c.*); 4·76 to 4·78 at 15° (Mitscherlich, *J.* 1855. 314). Insol. CS_2. H.C. $[Se,O^2]$ = 55,820; at. vol. = 16·5; change from amorphous Se to this form is accompanied by slight production of heat and contraction (Petersen, *Z. P. C.* 8, 601).

(ii.) *Red crystalline Se.* Small, thin, transparent, lustrous crystals; in thicker layers appears black and opaque. S.G. 4·46 to 4·5 at 15° (R., *l.c.*; M., *l.c.*; Rathke, *l.c.*). Melts at 217° (H., *l.c.*; D. a. M., *l.c.*). Insol. in CS_2. Petersen (*l.c.*) gives H.C. $[Se,O^2]$ = 56,200; and at. vol. = 17·7. This variety is a conductor of electricity, the conductivity increasing with increase of temp. and also by exposure to light. (For details, *v. infra.*) When heated to c. 110° this variety becomes black. The crystals are monoclinic, ratio of axes = 1·62:1:1·6 (M., *l.c.*; Regnault, *l.c.*); isomorphous with monoclinic S (R., *l.c.*). For S.H. *v.* beginning of this article.

(iii.) *Grey metallic Se.* Lustrous, grey, metal-like, granular solid, resembling grey pig-iron; somewhat malleable (Regnault, *l.c.*). Insol. in CS_2. S.G. 4·4 to 4·5 (R., *l.c.*). Melts at 217° (H., *l.c.*); on cooling, the vitreous variety is chiefly formed, but if the cooling is stopped at 210° after a time there is a sudden rise to 217°, and the whole solidifies in the metallic form. All varieties of Se are sol. Se_2Cl_2 and $SeEt_4$.

Action of heat on selenion. Any one of the crystalline varieties of Se melts at 217°; when the molten Se is allowed to cool slowly it gradually becomes less soft, a thermometer placed in the cooling substance continuously falls and shows no point of rest (Hittorf, *l.c.*; Regnault, *l.c.*); the final product is crystalline Se, but if the cooling is caused to take place rapidly the amorphous vitreous variety is formed; if the cooling is stopped at 210°, and that temperature is maintained for some time, there is a sudden rise to 217° and the Se again solidifies in the crystalline (metallic) form. When amorphous Se is heated it softens at c. 60°, and becomes gradually less viscous until at 250° it is quite liquid; if the heating is very gradual, there is a sudden evolution of heat at 96°-97° (Regnault, *l.c.*, found temperature rise to 200°-230°), and the metallic variety is produced. Se boils at 676°-683°, forming a reddish-yellow vapour, the V.D. of which does not become constant until 600°-700° above the b.p.

Effects of light and heat on the electrical conductivity of crystalline selenion. Amorphous Se does not conduct electricity; but when heated rapidly it begins to conduct at 165°-175°, and conductivity increases until it attains a maximum at c. 217° (Draper a. Moss, *C. N.* 33, 1). Crystalline Se conducts, the conductivity increasing proportionally with increase of temperature to 217°, after which it decreases and reaches a minimum at 250° (Hittorf, *P.* 84, 214; D. a. M., *l.c.*). If Se is heated for a considerable time to 200° and is then allowed to cool, conductivity decreases as temperature rises and increases as temperature falls (W. Siemens, *P.* 159, 117). This observation seems to show that at c. 200° a variety of Se is formed which behaves like a metal, and that on cooling this form remains mixed with the ordinary crystalline variety, so that the conductivity depends on the relative quantities of the two forms, and therefore on the temperature (*cf.* Kalischer, *W.* 31, 101). The electrical conductivity of crystalline Se increases enormously when the Se is exposed to light (Sale, *Pr.* 21, 283; Smith, *B.* 6, 204; Rosse, *P. M.* [4] 47, 161; Forssmann, *W.* 2, 513). Adams and Day (*Pr.* 24, 163) found that the resistance of Se varied directly as the square root of the intensity of the source of light; also that light caused an electric current in Se from the less to the more illuminated part (*Pr.* 25, 113; *cf.* Bidwell, *C. N.* 52, 191).

Se may be sublimed and distilled *in vacuo*, or in an indifferent gas (Schuller, *J.* 1884. 1550); heated in air it is burnt to SeO_2. Se dissolves in conc. H_2SO_4, forming $SeSO_3$, and is ppd. again on adding water; Se is sol. in alkali solutions, forming alkali selenides; also in KCNAq, in alkaline sulphite solutions, in Se_2Cl_2, Se_2Br_2, and $SeEt_4$; the amorphous varieties are sl. sol. CS_2

Se resembles S and Te in its chemical character; it is somewhat less negative than S and more negative than Te; it shows distinct analogies with Cr, Mo, W, and U (*v.* OXYGEN GROUP OF ELEMENTS, vol. iii. p. 705; and CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168).

The atomic wt. of Se has been determined (1) by analysing $SeCl_4$ (Berzelius, *P.* 8, 21 [1818]); (2) by analysing K_2SeO_4 (Mitscherlich a. Nitzsch, *P.* 9, 627 [1827]; (3) by oxidising Se to SeO_2, by reducing SeO_2 to Se, and by analysing $BaSeO_3$ (Sace, *A. Ch.* [3] 21, 119 [1847]); (4) by analysis of HgSe (Erdmann a. Marchand, *J. pr.* 55, 202 [1849]); (5) by converting Se into $SeCl_4$ (Dumas, *A. Ch.* [3] 55, 186 [1859]; (6) by reducing SeO_2 to Se and by analysing Ag_2SeO_3 (Pettersson a. Ekman, *B.* 9, 1210 [1876]; (7) by determining S.H. of Se (Regnault, *A. Ch.* [3] 46, 257); (8) by determining V.D. of, and analysing, SeH_2, SeO_2, Se_2Cl_2, $SeCl_4$, and $SeBrCl_3$.

The molecular wt. of Se has been found by determining the V.D. of Se at 860°, c. 1000°, and c. 1400°; the values at 1400° agree with the formula Se_2.

The atom of Se is divalent in the gaseous molecule SeH_2, and tetravalent in the gaseous molecules $SeCl_4$ and $SeBrCl_3$.

Reactions and Combinations.—1. *Water and ozone* produce H_2SeO_4 (Mailfert, *C. R.* 94, 860, 1186). Water alone does not react at 160° (Cross a. Higgin, *C. J.* 35, 249).—2. *Conc. sulphuric acid* dissolves Se on warming, forming H_2SeO_3, and some H_2SeO_4, and giving off SO_2. *Fuming sulphuric acid* forms a greenish solution containing $SeSO_3$ (*v. Thio-oxide*, *p.* 441); on boiling H_2SeO_3 is formed and SO_2 evolved (Divers a. Shimosé, *B.* 18, 1209).—3. *Hot conc. nitric acid* oxidises Se to H_2SeO_3, with evolution of NO. *Hydrochloric acid* does not react with Se.—4. Se dissolves in *alkali solutions*, forming alkali selenides; *fusion with alkalis* produces the same compounds.—5. *Fusion with nitre or potassium chlorate* forms K_2SeO_4.—6. *Potassium cyanide solution* dissolves Se to KCNSeAq. 7. *Solutions of alkali or alkaline earth sulphites* dissolve Se, forming thioselenates (Rathke a. Zschiesche, *J. pr.* 92, 141; Uelsmann, *A.* 116, 123; *v.* also THIOSELENATES, p. 434).—8. Se vapour passed over heated *lead fluoride* forms Se fluoride (Knox, *Pr. Irish Acad.* 1841. 299).—9. Se combines with *oxygen* to form SeO_2, when heated in O or air.—10. Se combines with *chlorine*, *bromine*, and *iodine* at the ordinary temperature.—11. Heated to low redness with *hydrogen*, H_2Se is formed (Uelsmann, *A.* 116, 122).—12. *Phosphorus* combines at the ordinary temperature.—13. Se combines with *arsenic* and *antimony*, by heating the elements together.—14. Selenides of most metals are formed by heating Se with *metals* (*v.* SELENIDES, p. 436). Sometimes the combination is effected without heat, under the influence of light (*v.* Bidwell, *P. M.* [5] 20, 178; Moss, *C. N.* 33, 203).—15. Se dissolves in molten *sulphur*, but no definite compounds are formed in this way.—16. With *sulphuric anhydride* Se combines to form $SeSO_3$ (*v. Thio-oxide*, p. 441).

Selenion, acids of. *Selenhydric acid* H_2Se, vol. ii. p. 724; *selenic acid* H_2SeO_4, p. 435; *selenious acid* H_2SeO_3, p. 445; *Selenocyanhydric acid* HCNSe, vol. ii. p. 348; also *Selenocyanic acid*, this vol. p. 443; *salts of thioselenic acids*, H_2SeSO_3 and $H_2SeS_2O_6$, are known, p. 434; and *salts of selenosamic acids*, $Se(NH_2)OM^I$ and $2SeO(NH_2).OH.OM^I$, have been isolated, p. 446.

Selenion, antimonide of; *v.* vol. i. p. 283, ANTIMONY, *Combinations of*, No. 6.

Selenion, arsenides and arsenosulphides of; *v.* vol. i. p. 303, ARSENIC, *Combinations of*, No. 7.

Selenion, boride of. A yellow-grey solid is formed by strongly heating amorphous B in a stream of H_2Se; the solid is decomposed by water with rapid evolution of H_2Se (Sabatier, *C. R.* 112, 865). As S. gives the formula B_2S_3 to the boron sulphide formed by passing H_2S over B, it is probable that the Se compound has the composition B_2Se_3.

Selenion, bromides of. Two compounds of Se and Br are known, Se_2Br_2 and $SeBr_4$; both are formed by the direct union of the elements. Both are decomposed by heat, but they are more stable towards heat than the corresponding S compounds (Evans a. Ramsay, *C. J.* 45, 62). As the V.D. of neither has been determined, the formulæ are not necessarily molecular; but from the analogy of Se_2Cl_2 and $SeCl_4$, which formulæ represent the compositions of gaseous molecules of these chlorides, it is probable that the mol. wts. of the bromides correspond with the formulæ Se_2Br_2 and $SeBr_4$.

SELENIOUS BROMIDE Se_2Br_2. (*Selenion monobromide.*) Formula probably molecular, from analogy of Se_2Cl_2. To 15·9 parts powdered Se covered with three times its weight of dry CS_2, 16 parts Br are gradually added; after a time the CS_2 is distilled off; and Se_2Br_2 remains as a thin oily liquid, having a dark reddish-brown

colour (appearing black in a thickish layer), and an unpleasant smell resembling that of S_2Cl_2 (Serullas, *A. Ch.* [2] 35, 349; Schneider, *P.* 128, 327). A thin layer of Se_2Br_2 transmits rose-red light; the absorption spectrum has been examined by Gernez (*C. R.* 74, 1190). S.G. of Se_2Br_2 = 3·604 at 15°. Br is given off on heating, then a little $SeBr_4$, and at 225°–230° most of the Se_2Br_2 distils over, and finally some Se is obtained (Schneider, *l.c.*). Se_2Br_2 dissolves in all proportions in CS_2, less easily in $CHCl_3$, EtBr, and EtI. It sinks in *water*, and then decomposes to H_2SeO_3Aq, HBrAq, and Se. *Absolute alcohol* forms $SeBr_4$ (which remains dissolved) and Se. Se_2Br_2 dissolves Se (c. 22 p.c.), on adding CS_2 the Se separates. Br is absorbed by Se_2Br_2, with formation of $SeBr_4$. A solution of Se_2Br_2 in CS_2 shaken with dry AgCN forms a little Se cyanide (Schneider, *P.* 129, 634).

SELENIC BROMIDE $SeBr_4$. (*Selenion tetrabromide.*) Formula probably molecular, from analogy of $SeCl_4$. To a solution of 1 part Se_2Br_2 in CS_2 1¼ parts Br are gradually added, the $SeBr_4$ which separates is allowed to stand in contact with the CS_2 for some days, whereby it becomes crystalline, and the CS_2 is distilled off; the compound obstinately retains some CS_2. By heating to 75°–80° Br is given off, and the $SeBr_4$, containing Se_2Br_2, sublimes in black, lustrous, six-sided leaflets, mixed with a little pure $SeBr_4$ in dark-orange crystals, and Se_2Br_2 remains (Schneider, *P.* 129, 450). $SeBr_4$ is also obtained by dissolving 1 part powdered Se in 10–12 parts Br, pressing the crystalline mass between filter-paper, and removing excess of Br by gently warming. $SeBr_4$ dissolves in CS_2, $CHCl_3$, and EtBr; it dissolves with decomposition in alcohol, also in HClAq. $SeBr_4$ is very hygroscopic; in moist air it gives Br and Se_2Br_2; in much water it forms H_2SeO_4Aq and HBrAq. Combines with SO_3 to form $SeCl_4.SO_3$ (*v.* SELENION THIO-OXYCHLORIDE, p. 441). Forms compounds with KBr and NH_4Br, K_2SeBr_6 and $(NH_4)_2SeBr_6$ (*v.* Muthmann a. Schäfer, *B.* 26, 1008).

Selenion, bromochlorides of. Two compounds of Se, Br, and Cl were obtained by Evans and Ramsay (*C. J.* 45, 68) by the interactions of Se_2Cl_2 and Br, and Se_2Br_2 and Cl. The bromochlorides thus formed are $SeBrCl_3$ and $SeBr_3Cl$.

SELENION TRIBROMOCHLORIDE $SeBr_3Cl$. Orange, hygroscopic crystals formed by adding 2·1 parts Br, in CS_2, to 1 part Se_2Cl_2, crystallising from CS_2, and gently warming in a current of air to remove adhering CS_2 ($Se_2Cl_2 + 3Br_2 = 2SeBr_3Cl$). Decomposes when heated, giving off Br; as V.D. at 200° was c. half that calculated for $SeBr_3Cl$, dissociation is probably complete at that temperature.

SELENION BROMOTRICHLORIDE $SeBrCl_3$. Mol. w. 264·66. V.D. at 179° and 754 mm. pressure = 131·5; dissociation begins at c. 190°–200°. Yellow-brown crystals; obtained by passing Cl into Se_2Br_2 in CS_2, washing the pp. with CS_2, and drying in a current of warm air. Gives off Br when heated above c. 190°, and yields sublimate of $SeBr_4$.

Selenion, carbide of, *v.* CARBON SELENIDE, vol. i. p. 693.

Selenion, chlorides of. Two chlorides are formed by passing Cl over heated Se; using an excess of Se the product is Se_2Cl_2, and with an excess of Cl the product is $SeCl_4$. Attempts to form $SeCl_2$, corresponding with SCl_2, have been unsuccessful.

SELENIOUS CHLORIDE Se_2Cl_2. (*Selenion monochloride. Selenion selenochloride.*) Mol. w. 228·34. V.D. 110 at 200°–250° (Evans a. Ramsay, *C. J.* 45, 62; Chabrié, *Bl.* [3] 2, 803). S.G. 2·906 at 17·5° (Divers a. Shimosé, *C. J.* 45, 198). Boiling begins at c. 145°, but no definite b.p. can be given (E. a. R., *l.c.*). H.F. $[Se^2,Cl^2]$ = 22,150 (*Th.* 2, 405).

Formation.—1. By passing Cl over excess of heated Se.—2. By heating $SeCl_4$ with Se at 100° (Berzelius, *P.* 9, 225).—3. By passing HCl into a solution of Se in fuming H_2SO_4 (Divers a. Shimosé, *C. J.* 45, 194, 198).

Preparation.—HCl gas is passed into a solution of Se in fuming H_2SO_4 till a deep-red liquid is deposited and the mother-liquor is yellowish-brown; the mother-liquor is then poured off, the red liquid is dissolved in fresh fuming H_2SO_4 and HCl is passed in; this process is repeated again; finally, the red liquid is digested, in a closed vessel, with dry KCl (to remove H_2SO_4) and decanted (D. a. S., *l.c.*). The reactions are probably (1) $2SeSO_3 + 2HCl = SeSO_3.SeCl_2 + H_2SO_3$; (2) $SeSO_3.SeCl_2 + HCl = Se_2Cl_2 + SO_2.Cl.OH$ (D. a. S.).

Properties, Reactions, and Combinations.—Se_2Cl_2 is a heavy, deep-red liquid, smelling something like S_2Cl_2; S.G. 2·906 at 17·5°; somewhat volatile at ordinary temperatures, giving off orange-coloured vapour at 100°, beginning to boil at c. 145°, but exhibiting no fixed b.p. (E. a. R., *l.c.*). V.D. determined at c. 200° gave results agreeing with Se_2Cl_2. For absorption spectrum of vapour *v.* Gernez, *C. R.* 74, 1190. Se_2Cl_2 is easily sol. CS_2, $CHCl_3$, C_6H_6, and CCl_4. It is slowly decomposed by H_2O, EtOH, and Et_2O; a solution in CS_2 shaken with water gives H_2SeO_3Aq, HClAq, and Se. Warm Se_2Cl_2 dissolves Se freely; on cooling the Se is partly ppd. in the metal-like form (Rathke, *A.* 152, 181). Se_2Cl_2 is decomposed by shaking with Hg or Ag (D. a. S., *l.c.*); with P it gives PCl_3 and Se (Baudrimont, *A. Ch.* [4] 2, 5). Se_2Cl_2 combines with PCl_5 to form a yellow substance (B., *l.c.*).

SELENIC CHLORIDE $SeCl_4$. (*Selenion tetrachloride.*) Mol. w. 220·28. V.D. at 180° = 110 (Evans a. Ramsay, *C. J.* 45, 65). H.F. $[Se,Cl^4]$ = 46,160 (*Th.* 2, 405).

Formation.—1. By heating Se, or Se_2Cl_2, in excess of Cl.—2. By heating SeO_2 with PCl_5 (*v. Preparation*).—3. By the action of $SOCl_2$ on $SeOCl_2$.

Preparation.—To 13 parts PCl_5 in a long-necked flask 7 parts SeO_2 are added little by little, the reaction being allowed to cease after each addition before more SeO_2 is added ($SeO_2 + PCl_5 = SeOCl_2 + POCl_3$); the mass becomes liquid and then suddenly solidifies ($3SeOCl_2 + 2POCl_3 = 3SeCl_4 + P_2O_5$); excess of $POCl_3$ is now removed by heating the flask while a rapid stream of dry CO_2 is passed through it; a wide tube is then fitted by a cork into the neck of the flask, and the flask is placed in a tray containing hot sand (if the flask is allowed to cool the condensing P_2O_5 may cause it to crack) (Michaelis, *J. Z.* 6, 79).

Properties, Reactions, and Combinations. A slightly yellow crystalline solid; volatilises when heated, without melting, in yellow vapours. Evans a. Ramsay (*C. J.* 45, 65) found V.D. at 180° to be 110, agreeing with the formula $SeCl_4$; dissociation to Se_2Cl_2 and Cl began at c. 210°, and at 350° c. 66 p.c. was decomposed. Clausnizer (*B.* 11, 2007) got the value 57 for V.D. at 218°, at which temperature E. a. R.'s value was c. 86; at 368° Chabrié (*Bl.* [3] 2, 803) obtained the number 57, which agrees fairly with the results of E. a. R. $SeCl_4$ is nearly insol. CS_2. In moist air $SeOCl_2$ and HCl are produced (Weber, *P.* 108, 615); water forms H_2SeO_3Aq and HClAq. H_2S produces HCl and Se sulphide; SO_2 has no action. NH_3Aq produces Se, N, and H at ordinary temperatures, and N selenide at a low temperature (Verneuil, *Bl.* [2] 38, 548). Dry NH_3 combines with $SeCl_4$ at −20°, forming a very unstable compound, probably $SeCl_4.4NH_3$ (V., *l.c.*). With PCl_5 the compound $SeCl_4.2PCl_5$ is formed (Baudrimont, *A. Ch.* [4] 2, 5).

Selenion, chlorobromides of, *v.* Selenion bromochlorides, p. 439.

Selenion, cyanide of; *v.* Cyanogen selenide, vol. ii. p. 358.

Selenion, fluoride of. No definite compound of Se and F has been isolated. According to Knox (*Pr. Irish Acad.* 1841. 299) a fluoride of Se sublimes when Se vapour is passed over molten PbF_2.

Selenion, haloid compounds of. Se combines with the halogens to form two types of compounds, Se_2X_2 and SeX_4 (the fluorides have not been examined); the formulæ are probably molecular, as the V.D.s of Se_2Cl_2 and $SeCl_4$ have been determined. The compounds Se_2X_2, where X = Cl or Br, are liquids at ordinary temperatures; the other compounds are solids. All the compounds are fairly easily decomposed by heat, but less easily than the corresponding S haloid compounds.

Selenion, hydride of; *v.* Hydrogen selenide, vol. ii. p. 724.

Selenion, hydroxides of. The hydroxides of Se, $SeO(OH)_2$, and $SeO_2(OH)_2$ are acids; *v.* Selenious acid, p. 445, and Selenic acid, p. 435.

Selenion, iodides of. Two compounds of Se and I are known, Se_2I_2 and SeI_4, corresponding with the bromides and chlorides.

Selenious iodide Se_2I_2. (*Selenion mono-iodide.*) Formula probably molecular, from analogy of Se_2Cl_2. Formed by heating the elements together in the ratio Se:I(1:1·61); also by heating Se_2Br_2 and EtI at 100° in a sealed tube (Schneider, *P.* 129, 627). Crystalline, steel-grey, somewhat metal-like solid; melting to a dark-brown liquid at 68°–70°. Decomposed to Se and I by continued heating at 100°; also by solvents of I. Water forms H_2SeO_3Aq, HIAq, and Se.

Selenic iodide SeI_4. (*Selenion tetra-iodide.*) Formula probably molecular, from analogy of $SeCl_4$. Formed by heating together Se and I in the ratio Se:4I(1:6·44); also by mixing $SeBr_4$ and EtI in the ratio $SeBr_4$:4EtI, the SeI_4 separates after a little. Best prepared by adding HIAq to conc. H_2SeO_3Aq as long as a pp. is produced; the pp. is washed, pressed, and dried over H_2SO_4 (Schneider, *l.c.*). A dark-grey solid, melting at 75°–80° to a blackish-brown liquid. Gives up all I when heated to c. 100°, or treated with solvents of I; slowly decomposed by water. Attempts to form an *iodochloride of selenion* were unsuccessful (*v.* Evans a. Ramsay, *C. J.* 45, 70).

Selenion, nitride of; *v.* Nitrogen selenide, vol. iii. p. 570.

Selenion, oxides of. Only one oxide of Se has been isolated with certainty; this oxide is SeO_2. Berzelius thought that an oxide SeO was formed, along with SeO_2, by heating Se in air or O, by heating Se and SeO_2, and by the partial oxidation of Se sulphide by HNO_3. According to Chabrié (*A. Ch.* [6] 20, 202) Se takes up O approximately corresponding with that required to form SeO, when heated in air to 180°. Attempts to prepare SeO_3 have failed. By passing gaseous SeO_2 and O over hot spongy Pt, von Gerichten (*A.* 168, 214) obtained a white sublimate that dissolved in water with a hissing sound, forming H_2SeO_4, but Cameron a. Macallan (*Pr.* 46, 32) failed to confirm this result; C. a. M. (*l.c.*) did not get SeO_3 by passing O over hot Pt sponge mixed with Se, nor by the action of ozone on SeO_2, nor by heating selenate of Sb, Bi, Fe, Pb, Hg, or Ag. By heating dry H_2SeO_4 with P_2O_5 in a closed flask they got a trace of a crystalline solid, analyses of which pointed to the composition SeO_3. A solution of Se in H_2SeO_4 perhaps contains Se_2O_3 (*v.* Selenic acid, *Reactions*, No. 6, p. 436).

Selenion dioxide SeO_2. (*Selenious oxide, Selenious anhydride.*) Mol. w. not determined. S.G. 3·9538 at 15° (Cameron a. Macallan, *Pr.* 46, 27; Clausnizer, *A.* 196, 265). [Se,O^2] = 57,250 from amorphous Se; 55,820 from black crystalline Se; 56,200 from red crystalline Se (Petersen, *Z. P. C.* 8, 601). Melts at 340° in a sealed tube; at ordinary pressure volatilises without melting, slowly at 250°, rapidly at 280° (Chabrié, *A. Ch.* [6] 20, 202; C. a. M., *l.c.*). For absorption-spectrum of SeO_2 vapour *v.* Gernez (*C. R.* 74, 803).

Preparation.—1. Se is placed in the lower part of a V-tube with one limb longer than the other, and the longer limb drawn to a fine opening; the shorter limb is connected with a gasholder, from which a stream of dry O is passed into the V-tube; the tube is heated till the Se burns; the SeO_2 condenses in the longer limb of the tube.—2. Se is dissolved in conc. HNO_3Aq, the solution is evaporated to dryness, best in a retort (solidification occurs suddenly, with evolution of heat); the dry H_2SeO_3 is heated in the retort till sublimation begins, then let cool, and dissolved in water; the solution is ppd. by BaOAq; the solution, after filtering, is evaporated to dryness, and the residue is heated, when SeO_2 sublimes; traces of H_2SeO_4 and H_2SO_4 are thus removed, excess of BaO remains in the residue (Thomsen, *B.* 2, 598; *cf.* Wohlwill, *A.* 114, 176; Fischer, *P.* 67, 412).

Properties and Reactions.—Long, white, lustrous, four-sided needles (for m.p. &c. *v.* beginning of this article). 1. Slowly withdraws water from *moist air*, forming H_2SeO_3; dissolves in *water*, forming same acid, with disappearance of heat, $[SeO^2,Aq] = -920$ (*Th.* 2, 405).—2. Sl. sol. boiling *acetic anhydride*, crystallising unchanged; heated to 180°–200° oxidation of the Ac_2O occurs (to CO_2, &c.) and Se separates (Hinsberg, *A.* 260, 40).—3. Dissolves in *aqueous acetic acid*, H_2SeO_3 separating on cooling (H., *l.c.*).—4. Dissolves in *alcohol of* 96 *p.c.*, and is re-obtained on evaporation over H_2SO_4 (H., *l.c.*). 5. Reacts with *phosphoric chloride* to give $SeCl_4$, P_2O_5, and $POCl_3$; heated with *phosphoryl chloride* gives $SeOCl_2$ and P_2O_5 (Michaelis, *J. Z.* 6, 79).—6. Heated with *sodium chloride* yields $SeOCl_2$ and Na_2SeO_3 (Cameron a. Macallan, *Pr.* 46, 35).—7. Heated with *selenion tetrachloride* in a closed tube produces $SeOCl_2$; with $SeBr_4$ probably forms $SeOBr_2$ (Schneider, *P.* 129, 450). 8. Decomposed by dry *ammonia* to H_2O, Se, and N; when NH_3 is passed into SeO_2 in absolute alcohol, $SeO(NH_2).ONH_4$ is formed (*v.* SELENOSAMIC ACIDS, SALTS OF, p. 446).—9. Heated with dry HCN and Ac_2O, Se cyanide is probably formed (Hinsberg, *A.* 260, 40).—10. *Hydriodic acid* reduces SeO_2 to Se and H_2O, even at 10°.—11. SeO_2 and *sulphur dioxide* do not react at any temperature (Schulze, *J. pr.* [2] 32, 390).—12. The compounds K_2SeBr_6 and $(NH_4)_2SeBr_6$ are produced by dissolving SeO_2 in *hydrobromic acid and adding potassium or ammonium bromide* (*v.* Muthmann a. Schäfer, *B.* 26, 1008).

Combinations.—1. According to Ditte (*A. Ch.* [5] 10, 82), SeO_2 combines with dry *hydrogen chloride* to form two compounds, one of which, $SeO_2.2HCl$, is liquid, and the other, $SeO_2.4HCl$, is solid, at the ordinary temperature. With *hydrogen bromide* $SeO_2.4HBr$ is formed, and when this is kept very cold and HBr is passed over it, D. says that $SeO_2.5HBr$ is produced. *Hydrogen fluoride* is said also to combine with SeO_2, but the product has not been examined.—2. With *alkali halides* the compounds $MX.2SeO_2.2H_2O$ are formed (Muthmann a. Schäfer, *B.* 26, 1008).—3. Hinsberg (*A.* 260, 40) described a compound with *alcohol*, $SeO_2.C_2H_6O$, obtained by evaporating SeO_2 in absolute alcohol over $CaCl_2$.—4. Large white crystals of the compound $SeO_2.SO_3$ are obtained by warming SeO_2 and pure *sulphuric anhydride* to 100°, distilling off excess of SO_3 at 60°–70°, and allowing to cool. At 100° the compound gives up SO_3 (Weber, *B.* 19, 3185).

SELENION THIO-OXIDE $SeSO_3$. (*Selenion sulphoxide. Selenion-sulphur trioxide.*) Mol. w. not determined. Magnus (*P.* 10, 491) noticed that Se dissolved in fuming H_2SO_4 to produce a green solution; Weber (*P.* 156, 531) separated and analysed the green compound, and gave it the formula $SeSO_3$. Divers a. Shimosé (*C. J.* 45, 201) further examined this substance. Powdered Se is placed in liquid SO_3; heat is given off, and a dark-green liquid is formed; after a time the whole solidifies; after warming to 30°–40° for a few minutes the liquid part is drained off, and the adhering SO_3 is removed by the use of a Sprengel pump (for details *v.* D. a. S. on $TeSO_3$, *C. J.* 43, 324). $SeSO_3$ is a green solid, which may be heated to c. 35° without change; decomposition begins at c. 40°, and at c. 120° SO_2 and O are rapidly evolved and Se separates; by heating slowly *in vacuo* it changes to a yellow powder, which D. a. S. think to be a modification of the thio-oxide. $SeSO_3$ is sol. conc. H_2SO_4; on adding much water Se is ppd., and H_2SeO_3 and H_2SO_4 go into solution. HCl reacts with $SeSO_3$ in H_2SO_4 to form Se_2Cl_2 and $SO_2.Cl.OH$ (*v.* SELENIOUS CHLORIDE, *Preparation*, p. 439). Schulz-Sellack (*B.* 4, 113) observed that the vapours of SO_3 react with Se to form a yellow powder.

Selenion, oyacids of, and their salts. The oxyacids of Se are *selenious acid* H_2SeO_3 (*v.* p. 445) and *selenic acid* H_2SeO_4 (*v.* p. 435); salts of the *thioselenic acids* H_2SeSO_3 and $H_2SeS_2O_6$ have been isolated (*v.* p. 434); and salts of the *selenosamic acids* $SeO(NH_2).OH$ and $2SeO(NH_2).(OH)_2$ are known (*v.* p. 439).

Selenion, oxybromide of. By melting together SeO_2 and $SeBr_4$ Schneider (*P.* 129, 450) obtained needles which were probably $SeOBr_2$, corresponding with $SeOCl_2$ formed in a similar way.

Selenion, oxychlorides of. The oxychloride of Se, $SeOCl_2$, corresponds with sulphuryl chloride $SOCl_2$; an oxychloride containing Se and S, and corresponding with $S_2O_3Cl_4$, has also been isolated.

SELENYL CHLORIDE $SeOCl_2$. (*Selenion oxychloride.*) Mol. w. not determined.

Preparation.—1. Equivalent weights of $SeCl_4$ and SeO_2 are heated in a sealed tube to 150°, and the product is purified by repeated distillation (Weber, *P.* 118, 615).—2. SeO_2 and PCl_5 are brought together in the ratio $SeO_2:PCl_5$; $SeOCl_2$ and $POCl_3$ are produced, but the heat evolved suffices to cause a secondary reaction, which yields $SeCl_4$ and P_2O_5, so that very little $SeOCl_2$ can be obtained by this method (Michaelis, *J. Z.* 6, 79; *cf.* SELENIC CHLORIDE, *Preparation*, p. 439).—3. By distilling SeO_2 and NaCl in the ratio $SeO_2:NaCl$ (Cameron a. Macallan, *Pr.* 46, 35).

Properties.—A yellowish liquid, fuming in the air, boiling at 179·5°, and solidifying below 0° to colourless crystals, which melt at 10° (M., *l.c.*).

Reactions and Combinations (M., *l.c.*).—1. *Water* decomposes $SeOCl_2$, forming H_2SeO_3Aq and HClAq.—2. *Ammonia* produces SeO_2, Se, N, NH_4Cl.—3. *Sulphuryl chloride* produces $SeCl_4$ and SO_2.—4. *Phosphoryl chloride* forms $SeCl_4$ and P_2O_5 (*v. Preparation of selenic chloride*, p. 439).—5. With *phosphorous chloride* $POCl_3$, $SeCl_4$ and Se_2Cl_2 are produced.—6. $SeOCl_2$ combines with *stannic chloride* to form $3SeOCl_2.SnCl_4$; also with *titanic chloride* and *antimonic chloride* to form $2SeOCl_2.TiCl_4$ and $2SeOCl_2.SbCl_5$ (Weber, *P.* 125, 325).

SELENION, THIO-OXYCHLORIDE OF, $SeSO_3Cl_4$. (*Pyrothioselenyl chloride. Selenion sulphooxytetrachloride.*) Mol. w. not determined.

Formation.—1. By the interaction of SO_3 and $SeCl_4$ (H. Rose, *P.* 44, 315).—2. By dissolving $SeCl_4$ in Nordhausen sulphuric acid (Clausnizer, *B.* 11, 2007).—3. By heating SO_2Cl_2 and $SeOCl_2$ in a sealed tube to 170°–180° (C., *l.c.*).—4. By the interaction of $SO_2.OH.Cl$ and SeO_2, $SeOCl_2$, or $SeCl_4$ (C., *l.c.*).

Preparation.—$SeCl_4$ and $SO_2.OH.Cl$ are warmed together in the ratio $SeCl_4:2(SO_2.OH.Cl)$ till the $SeCl_4$ is quite dissolved:

$$SeCl_4 + SO_2.OH.Cl = SO_2.Cl.OSeCl_3 + Cl.$$

(Excess of $SO_2.OH.Cl$ is needed to hasten the reaction and to serve as a solvent.) The reddish solution solidifies on cooling; the white needles are separated by pressing between porous plates, and dried over H_2SO_4.

Properties and Reactions.—Small white needles; unchanged *in vacuo* or on gentle warming; deliquesces in moist air; melts at 165° and boils at 183°; V.D. at 209° = 48·5, calculated for $SeSO_3Cl_4 = 150$; dissociation has therefore occurred, perhaps thus: $2SeSO_3Cl_4 = 2SO_3 + Se_2Cl_2 + 3Cl_2$ (C., *l.c.*). Decomposed by *water*, at once, to H_2SO_4Aq, H_2SeO_3Aq, and HClAq.

Selenion, phosphides of; *v.* PHOSPHORUS SELENIDES, p. 144.

Selenion, sulphides of. The only compound of Se and S that has been isolated is SeS. Divers a. Shimidzu (*C. J.* 47, 446) say that this is the only compound of the two elements that exists, but Rathke (*B.* 18, 1534) considers that others exist, although none but SeS has been obtained in a state of purity. Se and S may be melted together in all proportions, but no compound is produced (Bettendorff a. von Rath, *P.* 139, 329; Rathke, *P.* 141, 590). Isomorphous mixtures of the two elements crystallise from solutions of Se and S in CS_2 (B. a. von R., *l.c.*). The pp. formed by passing H_2S into H_2SeO_3 contains Se and S in the ratio SeS_2, but it is a mixture of SeS with S (H. Rose, *P.* 107, 186; D. a. S., *l.c.*; Rathke, *B.* 18, 1534). The pp. containing Se and S in the ratio Se_2S obtained by passing H_2Se into H_2SO_3 is merely a mixture (D. a. S., *l.c.*).

SELENION MONOSULPHIDE SeS. Mol. w. not determined. Very dilute H_2SeO_3Aq, cooled to 0°–5°, is saturated with H_2S, which is first passed through a flask filled with pieces of ice; the yellow pp. which forms is washed, dried *in vacuo*, moistened with CS_2, and allowed to stand for some days till the mass becomes crystalline, the CS_2 withdrawing S; CS_2 is added to the crystals, after a few minutes the CS_2 is decanted, and the residue is washed with C_6H_6 and then with alcohol. SeS forms small, orange-yellow, lustrous tablets; S.G. 3·056 at 0°, 3·035 at 52°; S.H. ·1274. On heating it melts, gives off S vapour, and then vapour of S and Se. Sol. CS_2, but not crystallisable therefrom by evaporation; insol. water and ether (Ditte, *C. R.* 73, 625, 660).

Selenion, sulphoxide of; *v. Selenion thio-oxide*, under SELENION OXIDES, p. 441.

Selenion, sulphoxychloride of; *v. Selenion thio-oxychloride*, under SELENION OXYCHLORIDES, p. 441.

Selenion, thio-oxide of; *v.* SELENION OXIDES, p. 441.

Selenion, thio-oxychloride of; *v. Selenion oxychlorides*, p. 441. M. M. P. M.

SELENION, ORGANIC COMPOUNDS OF.

Methyl selenide or Selenion methide Me_2Se. Mol. w. 109. (58°). Formed by distilling a solution of barium methyl sulphate with K_2Se (Wöhler a. Dean, *A.* 97, 5) or of $KMeSO_4$ with Na_2Se (C. L. Jackson, *A.* 179, 1). Heavy oil with nasty smell. Burns with bluish flame. $PtCl_4$ forms $(Me_2Se)_2PtCl_4$, crystallising from alcohol in yellow plates. Conc. HNO_3 forms $(Me_2SeO)HNO_3$ [91°], whence HClAq produces Me_2SeCl_2 [60°], while HBrAq gives Me_2SeBr_2 [82°] and KIAq ppts. Me_2SeI_2.

Methylo-iodide Me_3SeI. *Tri-methyl-selenonium iodide.* Yields $(Me_3SeCl)_2PtCl_4$, crystallising from water in dark-red octahedra (Jackson, *B.* 7, 1277).

Di-methyl diselenide Me_2Se_2. Formed from $KMeSO_4$ and K_2Se_2 (W. a. D.; Rathke, *A.* 152, 211). Heavy reddish-yellow oil, with unpleasant odour, sol. HNO_3Aq.

Methane selinic acid $CH_3.SeO_2H$. [122°]. Formed by oxidising Me_2Se_2 with HNO_3 (W. a. D.). Deliquescent crystals, v. sol. alcohol. Gives with HCl crystalline CH_4SeO_2Cl.—AgA′: prisms.

Ethyl selenide Et_2Se. (108°). (Rathke; Pieverling, *A.* 185, 331). Oil, without unpleasant odour. HCl added to its solution in dilute HNO_3 ppts. Et_2SeCl_2, whence NH_3Aq forms $(Et_2Se)_2OCl_2$ (Joy, *A.* 86, 35).

Ethyl iodide Et_3SeI. Crystalline. Converted by moist Ag_2O into a strongly alkaline base which forms crystalline salts.—$(Et_3SeCl)_2ZnCl_2$ thin plates.—$(Et_3SeCl)_2PtCl_4$.

Di-ethyl diselenide Et_2Se_2. (186°). Liquid with disgusting odour. HCl added to its solution in dilute HNO_3 gives monoclinic crystals of $C_2H_6SeO_2Cl$.

Ethane selinic acid $Et.SO_2H$. Yields with HCl monoclinic crystals of $C_2H_6SeO_2Cl$.

Ethyl selenhydrate EtSeH. *Selenion-mercaptan.* Formed from KSeH and $Ca(EtSO_4)_2$ (Siemens, *A.* 61, 360). Heavy oil, boiling much below 100° and having an unpleasant odour. Reacts with HgO.

Ethyl selenite $SeO(OEt)_2$. (184°). S.G. $^{\underline{10}}$ 1·49. Formed from Ag_2SeO_3 and EtI, and got also by heating $SeOCl_2$ with NaOEt and dry ether at 180° (Michaelis, *A.* 241, 158). Thick liquid, miscible with water and alcohol. The *chloride* SeO(OEt)Cl [10°] (175°), formed from $SeOCl_2$ and alcohol, crystallises in needles.

Selenide of carbon CSe_2. Formed in small quantity by passing a mixture of CCl_4 and H_2Se through a red-hot tube (Rathke, *A.* 152, 199). Pungent yellow liquid. Converted by alcoholic potash into $EtO.CSe_2K$, crystallising in yellow needles, v. sol. water and alcohol.

Selenido-di-acetic acid $Se(CH_2.CO_2H)_2$. Formed from ammonium chloro-acetate and alcoholic $(NH_4)_2Se$ (Ulrich, *B.* 8, 773). Monoclinic tables.—×$(NH_4)_2A''$: insol. alcohol—×CuA″: bluish-green pp.

Amide.—Formed from $ClCH_2.CONH_2$ and alcoholic $(NH_4)_2Se$. Prisms, m. sol. cold water.

Di-phenyl selenide $SePh_2$. S.G. $^{\underline{20}}$ 1·450. V.D. 8·17 (calc. 8·09). Formed, together with selenophenol and $Se_2Ph_3.C_6H_4Cl$ (240°–250° *in vacuo*), from $SeCl_4$ and benzene in presence of $AlCl_3$ (Chabrié, *C. R.* 109, 183; *Bl.* [2] 50, 133; [3] 2, 788). Oil. Boils at 227° under a few cm. pressure. Bromine forms $Se(C_6H_4Br)_2$ [112°], crystallising from alcohol in colourless hexagonal plates. H_2O_2, in presence of HCl and a current of air, forms $Se(C_6H_4Cl).C_6H_4OH$ [145°] converted by HNO_3 into a crystalline product [188°].

Phenyl selenhydrate C_6H_5SeH. *Selenophenol.* [60°]. Formed from benzene, $SeCl_4$, and $AlCl_3$ (Chabrié, *C. R.* 109, 183; *Bl.* [3] 2, 788). Sol. alcohol, insol. water.

Tetra-methyl-di-amido-di-phenyl-selenide $Se(C_6H_4NMe_2)_2$. [124°]. Formed from $SeOCl_2$ and di-methyl-aniline in ether (Godchaux, *B.* 24, 765). Yellowish needles, m. sol. cold alcohol and ether.—$B''H_2SO_4$. [55°]. Colourless needles, v. e. sol. water.—$B''2C_6H_2(NO_2)_3OH$. [135°]. Yellow plates.

Tetra-ethyl-di-amido-di-phenyl-selenide $Se(C_6H_4NEt_2)_2$. [83°]. Formed from $SeOCl_2$ and $PhNEt_2$ in ether. Silky needles, v. e. sol. hot ether and alcohol.—$B''H_2Cl_2$. [73°].—$B''2C_6H_2(NO_2)_3OH$. [135°]. Yellow plates and needles.

Di-phenyl-selenone $SeOPh_2$. (230° at 65 mm.). S.G. $\frac{19\cdot6}{}$ 1·48. Formed, together with the compound $PhSeO(C_6H_4Cl)$ [94°], from $SeOCl_2$, benzene, and $AlCl_3$. Amber-yellow liquid. Not attacked by cold HNO_3. Bromine-water yields $SeO(C_6H_4Br)_2$ [120°]. H_2O_2, HCl, and a current of air form $SeO(C_6H_4Cl)_2$ [159°].

Phenyl seleno-carbimide Ph.NC.Se. Formed by shaking Na_2Se with the chloride of phenyl-carbamine, $PhNCCl_2$, and ether for a day, filtering, distilling with steam, and drying the oil *in vacuo* over H_2SO_4 (Stolte, *B.* 19, 2350). Pale yellowish-red oil, v. sol. alcohol and ether.

Phenyl-seleno-urea $NHPh.CSe.NH_2$. [182°]. Formed by passing NH_3 into Ph.NC.Se dissolved in ether, and also by the action of H_2Se on phenyl-cyanamide in benzene (Stolte, *B.* 19, 1579, 2350). Crystals (from alcohol).

Di-phenyl-seleno-urea $CSe(NHPh)_2$. [186°]. Formed from aniline and phenyl seleno-carbimide (Stolte, *B.* 19, 2351). Crystals (from alcohol), sl. sol. ether.

Selenaldine $C_6H_{13}NSe_2$. Formed by passing SeH_2 into an aqueous solution of aldehyde-ammonia in absence of air (Wöhler a. Liebig, *A.* 61, 11). Colourless crystals, with slight odour, sl. sol. water, v. sol. alcohol and ether. Its solutions are turned brown by air.

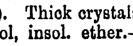
Amido-selenazole $C_3H_4N_2Se$ *i.e.*

$\left.\begin{matrix}\mathrm{Se\ .C(NH_2)}\\ \mathrm{CH{:}CH}\end{matrix}\right>\mathrm{N}$. *Selenazylamine.* [121°]. Formed by warming seleno-urea with di-chloro-di-ethyl oxide and aqueous NaOEt (G. Hofmann, *A.* 250, 308). White needles, v. sol. alcohol and ether, m. sol. benzene and water. Decomposed by prolonged boiling with water.—$B'_2H_2PtCl_6$: orange-red pp.

Acetyl derivative $C_3H_3AcN_2Se$. [c. 210°]. Needles.

Oxy-amido-selenazole

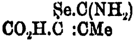
$\left.\begin{matrix}\mathrm{Se\ .C(NH_2)}\\ \mathrm{CH{:}C(OH)}\end{matrix}\right>\mathrm{N}$. *Seleno-hydantoïn.* [190°]. Formed by boiling seleno-urea with chloro-acetic acid and alcohol (G. Hofmann, *A.* 250, 312). Thick crystals, m. sol. hot water and alcohol, insol. ether.—B'HCl: needles.

Di-oxy-selenazole

$\left.\begin{matrix}\mathrm{Se\ .C(OH)}\\ \mathrm{CH{:}C(OH)}\end{matrix}\right>\mathrm{N}$. [147°]. Formed by boiling oxy-amido-selenazole with NaOHAq (Hofmann). Prisms, v. sol. alcohol, m. sol. water.

Amido-methyl-selenazole

$\left.\begin{matrix}\mathrm{Se\ .C(NH_2)}\\ \mathrm{CH{:}CMe}\end{matrix}\right>\mathrm{N}$. [80°]. Formed from seleno-urea and chloro-acetone (G. Hofmann, *A.* 250, 305). Needles, v. sol. alcohol and ether. Alkaline in reaction.—B'HCl: prisms (from water).—$B'_2H_2PtCl_6$: orange-red crystalline pp.

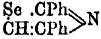
Acetyl derivative $C_4H_5AcN_2Se$. [122°]. Needles (from benzene), sl. sol. water.

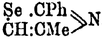
Amido-methyl-selenazole carboxylic acid

$\left.\begin{matrix}\mathrm{Se.C(NH_2)}\\ \mathrm{CO_2H.C\ {:}CMe}\end{matrix}\right>\mathrm{N}$. [195°]. Formed by heating seleno-urea with chloro-acetoacetic ether (G. Hofmann, *A.* 250, 309). Needles, m. sol. water, v. sol. alcohol and ether.—HA'HCl: plates, v. e. sol. water.

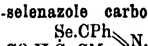
Acetyl derivative $C_5H_5AcN_2SeO_2$. [220°]. Needles, almost insol. hot water.

Amido-phenyl-selenazole $C_9H_8N_2Se$ *i.e.*

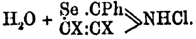
$\left.\begin{matrix}\mathrm{Se\ .C(NH_2)}\\ \mathrm{CH{:}CPh}\end{matrix}\right>\mathrm{N}$. [132°]. Formed from bromo-acetophenone and seleno-urea (G. Hofmann, *A.* 250, 307). Needles or prisms, insol. water, sol. alcohol and acids.—B'HBr: yellowish plates, sl. sol. cold water.

Di-phenyl-selenazole $C_{15}H_{11}NSe$ *i.e.*

$\left.\begin{matrix}\mathrm{Se\ .CPh}\\ \mathrm{CH{:}CPh}\end{matrix}\right>\mathrm{N}$. [99°]. Formed from ω-bromo-acetophenone and seleno-benzamide (G. Hofmann, *A.* 250, 317). Plates, v. sol. alcohol and ether. Its salts are decomposed by water.—$B'_2H_2PtCl_6$: pale-yellow pp.

Phenyl-methyl-selenazole $C_{10}H_9NSe$ *i.e.*

$\left.\begin{matrix}\mathrm{Se\ .CPh}\\ \mathrm{CH{:}CMe}\end{matrix}\right>\mathrm{N}$. (283°) at 737 mm. Formed from $PhCSe.NH_2$ [126°] and chloro-acetone (G. Hofmann, *A.* 250, 316). Yellow oil.—$B'_2H_2PtCl_6$: pale-yellow needles.

Phenyl-methyl-selenazole carboxylic acid $C_{11}H_9SeNO_2$ *i.e.*

$\left.\begin{matrix}\mathrm{Se.CPh}\\ \mathrm{CO_2H.C\ {:}CMe}\end{matrix}\right>\mathrm{N}$. [207°]. Formed by saponifying its ether, which is got from seleno-benzamide and chloro-acetoacetic ether (Hofmann, *A.* 250, 318). Small needles (from benzene), m. sol. alcohol.—AgA'.

Ethyl ether EtA'. [124°]. Plates.

Seleno-benzoic acid. *Amide* $C_6H_5.CSe.NH_2$. [126°] Formed by passing H_2Se into an alcoholic solution of benzonitrile made slightly alkaline with NH_3 (Dechend, *B.* 7, 1273; G. Hofmann, *A.* 250, 314). Golden needles (from water or ether). Reacts with α-chloro-ketones, forming selenazoles; *e.g.* X.CO.CHCl.X + CPh(SeH):NH = H_2O +

$\left.\begin{matrix}\mathrm{Se\ .CPh}\\ \mathrm{CX{:}CX}\end{matrix}\right>\mathrm{NHCl}$.

Seleno-benzoic aldehyde *v.* BENZYLIDENE SELENIDE.

Selenocyanic acid HSeCN. The K salt is got by fusing K_4FeCy_6 (3 pts.) with Se (1 pt.) (Crookes, *A.* 78, 177; *cf.* Berzelius, *S. J.* 31, 60). The free acid is obtained, in solution, by decomposing the lead salt by H_2S. It is decomposed by acids into Se and HCy. $FeCl_3$ does not give a red colour, but ppts. Se. Iodine added to a solution of KSeCN ppts. $KC_3N_3Se_4$. Air containing a little chlorine passed over a 10 p.c. solution of KSeCN forms a red crystalline pp. $KSe_4C_3N_3$ aq changing to yellow Se_3Cy_2, which separates from chloroform in yellow plates, and is decomposed by water into HCy, SeO_2, and Se, and yields *in vacuo* at 108° a crystalline sublimate of Se_2Cy_2, decomposed by hot water into HCy, SeO_2, and Se (Verneuil, *C. R.* 103, 144). Alcohol converts $KSe_4C_3N_3$ into Se and $KSe_2C_3N_3$, which forms brown crystals, sol. alcohol.

Salts.—KA'. Formed as above, and also by dissolving Se in aqueous KCy (Wöhler; Schiellerup, *A.* 109, 125; G. Hofmann, *A.* 250, 296). Very deliquescent needles, alkaline to litmus.—NH_4A' (Cameron a. Davy, *C. N.* 44, 68).—$KA'HgCl_2$: white pp.—$KA'HgBr_2$.—$KA'HgI_2$.—$KHg_2A'_3$: prisms.—$KHgA'_3$.—$Hg_2A'_2$: olive-green pp.—HgA'_2: felt-like mass of yellowish crystals.—AgA'_2HgCl_2.—PbA'_2: lemon-yellow needles (from water).—$K_2PtA'_6$. Dark-red scales (Clarke, *B.* 11, 1325).—AgA'. Satiny crystals, blackened by light. Converted by ICy into volatile crystalline $SeCy_2$ (Linnemann, *A.* 120, 36).

Methyl ether MeA'. (158°). Yellow oil (Stolte, *B.* 19, 1577).

Allyl ether C_3H_5A'. Oil.

Methylene ether $CH_2A'_2$. [132°]. Formed from MeI and alcoholic KSeCN (Proskauer, *B.* 7, 1281). Rhombohedra (from alcohol). HNO_3 forms $CH_2(SeO_3H)_2$.

Ethylene ether $C_2H_4A'_2$. [128°]. HNO_3 forms, on boiling, deliquescent $C_2H_4(SeO_3H)_2$, which yields BaA'', sol. hot water. KOH yields diethylene tetraselenide [131°].

Propylene ether $CH_3.CH(SeCN).CH_2(SeCN)$. [66°]. Formed by heating KSeCN with propylene bromide and alcohol (Hagelberg, *B.* 23, 1091). White crystals.

Trimethylene ether $CH_2(SeCN).CH_2.CH_2(SeCN)$. [51°]. Converted by KOH into trimethylene diselenide [55°].

Benzyl ether v. vol. i. p. 502.

Selenocyano-acetic acid $CH_2(SeCN).CO_2H$. [85°]. Formed from chloro-acetic acid and potassium selenocyanide (G. Hofmann, *A.* 250, 300). Yellowish needles (from ether and chloroform), v. e. sol. water and alcohol.—BaA'_2: amorphous.

Selenocyano-acetoacetic ether $CH_3.CO.CH(SeCN).CO_2Et$. Formed from chloro-acetoacetic ether and KSeCN (H.). Liquid.

Selenocyano-acetone $CH_3.CO.CH_2.SeCN$. Formed from chloro-acetone and KSeCN (H.). Yellowish oil. Gives an oily phenyl-hydrazide and an oxim. Not more sol. alkalis than water.

Selenocyano-acetophenone $C_6H_5.CO.CH_2SeCN$. [85°]. Formed by boiling ω bromo-acetophenone with alcohol and KSeCN (Hofmann). Crystalline.

Selenocyano-ethyl-phthalimide $C_8H_4O_2:N.CH_2.CH_2.SeCN$. [125°]. Formed by heating bromo-ethyl-phthalimide with KSeCy and alcohol (Coblenz, *B.* 24, 2133). Crystalline mass. Converted by boiling dilute caustic potash into $Se_2(C_2H_4.NH.CO.C_6H_4.CO_2H)_2$ [119°], which forms yellowish crystals and is converted by HCl at 180° into $Se_2(C_2H_4NH_2)_2$, which yields B''2HCl [188°] and $B''2C_6H_3N_3O_7$ [178°], both being crystalline.

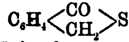
γ-Selenocyano-propyl-phthalimide $C_8H_4O_2:N.CH_2.CH_2.CH_2.SeCN$. [102°]. Formed by heating bromo-propyl-phthalimide with KSeCN and alcohol (Coblenz, *B.* 24, 2134). Converted by boiling dilute (10 p.c.) KOH into crystalline $Se_2(C_3H_6.NH.CO.C_6H_4.CO_2H)_2$ [84°], whence HCl at 180° forms $Se_2(C_3H_6NH_2)_2$, which yields B''2HCl [170°] and $B''2C_6H_3N_3O_7$ [165°].

ω-Selenocyano-o-toluic acid. *Nitrile* $CH_2(SeCN).C_6H_4.CN$. *o-Cyano-benzyl selenocyanide.* [121°]. Formed by warming the nitrile $CH_2Cl.C_6H_4.CN$ with KSeCN (Drory, *B.* 24, 2564). Long brownish needles (from alcohol) or prisms (from benzene). Converted by dilute H_2SO_4 into $Se_2(CH_2.C_6H_4.CN)_2$ [110°]. HClAq at 100° forms Se and *o*-cyano-benzyl chloride.

Selenocyanuric acid $H_3Se_3C_3N_3$. Formed from Cl_3Cy_3 and Na_2Se (Stolte, *B.* 19, 1578).

Methyl ether. [174°].

Seleno-phthalimidine $C_6H_4<\substack{C(NH)\\ CH_2}>Se$. Formed from $CH_2(SeCN).C_6H_4.CN$ and conc. H_2SO_4 (Drory, *B.* 24, 2566). Sol. alcohol.



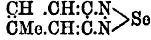
Reactions.—1. NaOH forms the compound $Se_2(CH_2.C_6H_4.CN)_2$, crystallising in needles [110°], sol. alcohol and CS_2, and converted by HCl at 160° into Se and phthalide.—2. When steam is blown through a mixture of selenophthalimidine, alcohol, and KOH there is formed selenophthalide $C_6H_4<\substack{CO\\ CH_2}>Se$, crystallising in broad plates [58°], insol. water, sol. alcohol.—3. Alcoholic potash and MeI form $CH_2(SeMe).C_6H_4.CN$ (180°-200°).

Salts.—B'HCl: needles, slightly sol. water and alcohol.—$B'_2H_2PtCl_6$. Orange powder.—$B'C_6H_3N_3O_7$.—B'HBr. [264°]. Needles: sl. sol. water.—$B'HI_2$ (?) [223°]. Formed by heating $CH_2(SeCy).C_6H_4.CN$ with HIAq at 100°. Dark-violet needles.—*Sulphate* [145°-150°].

Piaselenole $C_6H_4<\substack{N\\ N}>Se$. [76°]. Formed from *o*-phenylene-diamine and an aqueous solution of selenious acid (Hinsberg, *B.* 22, 2897). Needles, v. sol. alcohol and ether, sl. sol. water. Its salts are yellow and decomposed by much water with separation of the base. Iodine forms a green periodide.

Amido-piaselenole $C_6H_3(NH_2):N_2Se$. [150°]. Formed by adding H_2SeO_3 to a cool solution of tri-amido-benzene hydrochloride and NaOAc (Hinsberg, *B.* 22, 2898). Brownish-red needles, sl. sol. water, m. sol. alcohol. $SnCl_2$ separates Se.—B'HCl: reddish-brown needles, sl. sol.

Oxy-piaselenole. *Ethyl derivative* $C_6H_3(OEt):N_2Se$. [104°]. This is formed from $C_6H_3(OEt)(NH_2)_2$ and aqueous H_2SeO_3. Needles forming a yellowish-red solution in H_2SO_4.



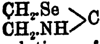
Methyl-piaselenole $\substack{CH\ .CH:C.N\\ CMe.CH:C.N}>Se$. [73°]. (267° uncor.). Formed from tolylene-diamine and aqueous SeO_2 at 80° (Hinsberg, *B.* 22, 863). Needles, sl. sol. cold water. $SnCl_2$ yields tolylene-*o*-diamine and Se. Does not react with nitrous acid or with Ac_2O.—$B'_2H_2PtCl_6$.

Chloro-methyl-piaselenole $C_6H_2ClMe:N_2Se$. [150°]. Formed by warming *o*-tolylene-diamine with SeO_2 and conc. HClAq (Hinsberg, *B.* 23, 1395). Small needles, volatile with steam.

Naphthopiaselenole $C_6H_4<\substack{CH:C.N\\ CH:C.N}>Se$. [129°]. Formed from (αβ)-naphthylene-diamine sulphate, aqueous NaOAc, and SeO_2 (Hinsberg, *B.* 22, 866). Needles, sl. sol. water, m. sol. alcohol, v. sol. ether. Conc. H_2SO_4 gives an intense yellow colour. $SnCl_2$ and HCl give Se and naphthylene-diamine.

Seleno-urea $CSe(NH_2)_2$. [c. 200°]. S. 11 at 19°. S. (alcohol) 3 at 18°. Formed by passing H_2Se into a 2 p.c. solution of cyanamide in ether (Verneuil, *C. R.* 99, 1154; 100, 1296; *Bl.* [2] 43, 58, 583). White needles, v. sol. hot water, sl. sol. alcohol and ether. Its solutions are decomposed by light, especially in presence of an alkali, with separation of selenium. In presence of air and HClAq it yields $(CSeN_2H_4)_3O2HCl$, which forms brown crystals with violet reflex, converted by baryta-water into Se, seleno-urea, and cyanamide. The compound $(CSeN_2H_4)_3O2HBr$ may be formed in like manner. When the 'oxy-triselenourea' hydrochloride is allowed to stand in the acid liquid in which it is formed, it changes into yellow crystalline $(CSeN_2H_4)_2Cl_2$. HIAq converts selenourea into $(CSeN_2H_4)_2I_2$. H_2SO_4 added to a saturated solution of selenourea forms scarlet crystals converted by heating with alcohol (100 pts.) and H_2SO_4 (4 pts.) at 50° into $(CSeN_2H_4)_2OH_2SO_4$, crystallising in pearly plates.

Ethylene-ψ-seleno-urea $C_3H_6N_2Se$ *i.e.*



$$\left.\begin{matrix} CH_2.Se \\ CH_2.NH \end{matrix}\right> C{:}NH$$

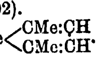
Formed by evaporating a solution of bromo-ethyl-amine hydrobromide (8 g.) with KSeCy (5 g.) to dryness on a water-bath (Baringer, *B.* 23, 1003). Unstable. Converted by bromine-water into ethylene-ψ-urea.—B'HBr. [170°]. Needles.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. [220°]. Needles.

Propylene-ψ-selenourea $C_4H_8N_2Se$. Obtained in like manner from β-bromo-propyl-amine.—$B'C_6H_3N_3O_7$. [110°].—$B'_2H_2PtCl_6$. Light-yellow plates.

Trimethylene-ψ-selenourea $C_4H_8N_2Se$. Formed from γ-bromo-propyl-amine and KSeCy.—B'HBr. [135°]. White crystals (from alcohol) soon turning red.—$B'C_6H_3N_3O_7$. [c. 53°]. Small concentric needles.

Seleno-isovaleric aldehyde $C_5H_{10}Se$. [57°]. Crystalline (Schröder, *B.* 4, 402).

Di-methyl-selenophene



$$Se\left<\begin{matrix} CMe{:}CH \\ CMe{:}CH \end{matrix}\right.$$

Selenoxene. (154° uncor.). Formed by heating acetonyl-acetone with phosphorus pentaselenide P_2Se_5 at 180°. Colourless mobile liquid of slight smell. With isatin and conc. H_2SO_4 it gives a carmine-red colouration. By Laubenheimer's reaction a reddish-brown colour is produced. Benzoyl-formic acid also produces a reddish-brown colouration (Paal, *B.* 18, 2255).

SELENIOUS ACID H_2SeO_3. Mol. w. not determined. This compound is the acid of the anhydride SeO_2.

Preparation.—Se is dissolved in hot conc. HNO_3Aq, the solution is evaporated to dryness, the residue is dissolved in water, BaOAq is added to ppt. traces of H_2SeO_4, the filtrate is evaporated to dryness in a retort, and the residue is heated till SeO_2 sublimes (Thomsen, *B.* 2, 598); the pure SeO_2 thus obtained is dissolved in c. $\frac{1}{5}$ its weight of hot water, on cooling large crystals of H_2SeO_3 separate (Weber, *P.* 118, 479). To prevent formation of H_2SeO_4 in the oxidation of Se, Divers a. Shimosé (*C. J.* 47, 439) recommend to dissolve Se in a large excess of conc. H_2SO_4 instead of using HNO_3.

Properties.—Large white crystals, resembling nitre; effloresces in air; withdraws water from moist air; S.G. 3·0066 at 15·7° (Clausnizer, *B.* 11, 2009). Poisonous. The acid crystallises unchanged from solution in aqueous acetic acid, or in aqueous C_6H_6 (Chabrié, *A. Ch.* [6] 20, 202). H.F. $[Se,O^2,Aq] = 56{,}160$ (*Th.* 2, 274). H_2SeO_3 is a dibasic acid; this is shown by the existence of two salts M^IHSeO_3 and $M^I_2SeO_3$ (*v.* Selenites), and also by the heat of neutralisation, which is given by Thomsen (*Th.* 1, 172) as follows: $[H^2SeO^3Aq, NaOHAq] = 14{,}770$, $[H^2SeO^3Aq\ 2NaOHAq] = 27{,}020$, $[H^2SeO^3Aq, 4NaOHAq, = 27{,}480$. As no derivative of H_2SeO_3 exists corresponding with $C_2H_5.SO_2.OH$, and as only one ethyl selenite $SeO(OEt)_2$ can be obtained, and as the compound SeO.Cl.OEt has been isolated, it appears that the acid is $SeO(OH)_2$ and not $SeO_2.OH.H$ (Michaelis a. Landmann, *B.* 13, 656; *A.* 241, 150).

Reactions.—1. *Heat* causes H_2SeO_3 to decompose to SeO_2 and H_2O.—2. Many *oxidisable bodies* remove O from H_2SeO_3. For instance, *sulphur dioxide* passed into H_2SeO_3Aq ppts. Se; the reduction is complete only when the compounds interact in the ratio $H_2SeO_3{:}2SO_2$ (Schulze, *J. pr.* [2] 32, 390); the presence of HCl hastens the reaction (*v.* Michaelis, *J. Z.* 6, 88; Rathke, *A.* 152, 194). When SO_2 and H_2SeO_3 interact in other proportions than $H_2SeO_3{:}2SO_2$, thioselenic acids are formed (*cf.* p. 435). *Hydrogen sulphide* ppts. Se and S in the ratio Se:2S (Divers a. Shimidzu, *C. J.* 47, 441). Various *metals*, such as Cu, Fe, Ag, or Zn, also reduce H_2SeO_3Aq in presence of HCl, with ppn. of Se. H_2SeO_3Aq is partly reduced by exposure to *air containing dust.* M. M. P. M.

SELENITES. Salts of selenious acid (H_2SeO_3), $M_2^ISeO_3$, and M^IHSeO_3. The alkali salts are formed by adding alkalis to H_2SeO_3Aq and evaporating; most of the other selenites are formed from the alkali salts by double decomposition.

Selenites give selenides, or metallic oxide and Se, when heated with charcoal. Heated with NH_4Cl, out of air, they give a sublimate of Se. Most selenites, except those of the alkalis, are insol. in water.

Many selenites combine with SeO_2 to form acid salts; many basic selenites are also known.

Boulzoureano (*Bl.* [2] 48, 209) found that many selenites can be obtained in well-formed crystals by adding Na_2SeO_3Aq to solutions of metallic salts, and heating the pp. so formed with very dilute H_2SeO_3Aq in sealed tubes at 200°; also by dissolving metallic carbonates in dilute H_2SeO_3Aq, adding water, and heating in sealed tubes at 200°. The older investigations of selenites were by Berzelius (*v. Lehrbuch*) and Muspratt (*C. J.* 2, 52). Boulzoureano (*l.c.*; also *A. Ch.* [6] 18, 289) has made a more thorough investigation of these salts. Nilson (*Bl.* [2] 21, 253; 23, 260, 353, 494) has also prepared and described many selenites.

It has been thought sufficient to give the names of the metals selenites of which have been analysed. Abstracts of B.'s papers will be found in *C. J.* 54, 220; 60, 262; and an abstract of Nilson's paper will be found in the *3rd Supp.* of the first edition of this Dictionary, p. 1786.—Al, Am, Sb, Ba, Be, Bi, Cd, Ca, Ce, Cr, Co, Cu, Di, In, Fe, La, Pb, Li, Mg, Mn, Hg (*cf.* Cameron a. Davy, *Trans. I.* 28, 146), Ni, K, Ag, Na, Sr, Tl, Th, U, Zn. M. M. P. M.

SELENO-ANTIMONATES *v.* Antimonates, vol. i. p. 286.

SELENOCYANHYDRIC ACID *v.* vol. ii. p. 348.

SELENOCYANIDES *v.* vol. ii. p. 348.

SELENOMETAHYPOPHOSPHITES R^IPSe and $R^{II}(PSe)_2$ *v.* Diphosphorus selenide, this vol. p. 145.

SELENOPYROPHOSPHATES $R_4{}^{I}P_2Se_7$ and $R_2{}^{II}P_2Se_7$ *v.* Phosphoric selenide, p. 145.

SELENOPYROPHOSPHITES $R_4{}^{I}P_2Se_5$ and $R_2{}^{II}P_2Se_5$ *v.* Phosphorous selenide, p. 145.

SELENOSAMIC ACIDS, SALTS OF. Selenosamic acid $SeO(NH_2)OH$ has not been isolated, but the NH_4 salt of this acid, and also the NH_4 salt of diselenosamic acid, $2SeO(NH_2).(OH)_2$, have been obtained.

Ammonium selenosamate $SeO(NH_2)ONH_4$ is formed by the action of dry NH_3 on SeO_2 dissolved in alcohol. It is a white, crystalline, deliquescent salt; very unstable, easily giving off NH_3 and forming diselenosamate. Water partially converts this salt into $(NH_4)_2SeO_3$.

Ammonium diselenosamate $2SeO(NH_2).OH.ONH_4$ is formed by boiling an alcoholic solution of the selenosamate, or by letting the solution stand over H_2SO_4 *in vacuo.* It crystallises from alcohol in large, deliquescent prisms (*v.* Cameron a. Macallan, *Pr.* 44, 112).

M. M. P. M.

SELENOTHIO-OXIDE $SeSO_3$ *v. Selenion thio-oxide*, under Selenion oxides, p. 441.

SELENOTHIO-OXYCHLORIDE $SeSO_3Cl_4$ *v.* Selenion thio-oxychloride, p. 441.

SELENOTHIOSULPHATES M_2SeSO_3 *v. Thioselenates*, under Selenates, p. 434.

SELENOTRITHIONATES $M_2SeS_2O_6$ *v. Dithiotriselenates*, under Selenates, p. 434.

SELENOTRITHIONIC ACID $H_2SeS_2O_6$ *v. Dithiotriselenic acid*, under Selenates, p. 435.

SELENYL BROMIDE and **CHLORIDE** *v.* Selenion oxybromide and Oxychloride, p. 441.

SEMINOSE *v.* Mannose.

SENEGIN *v.* Saponin.

SENNA *v.* Cathartic acid.

SENNITE is identical with **Pinite**, the methyl ether of dextrorotatory inosite.

SEPTYL. A name for Heptyl.

SEQUOIENE $C_{13}H_{10}$. [105°]. (290°–300°). V.D. 5·66 (obs.). Occurs, together with $C_{10}H_{16}$ (155°), S.G. $\underline{^{15}}$ ·852, $[\alpha]_D = 24°$, and oily $C_{18}H_{20}O_3$ (229°), in the leaves of *Sequoia gigantea* (Lunge a. Steinkauler, *B.* 13, 1656). White plates with characteristic smell, volatile with steam; sol. alcohol, ether, benzene, and chloroform.

SERICIC ACID $C_{15}H_{30}N_4O_7$. Formed by the action of conc. baryta-water on silk (Champion, *C. R.* 72, 330). Deliquescent, translucent mass. —BaA$'_2$.—PbA$'_2$: pp.

SERIN $C_3H_7NO_3$. *a-Amido-hydracrylic acid?* S. 3 at 10°; 5 at 20°. Formed by boiling silk with dilute H_2SO_4 (Crämer, *J. pr.* 96, 76; Baumann, *B.* 15, 1735; Melikoff, *C. C.* 1881, 354). Monoclinic crystals, insol. alcohol and ether. Converted by nitrous acid into glyceric acid.—CuA$'_2$.—HA'HCl: needles, v. e. sol. water.—HA'HNO_3: minute needles.

SERINE *v.* Proteïds.

SERUM ALBUMEN *v.* Proteïds.

SERUM CASEÏN *v.* Proteïds.

SERUM GLOBULIN *v.* Proteïds.

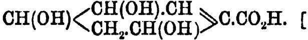
SESAME OIL. S.G. $\frac{20}{4}$ ·9191. $\mu_D = 1·474$ at 20° (Long, *Am.* 10, 392). A fatty oil obtained from the seeds of *Sesamum orientale.* It contains glycerides of oleïc and linoleïc acids (Pohl, *J. pr.* 63, 400; Hazura a. Grüssner, *M.* 10, 247). Gives a raspberry-red colour on warming with HClAq and cane-sugar (Zipperer, *Chem. Zeit.* 11, 1600). The oil contains ·05 p.c. of sesamin $C_{18}H_{18}O_5$ [118]. S. (alcohol) ·27 at 20°; 8·07 at 78°. S.G. 1·305. H_2SO_4 containing HNO_3 colours sesamin green and afterwards bright red (Tocher, *Ph.* [3] 23, 700).

SEXTYL. Another name for Hexyl.

SHEA BUTTER, obtained in West Africa from the nuts of *Bassia Parkii*, contains oleïn and stearin (Oudemans, *J. pr.* 89, 205).

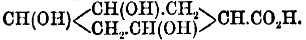
SHELLAC *v.* Lac.

SHIKIMIC ACID $C_7H_{10}O_5$ *i.e.*



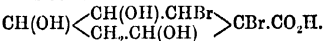
$\mathrm{CH(OH)}\!<\!\begin{array}{l}\mathrm{CH(OH).CH}\\ \mathrm{CH_2.CH(OH)}\end{array}\!\gg\!\mathrm{C.CO_2H}$. [184°]. S.G. $\underline{^{14}}$ 1·599. $\mu_{\infty} = 1·303$ at 14°. $[\alpha]_D = -186°$ in a 7 p.c. solution. S. (ether) ·015 at 23°; S. (alcohol) 2·25. Occurs in the fruit of *Illicium religiosum* (Japanese, shikimi) and Chinese star-anise (Eykman, *R. T. C.* 4, 49; 5, 299; *B.* 24, 1278). Crystalline powder composed of minute needles, sl. sol. alcohol and $CHCl_3$, nearly insol. ether. Lævorotatory. Yields *p*-oxy-benzoic acid when heated with HClAq.—NH_4A': crystals.

Dihydride



$\mathrm{CH(OH)}\!<\!\begin{array}{l}\mathrm{CH(OH).CH_2}\\ \mathrm{CH_2.CH(OH)}\end{array}\!>\!\mathrm{CH.CO_2H}$. [175°]. S.G. $\underline{^{2}}$ 1·47. $\mu_{\infty} = 1·324$ at 19°. $[\alpha]_D = -18°$. S. 14 in the cold. Formed by reducing the acid with sodium-amalgam in presence of HClAq. Monoclinic crystals. Converted by HCl into benzoic acid.

Dibromide



$\mathrm{CH(OH)}\!<\!\begin{array}{l}\mathrm{CH(OH).CHBr}\\ \mathrm{CH_2.CH(OH)}\end{array}\!>\!\mathrm{CBr.CO_2H}$. [c. 188°] $\mu_{\infty} = 1·295$. $[\alpha]_D = -58°$. Formed by adding Br to a cold solution of the acid. Tetrahedra. Converted by moist Ag_2O into $C_7H_9BrO_5$ [235°], S. 6·3 at 17°, $[\alpha]_D = +22°$, crystallising in hexagonal needles, sl. sol. ether, converted by baryta into oxyshikimic acid [156°].

SHIKIMIPICRIN $C_7H_{10}O_3$ (?). [200°]. S. 6·2 in the cold. Occurs in the fruit of *Illicium religiosum* (Eykman, *R. T. C.* 4, 53). Large crystals, m. sol. alcohol, sl. sol. ether.

SHIKIMOLE *v.* Safrole.

SIEGBURGITE. A fossil resin found near Siegburg. It contains styracin, metastyrene, and some free cinnamic acid (Klinger a. Pitschke, *B.* 17, 2742).

SIKIMINE. [175°]. A poisonous substance in the seeds of *Illicium religiosum* (Eykman, *Ph.* [3] 11, 1046). Prisms, sl. sol. water, ether, and $CHCl_3$, v. sol. alcohol and HOAc.

SILICA SiO_2. (*Silicon dioxide. Silicic anhydride.*) Mol. w. not known. S.G. *quartz* 2·647 to 2·652, *tridymite* 2·282 to 2·326, *amorphous* 2·20 at 15·6° (Schaffgotsch, *P.* 68, 147). S.H. *quartz* ·1737 at ord. temp., ·305 at c. 400°, constant from 400° to over 1000° (Pionchon, *C. R.* 106, 1344). H.F. $[\mathrm{Si,O^2}] = 219,240$ from amorphous Si; 211,120 from crystalline Si (Troost a. Hautefeuille, *C. R.* 70, 252).

Occurrence.—Compounds of SiO_2 are very widely distributed in large quantities; *quartz*, *flint*, *chalcedony*, *jasper*, *opal*, &c., are nearly pure SiO_2. Silica is the chief constituent of *sandstones*; *felspar*, *agate*, and a vast number of other minerals contain silica. Silica (or silicates) is also found in many plants.

Preparation.—(i) Amorphous silica.—1. Quartz is finely powdered, best by heating to redness and plunging into cold water, and heated with c. 6 times its weight of Na_2CO_3 in a Pt crucible till the whole fuses quietly; the cold mass is treated with water, the solution, when clear, is poured slowly into excess of fairly conc. HClAq, the liquid (after filtration, if necessary) is evaporated to dryness in a Pt dish, the residue is moistened with conc. HClAq, warmed, and allowed to stand for an hour or two; this treatment with acid is repeated two or three times; water is then added and, after warming and standing, the solution is filtered off, the residual SiO_2 is washed with hot water, dried, and heated to redness.—2. SiF_4 (*v.* p. 459) is passed into water, the gelatinous SiO_2 which is ppd. is pressed between linen, thoroughly washed, dried, and heated to redness.

(ii.) Crystalline silica.—1. Moist ppd. SiO_2—*e.g.* the pp. got by passing SiF_4 into water—is dissolved in boiling NaOHAq, and the solution is heated in a sealed tube; crystals of *tridymite* (*v. infra, Properties*) separate below 180°, and crystals of *quartz* separate above 180° (Maschke, *P.* 145, 549).—2. Small tubes of hard glass are half-filled with solutions of dialysed silicic acid (*v.* Silica, hydrates of, *infra*) containing c. 10 p.c. SiO_2, closed by fusion, and heated to 250° for some months; small crystals of *quartz* are thus obtained (Kroustchoff, *C. R.* 104, 602).—3. Any hydrate of SiO_2 yields crystalline silica by heating in a forge-fire (Fremy, *A. Ch.* [3] 38, 327).—4. Crystalline SiO_2 is formed by fusing silicates with microcosmic salt (G. Rose, *J. pr.* 101, 228), or with borax (G. Rose, *B.* 2, 388). For other methods of preparing crystalline silica *v.* Rammelsberg (*B.* 5, 1006), Hautefeuille (*C. R.* 86, 1133; 90, 830), Sénarmont (*A. Ch.* 42, 129), Friedel a. Sarasin (*Bl.* [2] 31, 481), and Daubrée (*Ann. M.* [5] 12, 297).

Properties.—The mol. w. of silica is unknown, but there is reason to think it is a considerable multiple of that indicated by the formula SiO_2. By applying the cryoscopic method to an aqueous solution of colloidal silicic acid (*v.* Metasilicic acid, *infra*) Sabanéeff (*J. R.* 21, 515; Abstract in *C. J.* 58, 1215) obtained numbers pointing to silica being a very high polymeride of SiO_2. The great infusibility and non-volatility of silica, especially when this compound is compared with CO_2, make it probable that the molecular formula of silica is $nSiO_2$, where *n* has a large value (*v.* Mendeléeff's *Principles of Chemistry*, vol. ii. p. 93).

Crystalline silica. SiO_2 crystallises as *quartz* in colourless, transparent, hexagonal, six-sided prisms having the axes-ratio 1:1·0999 (S.G. c. 2·65), and as *tridymite* in hexagonal forms with the axes-ratio 1:1·631 (S.G. c. 2·3). Crystalline SiO_2 is insol. or almost insol. in alkali solutions; it is attacked by HFAq slowly and without notable rise in temperature.

Amorphous silica is a white, loose, tasteless powder; S.G. 2·2. It dissolves in hot alkali solutions; after continued heating to a high temperature it is less sol. or nearly insol., owing to change into the crystalline form. Dissolves in HFAq, with intumescence and considerable rise of temperature.

Silica is fusible in the O-H flame to a colourless glass; when fused it may be drawn into extremely fine threads. Cramer (*Zeit. für angewand. Chem.*) finds that quartz is volatile at a temperature whereat Pt boils (*v. Abstract* in *C. J.* 64, ii. 164). SiO_2 is insol. in acids, except in HFAq. It is slightly volatilised in steam (*v.* Jeffreys, *A.* 39, 255). Silica is insoluble in molten microcosmic salt ($NaNH_4HPO_4$).

Reactions.—1. Fused with *alkalis*, alkali silicates are formed; with *alkali carbonates* CO_2 is evolved.—2. Decomposes most solid *salts* by fusion with them with formation of silicates (*cf.* Silicates, p. 448). According to Mills a. Meanwell (*C. J.* 39, 533) SiO_2 does not react with *pure* Na_2SO_4 or K_2SO_4 even at a very high temperature.—3. SiO_2 is decomposed by *potassium* at a red heat, forming K silicate and silicide; it is also reduced at red heat by *calcium*, *strontium*, and *magnesium* (Bunsen a. Matthiessen, *A.* 94, 111; Phipson, *Pr.* 13, 217; Parkinson, *C. J.* [2] 5, 128; Winkler, *B.* 23, 2642).—4. Heated with *carbon and certain metals*, SiO_2 is reduced, with formation of silicides of the metals; Ir, Pd, Pt, and Ru react in this way (Boussingault, *C. R.* 82, 591; *cf.* Warren, *C. N.* 60, 5). Au and Ag reduce SiO_2 only when strongly heated therewith in presence of Na_2SiF_6 and Na (W., *l.c.*).—5. Dry SiO_2 (prepared from SiF_4) which has not been strongly heated reacts with molten *metaphosphoric acid* to form $SiO_2.P_2O_5$ and $SiO_2.2P_2O_5.4H_2O$ (Hautefeuille a. Margottet, *C. R.* 96, 1052; 104, 56; *v.* Silicophosphoric oxides, p. 462).—6. Mixed with finely divided *carbon and heated in hydrogen sulphide*, SiS_2 is formed (*v.* Silicon sulphide, p. 462).—7. A mixture of SiO_2 and *carbon heated in chlorine or hydrogen chloride* gives $SiCl_4$ and CO (*v.* Silicon tetrachloride, p. 458); when *bromine* or *hydrogen bromide* is used, $SiBr_4$ is formed (*v.* Silicon tetrabromide, p. 457).—8. With *hydrogen fluoride*, SiF_4 is obtained (*v.* Silicon tetrafluoride, p. 459).—9. Heated to low redness in vapour of *boron trichloride*, $SiCl_4$ and B_2O_3 are formed (Troost a. Hautefeuille, *A. Ch.* [5] 7, 476).

SILICA, HYDRATES OF. (*Silicic acids.*) The hydrates of SiO_2 act as weak acids. The compositions of these hydrates are very uncertain. The silicates $nSiO_2.mRO$ are derivable from hydrates of SiO_2, some of which have been isolated while others are hypothetical (*v* Silicates, p. 448).

Metasilicic acid $H_2SiO_3 = SiO_2.H_2O$. (*Silica monohydrate.*) Obtained by the action of moist air on $Si(OEt)_4$; $Si(OEt)_4 + 3H_2O = SiO_2.H_2O + 4EtOH$ (Ebelmen, *J. pr.* 37, 359). Also by dialysing a mixture of Na silicate and excess of HClAq until the liquid in the dialyser is free from chlorides, concentrating by boiling in a flask, allowing to gelatinise, and drying the jelly-like mass over H_2SO_4 for two days (Graham, *T.* 1861. 183). $SiO_2.H_2O$ is described by Graham as a transparent, glassy, lustrous solid; insol. water.

Orthosilicic acid $H_4SiO_4 = SiO_2.2H_2O$. (*Silica dihydrate.*) This hydrate of SiO_2 has not been isolated with certainty; it is supposed to exist in the solution obtained by dialysing a solution of K or Na silicate with excess of HClAq; but as the compositions of the silicates of K and Na are very doubtful, the argument based on the supposition that these silicates are ortho- salts—and, therefore, will yield ortho- acid —is not very trustworthy. Various esters of the form $Si(OX)_4$ exist where X is Me, Et, &c. The solution of $SiO_2.xH_2O$, when x is supposed to = 2, obtained by dialysing K or Na silicate solution with excess of HClAq till the liquid in the dialyser is free from chlorides, is described by Graham (*l.c.*) as a clear liquid, which may be boiled in a flask till it contains c. 13 p.c. SiO_2 without separation of any solid. The liquid soon becomes opalescent on keeping, and after a time sets to a transparent, colourless jelly, which is insol. water, and, dried over H_2SO_4, gives $SiO_2.H_2O$ (*v.* METASILICIC ACID, p. 447). The solution of $SiO_2.xH_2O$ is coagulated by a minute trace of an alkali or alkaline earth carbonate, also by CO_2, but not by dil. H_2SO_4Aq, HNO_3Aq, or $H.C_2H_3O_2Aq$. The solution reddens litmus (*cf.* Doveri, *A.* 64, 256; Liebig, *A.* 94, 373; Karsten, *P.* 6, 357; Fuchs, *A.* 82, 119; Struckmann, *A.* 94, 341; Rose, *P.* 108, 20; Kühn, *J. pr.* 59, 1; Fremy, *A. Ch.* [3] 38, 314; Maschke, *J. pr.* 68, 234).

TRISILICIC DIHYDRATE $3SiO_2.2H_2O = H_4Si_3O_8$. By decomposing K or Na silicate solution by CO_2, or SiF_4 by H_2O, and drying the gelatinous pp. so formed *in vacuo*, Fremy (*l.c.*) obtained a hydrate containing 16·2 to 16·8 p.c. water ($3SiO_2.2H_2O$ requires 16·67 p.c. water). Several naturally occurring silicates may be regarded as derived from this hydrate (*v.* SILICATES, *infra*).

DISILICIC MONOHYDRATE $2SiO_2.H_2O = H_2Si_2O_5$. The gelatinous pp. formed by decomposing SiF_4 by water, after drying for six weeks in air at 20°–25°, was found by Merz (*J. pr.* 99, 1771) to contain from 13·1 to 13·5 p.c. water (the formula given requires 13·05 p.c. water).

OTHER HYDRATES. By drying the gelatinous pps. obtained by decomposing SiF_4 by water, or by decomposing alkali silicate solutions by weak acids and washing (*v.* Kühn, *J. pr.* 59, 1), solids are obtained of varying and uncertain composition (*v.* Carnelley a. Walker, *C. J.* 53, 80); hydrates of fair definiteness agreeing approximately with the formulæ $3SiO_2.H_2O = H_2Si_3O_7$, $9SiO_2.2H_2O = H_4Si_9O_{20}$, and $6SiO_2.H_2O = H_2Si_6O_{13}$, have been obtained (Fuchs, *A.* 82, 119; Gottlieb, *J. pr.* [2] 6, 185; Merz, *J. pr.* 99, 1771). For methods of preparing gelatinous pps. of $SiO_2.xH_2O$ *v.* Struckmann, *A.* 94, 337; Kuhlmann, *A.* 41, 231; Liebig, *A.* 94, 374; Guyton-Morveau, *A. Ch.* [2] 31, 246; Hautefeuille a. Margottet, *C. R.* 96, 1052. Concerning the absorption of water by SiO_2 *v.* van Bemmelen, *B.* 11, 2232; 13, 1466.

Thomsen (*Th.* 1, 215) has examined the thermal phenomena accompanying the interaction of NaOHAq and SiO_2Aq; the SiO_2Aq was prepared by adding exactly an equivalent of HCl in dilute solution to Na silicate solution of known composition. He gives the following tables:—

m	$[mNaOHAq,SiO^2Aq]$	x	$[NaOHAq,xSiO^2Aq]$
$\frac{1}{3}$	2652	$\frac{1}{4}$	1353
$\frac{1}{2}$	3241	$\frac{1}{2}$	2615
$\frac{2}{3}$	3555	$\frac{3}{4}$	3548
1	4316	1	4316
$\frac{3}{2}$	4731	$\frac{3}{2}$	5332
2	5230	2	6483
4	5412	3	7956

There seems to be no fixed point of neutralisation. Putting $[NaOHAq,xSiO^2Aq] = \frac{x.C}{x+n}$ where C and n are constants having the values C = 13,410 and $n = 2·13$, the calculated values agree very fairly with the observed so far as data go; if the formula is supposed to be accurate then the heat of neutralisation of SiO_2Aq, when SiO_2 is taken as = ∞ in the reaction NaOHAq + SiO_2Aq, is = 13,410, which is about the thermal value of the interaction of an acid with one molecular weight of NaOH. The *affinity* of SiO_2Aq is almost *nil*. M. M. P. M.

SILICATES. *Compounds of SiO_2 with basic radicles.* The basic radicles of silicates are generally oxygen-containing groups; sometimes they contain negative elements other than O. Silica, like other feebly acidic oxides, combines with bases in many proportions, forming compounds which may be represented as normal salts, and also compounds of the type of basic and acidic salts. The general composition of silicates is given by the formula $nSiO_2.mR$, where R = basic radicle. Most of the silicates occurring in rocks vary in composition between the limits $SiO_2.4MO$ and $2SiO_2.MO$, where M = a mono- or di-valent metal, and the limits $SiO_2.2M_2O_3$ and $6SiO_2.M_2O_3$ where M = a trivalent metal. The metals most commonly found in these silicates are Al, K, Na, Ca, Mg, Fe, and Mn. A fair number of natural silicates contain Cl or F as part of the basic radicle. Few pure silicates occur in rocks: the siliceous minerals are generally mixtures of isomorphous silicates; hence it is not possible to deduce satisfactory formulæ for naturally occurring silicates solely from the results of analyses of minerals.

Mendeléeff (*Principles of Chemistry*, 2, 111) compares the siliceous minerals to alloys. Several silicates which occur as mineral species have been formed artificially; the study of the alteration-products of natural silicates, and the comparison of silicates with carbon compounds (*v. e.g.* Mendeléeff, *l.c.*, *note* p. 111) throw light on the constitution of these bodies.

The most important memoirs on the constitution and chemical relations of the silicates are to be found in Groth's *Tabellarische Uebersicht der Mineralien nach ihren Krystallographisch-chemischen Beziehungen* (3rd ed.), pp. 89 *et seq.*, and in a series of papers by F. W. Clarke (*Am.* 10, 120; *Am. S.* [3] 38, 384; 40, 303; 43, 190), (*v.* also Clarke in *U.S. Geological Survey Bulletins*, No. 90 [1892]; also *A. C. J.* May 1893).

Groth and Clarke both look on the natural silicates as derived from a few fairly simple types. They are very stable compounds; most of them are formed at high temperatures, their number is not very great, and a few typical forms containing a small number of common metals are very widely distributed. Among the commoner silicates are $SiO_2.2MO$, $2SiO_2.3MO$, $3SiO_2.2MO$, where M is very frequently an alkaline earth metal; $3SiO_2.2R_2O_3$, $2SiO_2.R_2O_3$, $6SiO_2.R_2O_3.M_2O$, and $3SiO_2.R_2O_3.3MO$, where R is Al or Fe, and M is K, Na, or an alkaline earth.

The consideration of the probable constitution of the typical silicates may be approached by seeking to derive these salts from the silicic acids $n SiO_2.m H_2O$. *Metasilicic acid*, $SiO_2.H_2O$, has been isolated; the formula may be written H_2SiO_3 or $OSi(OH)_2$. *Orthosilicic acid*, $SiO_2.2H_2O = H_4SiO_4 = Si(OH)_4$, also probably exists. A few other hydrates of silica have been isolated, but their compositions are not quite definitely established; $2SiO_2.H_2O = H_2Si_2O_5$, and $3SiO_2.2H_2O = H_4Si_3O_8$, seem to be fairly certain.

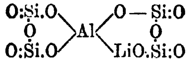
Silicates derivable from metasilicic acid $O{:}Si(OH)_2$. The typical empirical formulæ of normal salts of this class are $SiO_2.M_2O$, $SiO_2.MO$, $3SiO_2.M_2O_3$, $4SiO_2.R_2O_3.M_2O$, and $4SiO_2.R_2O_3.MO$. The atomic ratio of Si to O in these salts is 1:3; this ratio is maintained in the acid salts. Silicates of the forms $SiO_2.2MO$ and $SiO_2.M_2O_3$ may be represented as basic salts of this class; the atomic ratios of Si to O in these are 1:4 and 1:5. Examples of normal salts of this class are *sodium silicate* $O{:}Si(ONa)_2$, *wollastonite* $O{:}Si.O_2Ca$, and *leucite* $(O{:}Si.O_2)_4Al_2K_2$. The basic salts may be regarded as derived from $O{:}Si(OH)_2$ by replacing each H by a monovalent basic radicle, such as AlO or ZnOH; for instance, *siliceous calamine* $SiO_2.2ZnO.H_2O$ may be formulated $O{:}Si(O.ZnOH)_2$, and *kyanite* $SiO_2.Al_2O_3$ is probably $O{:}Si(OAl{:}O)_2$. If only one H is replaced in $O{:}Si(OH)_2$ the product will be an acid salt of the metasilicate class; *gyrolite*, for instance, $3SiO_2.2CaO.H_2O$ may be represented as

$$O{:}Si(OH)O.Ca.O.\underset{O}{Si}.O.Ca.O.(HO)Si{:}O.$$

Silicates derivable from hypothetical metadisilicic acid

$$2\left(O.Si(OH)_2\right) - HOH = HO.\underset{O}{Si}.O.\underset{O}{Si}.OH.$$

The typical empirical formulæ of normal salts of this class are $2SiO_2.M_2O$, $2SiO_2.MO$, $6SiO_2.R_2O_3$, and $8SiO_2.R_2O_3.M_2O$. The atomic ratio of Si to O in these salts is 2:5; this ratio is maintained in the acid salts. Silicates of the form $2SiO_2.2MO.H_2O$, wherein the atomic ratio of Si to O is 2:7, *may* be regarded as basic salts of this class. *Petalite* $8SiO_2.Al_2O_3.Li_2O$ is probably an example of a normal salt of the metadisilicate class; thus



Picrosmine $2SiO_2.2MgO.H_2O$ may perhaps be a basic salt of this class,

$$(HOMg)O.\underset{O}{Si}.O.\underset{O}{Si}.O(MgOH);$$

but it may also be regarded as an acid orthodisilicate (*v. infra*). One of the soluble glasses, $4SiO_2.Na_2O.H_2O$, may be written as an acid salt of this class,

$$HO.\underset{O}{Si}.O.\underset{O}{Si}.ONa.$$

Silicates derivable from orthosilicic acid $Si(OH)_4$. The typical empirical formulæ of normal salts of this class are $SiO_2.2M_2O$, $SiO_2.2MO$, $3SiO_2.2M_2O_3$, and $3SiO_2.M_2O_3.3M_2O$. The atomic ratio of Si to O in these salts is 1:4; this ratio is maintained in the acid salts. Salts of the forms $SiO_2.4MO.2H_2O$ and $SiO_2.2M_2O_3$, atomic ratio of Si to O = 1:8, may be formulated as basic orthosilicates. *Olivine* $SiO_2.2MgO$, and *zirconite* $SiO_2.ZrO_2$ are likely normal salts of this class;

$$Mg{<}{}^{O}_{O}{>}Si{<}{}^{O}_{O}{>}Mg \text{ and } Si(O_4Zr).$$

Xenolite $3SiO_2.2Al_2O_3$, is also a normal orthosilicate;

$$AlO_3{:}Si.\underbrace{OO_2}_{Al}{:}Si{:}\underbrace{O_2O}_{Al}.Si{:}O_3Al.$$

Andalusite $SiO_2.Al_2O_3$ is probably partly a basic salt and partly a normal salt of this class; $Si(O_3Al).O.AlO$. *Dioptase* $SiO_2.CuO.H_2O$ may be formulated as an acid salt of the orthosilicate class; $Si(OH)_2.O_2Cu$.

Silicates derivable from hypothetical orthodisilicic acid

$2Si(OH)_4 - H_2O = (HO)_3Si.O.Si(OH)_3$. The typical empirical formulæ of normal salts of this class are $2SiO_2.3M_2O$, $2SiO_2.3MO$, $2SiO_2.M_2O_3$, and $4SiO_2.M_2O_3.3M_2O$. The atomic ratio of Si to O in the normal and acid salts is 2:7. *Serpentine* $2SiO_2.3MgO$ is probably a normal salt of this class, $(MgO_2)\underset{O.Mg.O}{Si.\ O.\ Si}(O_2Mg)$. *Okenite* $2SiO_2.CaO.2H_2O$ seems to be an acid salt of this class, $HO.\underset{O_2Ca}{Si.O}.Si(OH)_3$; *picrosmine* $2SiO_2.2MgO.H_2O$ may also be an acid orthodisilicate, $MgO_2.(HO)Si.O.Si(OH).O_2Mg$; but it may be formulated as a basic metadisilicate (*v. supra*).

Silicates derivable from hypothetical orthotrisilicic acid. By removing $2H_2O$ from $3Si(OH)_4$ the acid

$$(HO)_3Si.O.\underset{(OH)_2}{Si}.O.Si(OH)_3$$

would remain. Some natural silicates may be looked on as salts of this hypothetical acid; *meerschaum*, for instance, $3SiO_2.2MgO.2H_2O$, may have the formula

$$MgO_2.(HO)Si.O.\underset{(OH)_2}{Si}.O.Si(OH).O_2Mg.$$

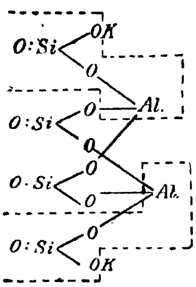
Groth (*l.c.*), however, thinks it is not necessary to call in a hypothetical trisilicic acid to express the composition of silicates.

Some silicates which do not fit into any of the classes already mentioned may be looked on as derived from more than one of the acids simultaneously. Others may be represented as salts of hypothetical acids formed by eliminating water from one or other of the acids that have been mentioned. *Orthoclase*, $6SiO_2.Al_2O_3.K_2O$, may be taken as an example of a silicate derived, according to Groth (*l.c.*), from two acids, metasilicic and metadisilicic; thus

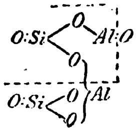
$$O.Si.{<}{}^{O}_{O}{>}Al.O.\underset{O}{Si}.O.\underset{O}{Si}.OK.$$

Groth urges that this formula is in keeping with the facts (1) that felspars of the *orthoclase* class are derived from silicates, such as *leucite*, which are metasilicates, and (2) that *orthoclase* readily yields *kaolinite* $2SiO_2.Al_2O_3$, which may be a basic metadisilicate. Writing *leucite* as a metasilicate, and *kaolinite* as a basic metadisilicate, it is seen that both contain the group $O{:}Si{<}{}^{O}_{O-Al=}$, a group which is represented as present in *orthoclase* also. Thus

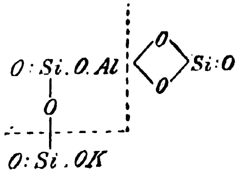
Leucite.



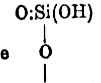
Kaolinite.



Orthoclase.

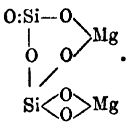


The group common to the three silicates is indicated by the dotted lines. If HHO were removed from orthodisilicic acid the product



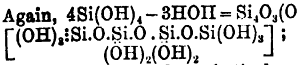
$$\begin{array}{l}\mathrm{O{:}Si(OH)}\\ \quad|\\ \quad\mathrm{O}\\ \quad|\\ \mathrm{Si(OH)_3}\end{array}$$

would be ; *augite*, $2SiO_2.2MgO$, may be derived from this acid,



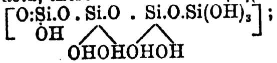
.

Again, $4Si(OH)_4 - 3HOH = Si_4O_3(OH)_{10}$



$$\left[\begin{array}{l}\mathrm{(OH)_3{\vdots}Si.O.Si.O\,.\,Si.O.Si(OH)_3}\\ \qquad\qquad\mathrm{(OH)_2(OH)_2}\end{array}\right]$$

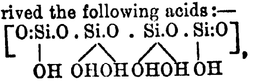
; if H_2O were removed from this hypothetical *orthotetrasilicic acid*, there would result $Si_4O_4(OH)_8$



$$\left[\begin{array}{l}\mathrm{O{:}Si.O\,.\,Si.O\,\,.\,\,Si.O.Si(OH)_3}\\ \quad\mathrm{OH}\\ \qquad\quad\mathrm{OHOHOHOH}\end{array}\right]$$

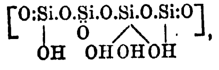
; and from this might be derived the following acids:—

$Si_4O_5(OH)_6$



$$\left[\begin{array}{l}\mathrm{O{:}Si.O\,.\,Si.O\,\,.\,\,Si.O\,.\,Si{:}O}\\ \quad|\qquad\quad\wedge\qquad\quad\wedge\qquad|\\ \mathrm{OH\ \ OHOH\ OHOH\ OH}\end{array}\right],$$

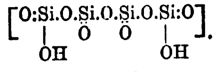
$Si_4O_6(OH)_4$



$$\left[\begin{array}{l}\mathrm{O{:}Si.O.Si.O.Si.O.Si{:}O}\\ \quad|\qquad\mathrm{O}\qquad\wedge\qquad|\\ \mathrm{OH\quad OH\,OH\,OH}\end{array}\right],$$

and

$Si_4O_7(OH)_2$



$$\left[\begin{array}{l}\mathrm{O{:}Si.O.Si.O.Si.O.Si{:}O}\\ \quad|\qquad\mathrm{O}\qquad\mathrm{O}\qquad|\\ \mathrm{OH}\qquad\qquad\qquad\mathrm{OH}\end{array}\right].$$

Some of the natural silicates may be represented as derived from one or other of these acids. Acids containing OH yield Cl derivatives wherein OH is replaced by Cl, generally by interaction with PCl_5. As Cl derivatives of some of the hypothetical silicic acids are known, the existence of these derivatives is an argument in favour of representing certain silicates as salts of acids which have not themselves been isolated. Thus, besides $SiCl_4$, which corresponds with orthosilicic acid $Si(OH)_4$, and $SiCl_3.SH$, which is derived from the hypothetical orthothiosilicic acid, there exists Si_2OCl_6 corresponding with ortho-disilicic acid $Si_2O(OH)_6$, $Si_4O_3Cl_{10}$ corresponding with ortho-tetrasilicic acid $Si_4O_3(OH)_{10}$, $Si_4O_4Cl_8$ corresponding with the acid $Si_4O_4(OH)_8$, and $Si_4O_5Cl_6$ corresponding with the acid $Si_4O_5(OH)_6$ (*v. supra*).

Clarke (*l.c.*), recognising the two main divisions of ortho- silicates and meta- silicates, seeks to derive the various members of each class as far as possible from the typical normal aluminium salts by substituting metals or basic groups, wholly or partially, for Al.

Orthosilicates. Clarke starts with normal Al orthosilicate, $3SiO_2.2Al_2O_3 = Al_4(SiO_4)_3$, which forms the mineral species *xenolite*; allied to *xenolite* are *fibrolite* $SiO_2.Al_2O_3 = Al_2SiO_5$, *topaz* $SiO_2.Al_2O_2F_2 = Al_2SiO_4F_2$, *muscovite* $6SiO_2.3Al_2O_3.K_2O.2H_2O = 2Al_3KH_2(SiO_4)_3$, *paragonite*, corresponding with *muscovite* but containing Na in place of K, and *eucryptite* $2SiO_2.Al_2O_3.Li_2O = 2AlLiSiO_4$. By trebling the formulæ given for *fibrolite* and *topaz*, using the simplest formula given for *muscovite* and *paragonite*, and trebling the simplest formula given for *eucryptite*, Clarke arrives at the following comparable formulæ for the six silicates:—

Xenolite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Fibrolite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}(AlO)_3}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Topaz.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}(AlF_2)_3}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Muscovite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}KH_2}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Paragonite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}NaH_2}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Eucryptite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}Li_3}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

These silicates are represented as derived from normal Al orthosilicate by substituting either metals, metals and hydrogen, or basic groups, for Al. If such substitution is carried further a series of silicates may be obtained, for some of which Clarke suggests the following formulæ:—

Dumortierite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}(AlO)_3}\\ \mathrm{O.Si{\vdots}O_3{\vdots}(AlO)_3}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Grossularite.

$$\mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O.Si{\vdots}O_3}\\ \mathrm{O.Si{\vdots}O_3}\end{array}\right\}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Prehnite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}CaH}\\ \mathrm{O.Si{\vdots}O_3{\vdots}CaH}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Natrolite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si{\vdots}O_3{\vdots}NaH_2}\\ \mathrm{O.Si{\vdots}O_3{\vdots}NaH_2}\\ \mathrm{O.Si{\vdots}O_3{\vdots}Al}\end{array}\right.$$

Fibrolite alters by hydration, giving *westanite* $4SiO_2.3Al_2O_3.H_2O = 2Al_3HSi_2O_9$, *kaolinite* $2SiO_2.Al_2O_3.2H_2O = Al_2Si_2H_4O_9$, and *montmorillonite* $4SiO_2.Al_2O_3.7H_2O = 2AlSi_2H_7O_9$. Clarke suggests the following formulæ for these products of alteration of fibrolite:—

Fibrolite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots(AlO)_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.$$

Westanite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.$$

Kaolinite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O.Si\vdots O_3\vdots H_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.$$

Montmorillonite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{O.Si\vdots O_3\vdots H_3}\\ \mathrm{O.Si\vdots O_3\vdots H_3}\end{array}\right.$$

If it is supposed that two groups $\mathrm{Al(O.Si\vdots O_3)_3}$ combine with elimination of one of the $\mathrm{O.SiO_3}$ groups ($=\mathrm{SiO_2+2O}$), then there remains the collocation of atoms,

$$\begin{array}{l}\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.SiO_3}\\ \mathrm{O.SiO_3}\\ \mathrm{O}\end{array}\right.\\ \qquad\quad >\mathrm{SiO_2}\\ \mathrm{Al}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{O.SiO_3}\\ \mathrm{O.SiO_3}\end{array}\right.\end{array}$$

from which a number of silicates, especially iron and magnesian micas, may be derived. Thus—

Annite.

$$\begin{array}{l}\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots FeH}\\ \mathrm{O.Si\vdots O_3\vdots FeH}\end{array}\right.\\ \quad\ \mathrm{O_2{:}Si{:}O_2{:}K_2}\\ \mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots FeH}\\ \mathrm{O.Si\vdots O_3\vdots FeH}\end{array}\right.\end{array}$$

Sodalite.

$$\begin{array}{l}\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Na_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.\\ \quad\ \mathrm{O_2{:}Si{:}O_2{:}Na_2}\\ \mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{Cl}\end{array}\right.\end{array}$$

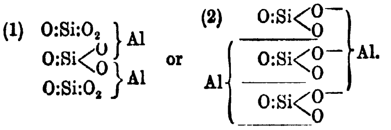
Noscan.

$$\begin{array}{l}\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Na_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.\\ \quad\ \mathrm{O_2{:}Si{:}O_2{:}Na_2}\\ \mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{SO_4.Na}\end{array}\right.\end{array}$$

Clarke (*Am.* 10, 126) suggests that *ultramarine* may be analogous to these silicates; thus,

$$\begin{array}{l}\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Na_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.\\ \quad\ \mathrm{O_2{:}Si{:}O_2{:}Na_2}\\ \mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{S.Na}\end{array}\right.\end{array}$$

The metasilicates are considered by Clarke (*l.c.*) in a way similar to that whereby he has elucidated the orthosilicates. The starting-point is Al metasilicate, $\mathrm{Al_2(SiO_3)_3}$. This salt is not itself known. The formula may be



$$(1)\quad \begin{array}{l}\left.\begin{array}{l}\mathrm{O{:}Si{:}O_2}\\ \mathrm{O{:}Si{<}^{O}_{O}}\end{array}\right\}\mathrm{Al}\\ \left.\begin{array}{l}\\ \mathrm{O{:}Si{:}O_2}\end{array}\right\}\mathrm{Al}\end{array}\quad \text{or}\quad (2)\quad \mathrm{Al}\left\{\begin{array}{l}\mathrm{O{:}Si{<}^{O-}_{O}}\\ \mathrm{O{:}Si{<}^{O-}_{O}}\\ \mathrm{O{:}Si{<}^{O-}_{O}}\end{array}\right\}\mathrm{Al.}$$

Inasmuch as many metasilicates of the form $\mathrm{AlM(SiO_3)_2}$, where M = Li, K, Na, H, may be simply derived from the first, but not from the second, formula given for $\mathrm{Al_2(SiO_3)_3}$, thus $\mathrm{O{:}Si{:}O_2{:}Al.O.\underset{OM}{Si}{:}O}$, Clarke thinks that the first formula may be taken to represent $\mathrm{Al_2(SiO_3)_3}$. Several other metasilicates may be formulated as derived from the Al salt by substituting metals or basic groups for one of the $\mathrm{AlSiO_3}$ groups; or many metasilicates containing divalent metals may bem ore simply derived from the normal form $\mathrm{M^{II}SiO_3}$, by doubling this formula and then replacing one $\mathrm{M^{II}}$ in the formula $\mathrm{M^{II}M^{II}(SiO_3)_2}$ by other metals or by basic groups.

The species *albite* and *orthoclase*, $\mathrm{AlMSi_3O_8}$, are looked on by Clarke as derived from the Al salt of the acid $\mathrm{H_4Si_3O_8}$ ($=\mathrm{3SiO_2.2H_2O}$), which acid has probably been isolated, in the same way as many orthosilicates are derived by him from the normal Al salt $\mathrm{Al_4(SiO_4)_3}$. The triclinic felspars are generally thought to consist of mixtures ranging between the limits marked by *albite* $\mathrm{AlNaSi_3O_8}$, and *anorthite* $\mathrm{Al_2Ca(SiO_4)_2}$; if these formulæ are trebled and written thus

Anorthite.

$$\mathrm{Al}\left\{\begin{array}{ll}\mathrm{O.Si\vdots O_3{\equiv}Ca_3{\equiv}O_3\vdots Si.O}\\ \mathrm{O.Si\vdots O_3\vdots Al}\quad\mathrm{Al\vdots O_3\vdots Si.O}\\ \mathrm{O.Si\vdots O_3\vdots Al}\quad\mathrm{Al\vdots O_3\vdots Si.O}\end{array}\right\}\mathrm{Al}$$

Albite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si_3O_7\vdots Na_3}\\ \mathrm{O.Si_3O_7\vdots Al}\\ \mathrm{O.Si_3O_7\vdots Al}\end{array}\right.$$

both silicates are represented by strictly comparable formulæ. Clarke also draws attention to the fact that the four silicates *muscovite* $\mathrm{6SiO_2.3Al_2O_3.K_2O.H_2O}$, *garnet* $\mathrm{3SiO_2.Al_2O_3.3CaO}$, *orthoclase* $\mathrm{AlKSi_3O_8}$, and *tourmaline* $\mathrm{4SiO_2.Al_2O_3.2M_2O_3(or\ 6MO)B_2O_3}$, are very frequently associated in granite veins. By halving the formula for *muscovite* and writing it $\mathrm{Al_3KH_2(SiO_4)_3}$, writing the formula for *garnet* $\mathrm{Al_2Ca_3(SiO_4)_3}$, trebling the formula for *orthoclase* and writing it $\mathrm{Al_3K_3(Si_3O_8)_3}$, halving the formula for *tourmaline* and writing it $\mathrm{AlR_2(BO_2)(SiO_4)_2}$, where R is a metal or group equivalent to Al, very suggestive relationships are disclosed between the four silicates; thus

Muscovite.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si\vdots O_3\vdots KH_2}\\ \mathrm{O.Si\vdots O_3\vdots Al}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.$$

Garnet.

$$\mathrm{Al}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O.Si\vdots O_3}\\ \mathrm{O.Si\vdots O_3}\end{array}\right\}\mathrm{Ca_3}\\ \mathrm{O.Si\vdots O_3\vdots Al}\end{array}\right.$$

Tourmaline.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{B{:}O_2}\\ \mathrm{O.Si\vdots O_3\vdots R}\\ \mathrm{O.Si\vdots O_3\vdots R}\end{array}\right.$$

Orthoclase.

$$\mathrm{Al}\left\{\begin{array}{l}\mathrm{O.Si_3O_7\vdots K_3}\\ \mathrm{O.Si_3O_7\vdots Al}\\ \mathrm{O.Si_3O_7\vdots Al}\end{array}\right.$$

In *Am. S.* for November 1889 ([3] 38, 384), and *A. C. J.* May 1893, Clarke has applied the substitution method, as sketched above, to the *mica* group of silicates, and in the same journal for March 1892 (*Am. S.* [3] 43, 190) he has applied the same method to the *chlorite* group.

The *micas* all fall within the limits of composition indicated by the two formulæ $\mathrm{Al_3R^I_3(SiO_4)_3}$ and $\mathrm{AlR_9^I(Si_3O_8)_3}$. The first formula is derived from $\mathrm{Al_4(SiO_4)_3}$ by substituting Al by one trivalent or three monovalent basic radicles; the second formula is derived from the hypothetical salt $\mathrm{Al_4(Si_3O_8)_3}$ by substituting one, two, or three Al atoms by equivalent basic radicles. When F is present it is regarded as forming part of one or other of the monovalent groups Mg.F or $\mathrm{Al{:}F_2}$. If the ratio of O to Si is greater than $\mathrm{4O{:}Si(SiO_4)}$ the excess of O is looked on as combined with metal to form a basic group, such as Al:O; if the ratio of O to Si is less than 4O:Si the group $\mathrm{Si_3O_8}$ is supposed to be present. The micas are all capable of being represented as isomorphous mixtures of various constituents, the compositions of which fall within the limiting formulæ.

The *chlorites* are treated by Clarke (*l.c.*) similarly to the micas. In *Am. S.* [3] 43, 198 he gives the following general formulæ which summarise the composition of the chief *micas* and *chlorites*:—

Normal orthosilicate $Al_4(SiO_4)_3$.

Micas.

Muscovite $Al_3(SiO_4)_3R_3$.
Normal Biolite $Al_2(SiO_4)_2R_6$.
Normal Phlogopite $Al_2(SiO_4)_6R_9$.
Clintonite $R^{II}:O_2:Al(SiO_4)R_3$.

Normal orthosilicate $Mg_4(SiO_4)_2$.

Chlorites.

Aphrosiderite $Mg_3(SiO_4)_2R_2$.
Orthochlorites $\left\{\begin{array}{l} Mg_2(SiO_4)_2R_4. \\ Mg(SiO_4)_2R_6. \end{array}\right.$
Amesite $O:Mg_2(SiO_4)R_2$.

Preparation of silicates.—Alkali silicates are formed by dissolving moist amorphous SiO_2 in boiling solutions of alkalis or alkali carbonates, also by fusing SiO_2 with alkalis or with alkali salts of acids which volatilise by heat. Many other silicates are obtainable by double decompositions between alkali silicates (which are sol. water) and metallic salt solutions; also by heating various metallic oxides or carbonates with SiO_2.

Some naturally occurring silicates have been prepared by the following methods:—1. *Emerald* Be_2SiO_4, *olivine* Mg_2SiO_4, and *enstatite* $MgSiO_3$, by heating SiO_2 with BeO or MgO mixed with boric acid in a porcelain-oven, till the boric acid volatilised (Ebelmen, *A. Ch.* [3] 22, 211).—2. *Anorthite* $Al_2Ca(SiO_4)_2$, *labradorite* $3SiO_2.Al_2O_3.K_2O$, and *oligoclase* $9SiO_2.2Al_2O_3.2K_2O$, by strongly heating SiO_2 with K_2CO_3 in boric acid, or by adding CaO to molten boric acid and SiO_2 at a very high temperature (E., *C. R.* 32, 710; Fouquet a. Lévy, *C. R.* 90, 620).—3. *Zirconite* $ZrSiO_4$, and *kyanite* $(AlO)_2SiO_3$, by heating to redness ZrO_2 in vapour of H_2SiF_6, or SiO_2 in vapour of AlF_3 (Deville a. Caron, *A. Ch.* [4] 5, 113; Fremy a. Feil, *C. R.* 85, 1032).—4. *Enstatite* $MgSiO_3$, and *leucite* $Al_2K_2(SiO_3)_4$, by heating Mg, or Al mixed with KOH, to low redness in H and $SiCl_4$ vapour (St. Meunier, *C. R.* 90, 349, 1009).—5. *Orthoclase* $AlKSi_3O_8$, *albite* $AlNaSi_3O_8$, *petalite* $AlLi(Si_2O_5)_2$, by fusing a mixture of Al_2O_3, SiO_2, and tungstate or vanadate of K, Na, or Li; with excess of Al_2O_3 *leucite* $Al_2K_2(SiO_3)_4$ is obtained (Hautefeuille, *C. R.* 90, 378, 541).—6. *Orthoclase* $AlKSi_3O_8$, by heating Al_2O_3 and SiO_2, in the ratio $Al_2O_3:6SiO_2$, with KVO_3 (Hautefeuille a. Perrey, *C. R.* 107, 786).—7. *Phenacite* $Be_2(SiO_4)$ mixed with a *lithia felspar*, *quartz*, and *tridymite*, was obtained by heating for fifteen days at 600°–700° a mixture of 4·8 g. SiO_2, 1·5 g. BeO, 20 g. $LiVO_3$, and 1·5 g. Li_2CO_3 (H. a. P., *C. R.* 106, 1800).—8. Crystals of *emerald* were prepared (H. a. P., *C. R.* 106, 1800) by heating a mixture of 12·506 g. SiO_2, 3·58 g. Al_2O_3, 2·64 g. BeO, ·6 g. Cr_2O_3, and 92 g. acid Li molybdate (ratio $= Li_2O:2\frac{1}{2}MoO_3$); the mixture was placed in a Pt crucible, which was heated in a muffle to low redness for twenty-four hours, when the temperature was raised to 800° and kept thereat for fourteen days. The product was washed with water.

Properties and Reactions of Silicates.—All silicates except those of the alkalis are insol. water; most of them are also insol. dil. acids. For the action of water on certain silicates when the mixtures were rapidly rotated in cylindrical vessels *v.* Daubrée (*C. R.* 64, 839). Many silicates are decomposed by evaporation with HClAq or HNO_3Aq, with separation of $SiO_2.xH_2O$, which is changed to SiO_2 by heating somewhat above 100°. Some of those silicates which are not thus decomposed are acted on, with separation of $SiO_2.xH_2O$, by evaporating with 8 parts conc. H_2SO_4 and 3 parts water. Almost all silicates are decomposed by heating with conc. HClAq or H_2SO_4 and a little water in sealed tubes to c. 200°. Heating with conc. HFAq, or in HF gas, decomposes silicates with formation of SiF_4; when a silicate is mixed with 3 parts AmF or 5 parts powdered CaF_2, and the mixture well moistened with H_2SO_4, and heated in a Pt dish, all the Si is given off as SiF_4. Fusion of a finely-powdered silicate with 4–6 parts mixed K_2CO_3 and Na_2CO_3 gives K and Na silicate (which is sol. water), while the metal remains as oxide. Silicates which contain F generally lose HF or silicofluoride when strongly heated; any alkali or alkaline metal, or Fe or Al, which was present in the silicate in combination with F remains as oxide (Rammelsberg, *W.* 7, 146). Clarke a. Schneider (*Am. S.* [3] 40, 303, 405, 452) have studied quantitatively the interactions of various natural silicates with HCl gas and also with HClAq; their results make it probable that in the magnesian silicates gaseous HCl attacks only the Mg which is present as the basic monovalent radicle Mg.OH.

The following account of individual silicates does not refer to silicates which occur in rocks, but only to those salts which have been prepared in the laboratory; the chief naturally occurring silicates that have been prepared artificially are mentioned under the heading *Preparation of silicates* (*supra*).

Barium silicates. The *normal meta- salt* $BaSiO_3.xH_2O$ is formed by ppg. dil. Na_2SiO_3Aq (*v. Sodium silicates, infra*) by dil. $BaCl_2$Aq or $Ba(NO_3)_2$Aq; not quite insol. hot water, easily sol. dil. HClAq; retains water at 100° (Ammon, *J.* 1862. 138). Lefort (*J. Ph.* [3] 39, 31) says that $BaO.3SiO_2.3aq$ (? $BaH_2Si_3O_8.2aq$) is formed by ppg. a dil. Ba salt solution by a dil. solution of $9SiO_2.2Na_2O$.

Calcium silicates. The compounds $3SiO_2.CaO$, $2SiO_2.CaO$, $3SiO_2.2CaO$, and $SiO_2.2CaO$, are said to be produced by very strongly heating mixtures of quartz and marble in the proper proportions. By adding $CaCl_2$Aq to solution of $3SiO_2.K_2O$, a gelatinous pp. is obtained which becomes crystalline after a time; dried at 100°, the solid is said to be $3SiO_2.CaO.2aq$ (? $CaH_2Si_3O_8.aq$). The *normal meta- salt* $CaSiO_3$ is said to be formed by ppg. Na_2SiO_3Aq by dil. $CaCl_2$Aq (*v.* A., *l.c.*; L., *l.c.*). Calcium silicates form the bases of most hydraulic cements (*v. Cements* in DICTIONARY OF APPLIED CHEMISTRY).

Cerium silicate. The *normal meta- salt* $Ce(SiO_3)_2$ is said to be formed by fusing Ce oxychloride with SiO_2 and $CaCl_2$ or NaCl (Didier, *C. R.* 101, 882).

Cobalt silicate. The *normal ortho- salt* Co_2SiO_4 is formed, according to Bourgeois (*C. R.* 108, 1177), by very strongly heating CoO with $CoCl_2$ and a large excess of SiO_2.

Nickel silicate. *Normal ortho- salt* Ni_2SiO_4 formed like the Co salt (B., *l.c.*).

Magnesium silicate. The gelatinous pp. obtained by adding $MgCl_2Aq$ to solution of $8SiO_2.K_2O$ is said to be $2SiO_2.MgO.2H_2O$ (? $MgH_2(SiO_3)_2$. aq *acid meta-salt*) (Heldt, *J. pr.* 94, 129, 157). The *normal meta-salt* $MgSiO_3.xH_2O$ is obtained, according to Ammon (*l.c.*), by ppg. Na_2SiO_3Aq by dil. $MgCl_2Aq$.

Potassium silicates. The *normal meta-salt* K_2SiO_3 is prepared by fusing 1 part SiO_2 with $2\frac{1}{4}$ parts dry K_2CO_3. If this product is dissolved in a little water, and alcohol is added, a gelatinous pp. is formed, which, if slightly washed and squeezed, is said to be $4SiO_2.K_2O$; but Fremy (*J.* 1856. 353) gives the composition $9SiO_2.2K_2O$ aq to this pp., and this is confirmed by Lefort (*J.* 1861. 205).

The name *potash water-glass* is given to the mixture of K silicates obtained by fusing together quartz and pearlash in a proportion about equal to $4SiO_2.K_2O$. Water-glass is a clear transparent solid, like glass; it is completely sol. hot water; a conc. solution, with c. 28 p.c. silicate, is syrupy, somewhat turbid, and has S.G. 1·25. The solution is decomposed by acids, even by CO_2, with separation of $SiO_2.xH_2O$; alkaline carbonates and chlorides, especially AmCl, ppt. $SiO_2.xH_2O$; BaO, SrO, CaO, Al_2O_3, and PbO decompose the solution, forming a double silicate with the whole of the silica and a portion of the K. The solution yields pps. with solutions of most of the salts of earth metals and heavy metals. Water-glass is also formed by boiling SiO_2 with KOHAq under pressure.

Sodium silicates. The *normal meta-salt* Na_2SiO_3 is prepared by fusing 1 part SiO_2 with $1\frac{3}{4}$ parts dry Na_2CO_3. The salt is obtained with $8H_2O$, in monoclinic crystals, by dissolving SiO_2 in an equivalent quantity of NaOH in solution, decanting, evaporating, as much as possible out of contact with air, till Na_2CO_3 begins to settle out, cooling to −22°, stirring till the whole solidifies, straining from mother-liquor, dissolving in a little water, and allowing to stand (Ammon, *J.* 1862. 138; *cf.* Ordway, *Am. S.* [2] 40, 186). By adding freshly ppd. AlO_3H_3 to a boiling solution of Na_2SiO_3 and NaOH, the *double salt* $Na_2SiO_3.Al_4(SiO_4)_3$ is obtained; and the salt $Na_2SiO_3.Al_2(SiO_3)_3$ is ppd. by adding Na_2SiO_3Aq to a hot solution of alum (A., *l.c.*). Mixtures of Na silicates are known as *soda water-glass* (*cf. supra, Potash water-glass*). For effect of time on composition of solutions of Na silicates *v.* Kohlrausch (*Z. P. C.* 12, 773).

Strontium silicate. The *normal meta-salt* $SrSiO_3$ is said to be formed by adding Na_2SiO_3Aq to dil. $SrCl_2Aq$ (Ammon, *l.c.*).

Thorium silicates. The *normal ortho-salt* $ThSiO_4$ and the *normal meta-salt* $Th(SiO_3)_2$ are formed, according to Troost a. Ouvrard (*C. R.* 105, 225), by fusing ThO_2 with SiO_2 and $CaCl_2$ and treating with dil. HClAq. $ThSiO_4$ is not isomorphous with $ZrSiO_4$ (T. a. O., *l.c.*).

Zinc silicates. The *normal meta-salt* $ZnSiO_3$ is obtained in rhombic crystals by ppg. $ZnSO_4Aq$ by Na_2SiO_3Aq, and strongly heating the dried pp. with boric acid for several days (H. Traube, *B.* 26, 2735).

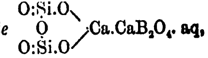
A systematic arrangement of the naturally occurring silicates will be found in Groth's *Tabell. Uebersichte*, pp. 103–151 [3rd ed.].

M. M. P. M.

SILICIC ACIDS *v.* **Silica, hydrates of, p. 447).**

SILICIDES. *Binary compounds of Si with metals.* These compounds are formed (1) by heating amorphous Si with metallic chlorides in presence of such a reducer as Na; (2) by heating K_2SiF_6 with metals; (3) by electrolysing a mixture of an alkali fluoride with a metallic oxide; (4) by heating metals with Si (*v.* Aluminium, Cerium, Copper, Iron, Magnesium, Manganese, Nickel, Platinum, silicides of). M. M. P. M.

SILICO-BORATES. Certain minerals consist of compounds of silicates and borates; the name silico-borate is sometimes applied to such compounds. *Datholite*



$$\begin{matrix} O{:}Si.O \diagdown \\ O \quad\quad Ca.CaB_2O_4.\,aq, \\ O{:}Si.O \diagup \end{matrix}$$

and *botryolite*, the same formula with 2aq, are examples of borosilicates. *Tourmalines* $Al(BO_2)(SiO_4)_2R^I_6$ are also silico-borates (R^I may be replaced by its equivalent of R^{II}).

M. M. P. M.

SILICO-BROMOFORM $SiHBr_3$. (*Silicon hydrogen bromide. Tribromo-silico-methane.*) Obtained, not quite pure, by Buff and Wöhler (*A.* 104, 99) by leading HBr gas over heated Si, distilling the product, shaking with Hg, and distilling again. Gattermann (*B.* 22, 193) obtained pure $SiHBr_3$ as follows. Crude Mg silicide, prepared as described under Silicon, *Preparation*, No. 1 (p. 456), is freed from MgO by powdering, adding little by little to HClAq (1:2), shaking with this acid for some hours, washing till the wash-water is neutral, and drying thoroughly. The Si thus obtained is heated in a tube in a stream of HBr, the tube being connected with a well-cooled receiver; the details and precautions described under Silicon tetrachloride, *Preparation*, No. 2 (p. 458) must be observed. The HBr required may be made by the action of H_2SO_4Aq on KBr; G. used a *cold* mixture of 45 c.c. conc. H_2SO_4 and 15 c.c. water, and let this drop on to 75 g. KBr; he dried the gas by H_2SO_4. The liquid is distilled, and then fractionated till a portion boils at 115°–117°; most of the remainder boils at c. 153° and is $SiBr_4$. A colourless liquid, boiling 115°–117°; S.G. 2·7 at ordinary temperature (G., *l.c.*). Fumes much in air, and takes fire, probably because the heat produced in the decomposition of a portion by the moisture of the air suffices to start rapid oxidation (G., *l.c.*). Ice-cold water forms *silico-formic anhydride* (*q. v.*, p. 455). Combines with PH_3, when compressed, to form a solid, unstable compound (Besson, *C. R.* 112, 530).

M. M. P. M.

SILICO-CHLOROFORM $SiHCl_3$. (*Silicon hydrogen chloride. Trichloro-silico-methane.*) Mol. w. 135·41. V.D. 67.

Formation.—1. Dry HCl gas is passed over Si heated below redness; the product is condensed in a flask in a freezing mixture and fractionated (Friedel a. Ladenburg, *A.* 143, 118; *cf.* Buff a. Wöhler, *A.* 104, 94).—2. Dry HCl gas is passed over siliceous pig-iron containing 15 p.c. Si (Warren, *C. N.* 60, 158).

Preparation.—Si, prepared by reducing sand by Mg (*v.* Silicon, *Preparation*, No. 1, p. 456) and removing MgO as described under Silico-bromoform (*supra*), is carefully heated in a stream of dry HCl gas in a tube connected with a receiver surrounded by a very good freezing mixture. The directions given for preparing $SiCl_4$ must be carefully followed (*v.* Silicon tetrachloride, *Preparation*, No. 2). [Gattermann recommends to make the HCl in a Kipp's generator, using conc. H_2SO_4 and fused NH_4Cl.] The liquid in the receiver is fractionated from a flask with a side tube 75 cms. long; if this is done, no condenser is required; the flask must be warmed by water at 90°, if a naked flame is used explosions of part of the $SiHCl_3$ may result (Gattermann, *B.* 22, 190).

Properties and Reactions.—A colourless, mobile liquid, with a very disagreeable smell; boils at 35°–39° (F. a. L., *l.c.*). Non-conductor of electricity.

The vapour takes fire very easily in *air*, *e.g.* by bringing a hot glass rod to the mouth of a vessel in which a little $SiHCl_3$ has been shaken. Mixture of the vapour with air is explosive. Decomposed to Si and HCl by passing through a narrow tube *heated to redness.* *Water* at 0° forms $Si_2O_3H_2$ (*v.* Silicoformic anhydride, p. 455) and HCl; at the ordinary temperature SiO_2xH_2O, HClAq, and H are produced. *Chlorine* reacts at ordinary temperatures, forming $SiCl_4$ and HCl; *bromine* reacts similarly at 100°. *Alcohol* produces $SiH(OEt)_3$ (*v.* Silicon tetrahydride, *Preparation*, No. 1, p. 460). Combines with *phosphorus hydride*, under pressure, to form a solid unstable body (Besson, *C. R.* 112, 530). M. M. P. M.

SILICO-ETHANE, PENTA-BROMO- DERIVATIVE OF, Si_2HBr_5. (*Disilicon hydrogen pentabromide. Pentabromo-silico-ethane.*) In making $SiBr_4$ by passing SiH_4 into Br, Mahn (*J. Z.* 5, 163) obtained a solid in the form of white needles, melting at 89° and boiling (out of contact with air) at 230°, and giving numbers on analysis agreeing with the formula Si_2HBr_5. Takes fire when heated in air. M. M. P. M.

SILICO-FLUORHYDRIC ACID H_2SiF_6Aq. (*Hydrofluosilicic acid.*) Known only in aqueous solution.

Preparation.—SiF_4, prepared by the interaction of CaF_2, SiO_2, and H_2SO_4 (*v.* Silicon tetrafluoride, p. 459), is passed into water, the exit tube dipping beneath a little Hg in the bottom of the vessel which contains the water; the vessel is shaken frequently to break up the gelatinous silica which forms in the water; when the liquid becomes thickish from separated silica, it is filtered through linen, the silica is pressed, and more SiF_4 is passed into the filtrate, as before.

(1) $SiF_4 + 3H_2O + Aq = SiO_2.H_2O + 4HFAq$;

(2) $4HFAq + 2SiF_4 = 2H_2SiF_6Aq$. The solution of H_2SiF_6 may be evaporated in a Pt vessel till it contains c. 34 p.c. of the acid.

To prepare the acid solution on a large scale, Tessié du Mothay recommends to fuse a mixture of fluorspar, silica, and charcoal in an oven, and to lead the gas that is given off through condensers containing water; c. 68 p.c. of the F in the fluorspar is thus obtained as H_2SiF_6 (*C. C.* 1868. 432).

Properties and Reactions.—H_2SiF_6Aq is a strongly-acid liquid, smelling like HClAq, and burning the skin. If kept in glass vessels it gradually withdraws alkali, lime, and iron oxide (H. Rose, *P.* 80, 403). Truchot (*C. R.* 98, 821) gives H.F. $[SiF^4,2HFAq] = 17,000$ (*cf.* Sabatier, *A. Ch.* [5] 22, 91). Thomsen gives $[SiO^2Aq,6HFAq] = 32,800$; and the heat of neutralisation as $[H^2SiF^6Aq,2NaOHAq] = 26,600$ (*Th.* 1, 236). The following table is given by Stolba (*J. pr.* 90, 193):—

S.G. H_2SiF_6Aq	P.c. H_2SiF_6	S.G. H_2SiF_6Aq	P.c. H_2SiF_6
1·0040	0·5	1·1559	18
1·0080	1	1·1653	19
1·0161	2	1·1748	20
1·0242	3	1·1844	21
1·0324	4	1·1941	22
1·0407	5	1·2038	23
1·0491	6	1·2136	24
1·0576	7	1·2235	25
1·0661	8	1·2335	26
1·0747	9	1·2436	27
1·0834	10	1·2537	28
1·0922	11	1·2639	29
1·1011	12	1·2742	30
1·1100	13	1·2846	31
1·1190	14	1·2951	32
1·1281	15	1·3056	33
1·1373	16	1·3162	34
1·1466	17		

The S.G. for any percentage of H_2SiF_6, when n = number of half-per-cents., is given by the formula; $S.G. = 1 + n \cdot 004 + \frac{n(n-3)+2}{100000}$.

By passing SiF_4 into fairly conc. HFAq until the liquid is saturated, hard, colourless, very hygroscopic crystals of the *hydrate* $H_2SiF_6.2H_2O$ separate; the crystals melt at 19°, and decompose at a higher temperature (Kessler, *C. R.* 90, 1285).

H_2SiF_6Aq acts as a dibasic acid (the heat of neutralisation confirms this), giving salts $M^I_2SiF_6$ and $M^{II}SiF_6$; with excess of a strongly basic metallic oxide it forms metallic fluoride and $SiO_2.H_2O$—thus

$$H_2SiF_6Aq + 3K_2O = SiO_2.H_2O + 6KFAq.$$

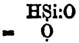
H_2SiF_6Aq is decomposed by conc. H_2SO_4, also by HCl gas, with formation of SiF_4 and withdrawal of water. Boric acid separates $SiO_2.xH_2O$ and forms *fluoboric acid* (*q.v.*, vol. i. p. 530). M. M. P. M.

SILICO-FLUORIDES. (*Hydrofluosilicates.*) Salts of H_2SiF_6 (*v.* preceding article). These salts are formed by dissolving various metals—*e.g.* Fe or Zn—in H_2SiF_6Aq, or by neutralising the acid solution by the proper quantities of basic oxides or hydroxides; if excess of a strongly basic oxide is added to H_2SiF_6Aq, $SiO_2.H_2O$ is separated and a fluoride is formed. Most of the silicofluorides are sol. water; the salts of Ba, K, Na, Ce, and a few elements allied thereto, are only slightly sol. water and insol. alcohol. Aqueous solutions of silicofluorides have an acid reaction to litmus. Silicofluorides are generally decomposed by heat, giving off SiF_4 and leaving fluorides; heated with AmCl, metallic chlorides remain (Stolba, *J. pr.* 101, 157). Some silicofluorides are decomposed by heating strongly with Fe or K, forming fluoride and Si. Conc. H_2SO_4 evolves H_2SiF_6, when heated HF is given off; conc. HClAq and HNO_3Aq react similarly, but more slowly and less completely; but H_2SiF_6Aq

partially decomposes most chlorides and nitrates in solution. Truchot (*C. R.* 98, 821, 1330) gives the heats of formation of alkali silicofluorides. M. M. P. M.

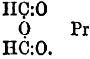
SILICO-FORMIC ACID. By the action of water on (?) SiI_2, Friedel a. Ladenburg (*A.* 203, 247) obtained a white solid that gave off H when treated with KOHAq; the amount of H obtained agreed fairly well with the formula SiH_2O_2. If this formula is correct, the compound is probably the Si analogue of formic acid. M. M. P. M.

SILICO-FORMIC ANHYDRIDE $H_2Si_2O_3$



$$= \begin{array}{l} HSi{:}O \\ \quad O \\ HSi{:}O. \end{array}$$

This body represents among Si compounds the hypothetical formic anhydride



$$\begin{array}{l} HC{:}O \\ \quad O \\ HC{:}O. \end{array}$$

Prepared by slowly distilling $SiHCl_3$ into water kept at 0°, filtering quickly the solid that separates, washing with ice-cold water, drying *in vacuo* over H_2SO_4 and then at 150°; the $SiHCl_3$ is distilled from a small flask and the distillation-tube is fused on to an inverted funnel which dips beneath the water; $2SiHCl_3 + 3H_2O = 6HCl + Si_2H_2O_3$ (Friedel a. Ladenburg, *A.* 143, 118; *cf.* Buff a. Wöhler, *A.* 104, 101; also Gattermann, *B.* 12, 186). A white, amorphous, light powder; floats in water, sinks in ether; sl. sol. water. Does not decompose at 300°, but at higher temperatures it glows and gives off H which takes fire explosively; burns when heated in O, emitting a brilliant light; burns when heated in a covered crucible, with formation of some amorphous Si. Heated in tube, SiH_4 is given off and a thin layer of amorphous Si remains. Not acted on by acids, except HFAq which dissolves it with rapid evolution of H. Alkali and alkali carbonate solutions, including NH_3Aq, dissolve this compound, giving off H, and forming alkali silicates. A freshly-prepared aqueous solution of $H_2Si_2O_3$ acts as an energetic reducer; $AuCl_3Aq$ is reduced to Au; Pd salts probably to Pd mixed with Pd silicate; SeO_2Aq, SO_2Aq, TeO_2Aq, and $HgCl_2Aq$ are reduced to Se, S, Te, and HgCl. CrO_3Aq, indigo solution, and salts of Pt and Ir are not reduced.

The substance obtained by Wöhler, by the action of light and water on the body he named *silicone* (*v.* SILICON, COMPOUNDS OF, WITH HYDROGEN AND OXYGEN, p. 459), and called by him *leukon* (*A.* 127, 268), and also the substance called by Geuther *silicium oxide* (*J. pr.* 95, 424), are probably identical with $Si_2H_2O_3$. M. M. P. M.

SILICO-IODOFORM $SiHI_3$. (*Silicon hydrogen iodide. Tri-iodo-silico-methane.*) Formula probably molecular, from analogy of $SiHCl_3$. Obtained in small quantities by the interaction of HI and crystalline Si at red heat (Buff a. Wöhler, *A.* 104, 99); better prepared by diluting the HI vapour with H; the product, which is a mixture of SiI_4 and $SiHI_3$, is repeatedly fractionated; SiI_4 boils at 290°, $SiHI_3$ at c. 200°. A mixture of SiI_4 and $SiHI_3$ is also obtained by heating SiH_4 with I (Mahn, *J.* 1869. 248). A colourless, refractive liquid; S.G. 3·362 at 0°, 3·314 at 20°; boils at c. 200°. Water produces $Si_2H_2O_3$ (Friedel, *A.* 149, 96) (*v.* SILICO-FORMIC ANHYDRIDE, *supra*). M. M. P. M.

SILICO-MOLYBDATES. Compounds containing SiO_2, MoO_3, and basic radicles; *v.* MOLYBDATES, vol. iii. p. 427.

SILICON. Si. (*Silicium.*) At. w. 28·3; mol. w. unknown. H.F. $[Si, O^2] = 219{,}240$ amorphous Si; 211,120 crystalline Si (Troost a. Hautefeuille, *C. R.* 70, 252). C.E. (linear at 40°) ·00000763 (Fizeau, *C. R.* 68, 1125). For other properties *v. Properties*, p. 456.

Historical.—The existence of a special earth in rocks that could be melted to glass-like substances was indicated by Pott in 1746. Scheele (*Opuscula*, 2, 67) and Bergmann (*Opuscula*, 2, 26) showed that this earth could not be changed into lime or alumina; Smithson in 1811 found that the earth acted like an acid; Berzelius, in 1823, isolated the element of this earth, and in 1854 Deville obtained the same element in crystalline form. The new element was shown to resemble carbon by the researches of Buff and Wöhler and of Friedel and Ladenburg. The name *silicon* was given from *acidum silicum* or *silex*.

Occurrence.—Si is not found uncombined; compounds of Si are very widely distributed in vast quantities; next to oxygen, Si (in combination) is the most widely distributed element. Silicates occur in very many rocks and soils and in plant-ashes; SiO_2 is found in many mineral springs and in sea-water (Forchhammer, *Pr. E.* 2, 303; Bunsen, *A.* 62, 7, 25), and in small quantities in various animal organisms (von Gorup-Besanez, *A.* 61, 46; Henneberg, *A.* 61, 261). Si is found in pig-iron; it is generally supposed to exist therein as crystallised Si, but the experiments of Jordan a. Turner (*C. J.* 49, 215) make it probable that the Si is combined with Fe as a silicide.

Formation.—Amorphous silicon.—1. By passing the vapour of $SiCl_4$ over heated K, removing excess of $SiCl_4$ by a current of dry air, and washing out KCl with water (Berzelius, *Lehrb.* (1st ed.) 3, 327).—2. By passing vapour of H_2SiF_6 over heated K, washing with water, heating the residue in a covered crucible (to remove H and C), washing with HFAq (to remove SiO_2) and then with water (B., *l.c.*).—3. By heating a mixture of K_2SiF_6 and K, and washing with water (B., *l.c.*); Wöhler (*A.* 104, 107) heats a mixture of Na_2SiF_6 with NaCl and Na.—4. By heating Mg in SiF_4 vapour (Warren, *C. N.* 58, 215).—5. By reducing SiO_2 by heating with Mg (*v. Preparation*, No. 1).—6. By electrolysing a fused silicate in a carbon crucible, with Pt as the positive, and gas-carbon as the negative, electrode (Hampe, *Chem. Zeitung*, 12, 841). *Crystalline silicon.*—7. By heating a mixture of K_2SiF_6, Na, and Zn (*v. Preparation*, No. 2).—8. By reducing K_2SiF_6 or a silicate by Al (*v. Preparation*, No. 3).—9. By passing H and $SiCl_4$ vapour over Zn heated to redness in a porcelain tube (Beketoff, *Bl.* 1, 22).—10. By heating a mixture of SiO_2, K_2CO_3, Iceland spar, and Na (Deville, *A. Ch.* [3] 49, 62).—11. By passing vapour of SiF_4 or $SiCl_4$ over Si heated to redness (Troost a. Hautefeuille, *C. R.* 73, 443).—12. By passing vapour of $SiCl_4$ over heated Na, or Al, and heating the product (Si with excess of Na or Al) in a carbon crucible (Deville, *A. Ch.* [3] 49, 62).—13. A piece of siliceous pig-iron is connected with the positive pole of a battery and immersed in dilute H_2SO_4Aq, in which a Pt plate connected with the negative pole of the battery is also placed; after some hours the iron has dissolved; the mixture of graphite, amorphous Si and SiO_2 which remains is heated to full redness for some time with Zn and the fused mass is treated with dilute HClAq (Warren, *C. N.* 57, 54).

Preparation.—Amorphous silicon.—1. An intimate mixture of 10 g. Mg powder and 40 g. thoroughly dry sand is placed in a test-tube, of fairly thick glass, c. 2·3 cms. diameter and c. 15 cms. long; the tube is heated throughout by a large flame, and then the lower part is very strongly heated, when reduction quickly occurs. If the tube is gradually moved downwards so that one part is strongly heated after another, the whole of the SiO_2 is reduced in a few minutes. The contents of the tube are shaken out, pulverised, and treated with HClAq (1:2), the solid being added to the acid in small successive quantities (to prevent explosion from evolution of SiH_4) (Gattermann, *B.* 22, 186). Crystalline silicon.—2. A mixture of 15 parts dry K_2SiF_6, 20 parts dry granulated Zn, and 4 parts dry Na in small pieces is placed in a clay crucible, which is covered and heated to redness; when the reduction of the K_2SiF_6 is effected (there is a visible, but not violent, reaction) the temperature is raised till the mass melts, care being taken not to heat to the b.p. of zinc, else considerable loss will occur. The crucible is broken when cold, the regulus is heated to the m.p. of zinc, the molten zinc is poured off, and SiO_2, Zn, &c., are removed by treatment, in succession, with conc. HClAq, conc. boiling HNO_3Aq, and HFAq. The Si, mixed with a little K_2SiF_6, thus obtained is placed in a crucible and covered with a layer of powdered glass; the crucible is set inside another, and heated to the m.p. of pig-iron (c. 1100°). When all is melted the crucible is allowed to cool to dull redness and is then plunged into water; the regulus is separated from the slag, and is treated with HFAq and then washed with water (Caron, *A. Ch.* [3] 63, 26; Deville a. C., *A. Ch.* [3] 67, 435).—3. A mixture of 1 part Al with 20-40 parts thoroughly dry K_2SiF_6 or Na_2SiF_6 is heated to c. 950° in a Hessian crucible, and the contents are kept molten for c. a quarter of an hour; the crucible is broken when cold, the regulus is separated, crushed, heated with conc. HClAq as long as H is given off, then with HFAq, and washed with water and dried (Wöhler, *A.* 97, 261). Or, a mixture of 10 parts powdered cryolite and 5 parts K_2SiO_3 or powdered glass is divided into two equal parts; one part is placed in a Hessian crucible, 1 part Al is added, the rest of the mixture is placed over this, and the whole is heated to redness for half an hour. The regulus is treated with conc. HClAq, HNO_3Aq, &c., as directed above.

Properties.—Si exists as a brown amorphous powder, and also as greyish-black, very lustrous, octahedral crystals.

Amorphous silicon is a lustrous, brown powder, which adheres to the fingers or to glass tenaciously. The S.G. has not been determined, but the powder is heavier than oil of vitriol; it is a non-conductor of electricity; burns when heated in air or O, but the SiO_2 formed soon stops the process; dissolves in cold HFAq, forming SiF_4 and H; also dissolves in warm alkali solutions; is oxidised with incandescence when thrown into molten nitre; combines with S when warmed therewith. After being strongly heated in a covered Pt crucible, and the SiO_2 formed has been removed by HFAq, amorphous Si is a dark chocolate-brown powder, which is not burnt by heating in air or O, is insol. HFAq and boiling alkali solutions, does not combine with S, and is not acted on by molten KNO_3 or $KClO_3$.

Crystalline silicon is obtained in leaflets or needles. The leaflets are opaque, very lustrous, metal-like, greyish black, resembling graphite; they consist of regular octahedra. The needles are also octahedral. Crystalline Si has S.G. 2·49 at 10° (Wöhler, *J.* 9, 437); 2·194 to 2·197 (Winkler, *J.* 17, 208). Scratches glass, but not topaz. According to Deville (*C. R.* 39, 321) crystalline Si 'conducts electricity like graphite.' M.P. between those of pig-iron and steel, *i.e.* between c. 1100° and c. 1300°. Crystalline Si is not changed when heated, even to whiteness, in O; it is unacted on by HFAq; dissolves in warm alkali solutions; combines with S vapour. When heated in the electric arc crystalline Si melts and then boils, and the ends of the electrodes become covered with crystals of SiC (Moissan, *C. R.* 117, 423).

For the lines in the emission spectrum of Si *v. B. A.* 1884. 441.

Deville (*A. Ch.* [3] 49, 70) thought that a graphite-like form of Si existed different from the ordinary crystalline (or diamond-like) form; but Miller (*P. M.* [3] 31, 397) showed that both the leaflets and the needles consisted of octahedra. Kopp (*A. Suppl.* 5, 72) found differences between the specific heats of crystalline Si and the graphite-like form prepared by the interaction of K_2SiF_6 and Al, and these differences were confirmed by Winkler (*J. pr.* 91, 198).

Warren (*C. N.* 63, 46) thought he had obtained a crystalline form of Si (oblique octahedra) different from the ordinary by the action of impure Al on K_2SiF_6 at a very high temperature; he described the crystals as very perfect, and sometimes half-an-inch across the faces.

Specific heat of silicon. Kopp, Regnault, and others obtained values for the S.H. of Si varying from ·138 to ·173 at c. 30°-100°. In 1875 Weber (*P. M.* [4] 49, 161, 276) showed that S.H. of crystallised Si increased rapidly from −40° to c. 200°, and attained an almost constant value at the latter temperature. Weber's results gave the following values for S.H. of crystallised Si:—

Temp.	S.H.
− 40°	·136
+ 57	·1833
128	·196
184	·2011
232	·2029

The *atomic weight* of Si has been determined (1) by finding the ratio of Si to SiO_2 formed therefrom (Berzelius, *P.* 1, 226 [1824]); (2) by converting $BaSiF_6$ into $BaSO_4$ (B., *P.* 8, 20

[1828]); (3) by ppg. Cl in $SiCl_4$ by Ag (Pelouze, *C. R.* 20, 1047 [1845]; Dumas, *A. Ch.* [3] 55, 183 [1859]); (4) by converting $SiCl_4$ into AgCl (Schiel, *A.* 120, 94 [1861]); (5) by decomposing $SiBr_4$ by water and determining SiO_2 produced (Thorpe a. Young, *C. J.* 51, 576 [1887]); (6) by finding V.D. of SiH_4, $SiCl_4$, $SiBr_4$, SiF_4, &c.; (7) by determining S.H. of Si. The atom of Si is tetravalent in the gaseous molecules SiH_4, $SiCl_4$, $SiBr_4$, SiF_4, $SiHCl_3$, &c. The molecular weight of Si is unknown.

Si is closely related to C, and less closely to Ti, Ge, Zr, Sn, Ce, Pb, and Th (*v.* CARBON GROUP OF ELEMENTS, vol. i. p. 682).

Reactions and Combinations.—I. Amorphous silicon which has not been heated.—1. Heated in *air* or *oxygen* burns to SiO_2, which coats the Si, so that the process soon stops.—2. Heated with *sulphur* forms SiS_2 (Berzelius).—3. In molten *nitre* forms potassium silicate, with incandescence.—4. Dissolves in cold solution of *fluorhydric acid* to form SiF_4 and H.—5. Dissolves in *conc. alkali solutions* on warming, forming H_2SiO_3Aq (or Na_2SiO_3Aq) and H. For differences between amorphous silicon before and after heating, *v. Properties of amorphous silicon*, p. 456.—II. Crystalline silicon.—6. Is not acted on by *oxygen*, nor by *fluorhydric acid*.—7. Heated in dry *chlorine* forms $SiCl_4$; in *bromine* vapour forms $SiBr_4$; in a mixture of *iodine* vapour and CO_2 forms SiI_4; takes fire in *fluorine*, forming SiF_4 (Moissan, *C. R.* 103, 256).—8. Heated with *sulphur* vapour forms SiS_2.—9. Strongly heated in *nitrogen* forms Si_3N_4.—10. Heated to c. 800° in a mixture of *oxygen and chlorine*, Si_2OCl_6 is formed (Troost a. Hautefeuille, *Bl.* [2] 35, 360). 11. Dissolves slowly in warm *alkali solutions* of medium concentration, giving off H.—12. Burns when heated with *alkali carbonates*, separating C, and giving off CO.—13. SiS_2 is produced (according to Sabatier, *Bl.* [2] 38, 153) by heating to bright redness in *hydrogen sulphide.*—14. Schutzenberger (*C. R.* 114, 1089) obtained a mixture of Si_3N_4 and a carbide (to which he gives the formula SiC) by heating to bright redness, in a carbon crucible placed inside another crucible packed with lamp-black, a mixture of 1 part Si and 2 parts SiO_2.—*The following reactions apply generally to silicon.*—15. Heated in *hydrogen chloride* $SiHCl_3$ is formed; in *hydrogen iodide* mixed with H, $SiHI_3$ is produced; and $SiHBr_3$ is obtained by heating in *hydrogen bromide.*—16. Heated with *silicon tetrachloride*, Si_2Cl_6 (and ? $SiCl_2$) is formed.—17. Oxidised by *hydrogen iodide solution* (*v.* Ditte, *Bl.* [2] 13, 322).—18. With *molten caustic soda* or *potash*, H is given off and a silicate formed; similar but slower reactions occur with *baryta* and *lime* (*v.* Berzelius, *A.* 49, 247).—19. Heated with several *metallic oxides*, such as PbO or Ag_2O, reduction occurs, generally with formation of a silicide. If a mixture of powdered Si, Al, and PbO is heated, a violent explosion occurs.—20. According to Colson (*Bl.* [2] 38, 56), Si_2C_2O is formed by heating Si in *carbon dioxide*; SiS, SiSO, and Si_4C_4S are formed by heating Si to white heat in *carbon disulphide*; $SiCO_2$ is formed by heating with *benzene*; and $Si_2C_2O_2$ is produced when Si is *heated to whiteness in a carbon crucible.*

Silicon, amidonitride of. By the interaction of NH_3 and $SiCl_4$ or SiF_4 Harris (*C. C.* 1889 [ii.] 283) obtained a snow-white powder, to which he gave the formula $Si.NH_2.N$.

Silicon, carbide of. According to Schutzenberger (*C. R.* 114, 1089), a compound of Si and C, having the composition of SiC, is formed along with a little Si_3N_4, by placing a mixture of 1 part crystallised Si and 2 parts SiO_2 in a covered gas-carbon crucible, imbedding this in lamp-black in a larger crucible, and this again in more lamp-black in another larger crucible, and heating to bright redness for some hours; boiling with moderately conc. HFAq dissolves SiO_2 and Si_3N_4, and leaves the SiC. Heated to low redness in *chlorine*, SiC is said to give $SiCl_4$ and C. Moissan (*C. R.* 117, 425) obtained colourless crystals of SiC by fusing C and Si in an electric furnace. The crystals are very hard, act strongly on polarised light, S.G. 3·12; they are not acted on by O or S vapour at 1000°; Cl begins to react at c. 600° and the action is complete at 1200°; the crystals are not acted on by boiling HClAq, HNO_3, H_2SO_4, *aqua regia*, or a mixture of HNO_3 and HFAq, nor by fused KNO_3 or $KClO_3$; molten KOH gradually forms K_2CO_3 and K silicate.

Silicon, bromides of. Two bromides of Si are known, Si_2Br_6 and $SiBr_4$.

DISILICON HEXABROMIDE Si_2Br_6. (*Silicon tribromide* $SiBr_3$.) Formula probably molecular from analogy of Si_2Cl_6. A colourless liquid, boiling at c. 240°. Formed by adding the proper quantity of Br to Si_2I_6 in CS_2, pouring off from I, purifying by shaking with Hg, filtering in dry air, and fractionating (Friedel a. Ladenburg, *A.* 203, 254).

SILICON TETRABROMIDE $SiBr_4$. Mol. w. probably 347·3.

Preparation.—Amorphous Si, prepared as described under SILICON, *Preparation*, No. 1 (p. 456), after being partially purified from SiO_2 by HClAq, washing, and drying, is heated in a glass tube, while Br vapour is passed over it; the tube passes into a small flask, which is surrounded by cold water. A mixture of $SiBr_4$ and Br collects in the flask; this is fractionated, and the last traces of Br are removed by shaking with Hg and distilling (Gattermann, *B.* 22, 186). $SiBr_4$ may also be prepared by heating a mixture of SiO_2 and C (*cf.* SILICON TETRACHLORIDE, p. 458) in Br, shaking with Hg, and fractionating (Serullas, *P.* 24, 341; modified by Reynolds, *C. J.* 51, 590).

Properties and Reactions.—A colourless liquid, having a disagreeable odour, and fuming much in air. S.G. 2·8128 at 0°. B.p. 153·4° at 762·5 mm. (Pierre, *A. Ch.* [3] 20, 26; Freyer a. Meyer, *Zeit. für anorgan. Chemie*, 2, 1); 148° to 150° (Serullas, *l.c.*). Solidifies at c. −12°. (F. a. L., *l.c.*). Decomposed by *water* to HBrAq and SiO_2; shaken with *conc. sulphuric acid*, slowly changes to Br and SiO_2. Heated to 250° with *lead oxide* gives $PbBr_2$ and Pb silicate (Friedel a. Ladenburg, *A.* 147, 362). *Ammonia* probably forms $SiBr_4.NH_3$ (Persoz, *A. Ch.* [2] 44, 315). *Phosphorus hydride* forms a white amorphous compound, by repeated compression with $SiBr_4$, the pressure being maintained for some hours (Besson, *C. R.* 110, 240).

For the compounds $SiBr_3H$ and Si_2Br_5H *v.*

SILICOBROMOFORM, and SILICO-ETHANE, PENTABROMO- DERIVATIVE OF, pp. 453, 454.

Silicon, bromochlorides of. Three compounds of Si with Br and Cl have been isolated. The V.D. of $SiBr_3Cl$, and also that of $SiBrCl_3$, has been determined; the formulæ of all are probably molecular.

SILICON BROMO-TRICHLORIDE $SiBrCl_3$. Mol. w. 214·16. A colourless liquid, boiling at c. 80°, fuming in air, and decomposed by water. Prepared by heating Br and $SiHCl_3$ at 100°; $SiHCl_3+Br_2=SiBrCl_3+HBr$ (Friedel a. Ladenburg, *A.* 145, 187). Also by the interaction of Br and $SiCl_3SH$ (? $SiCl_3SH+3Br=SiBrCl_3+SBr+HBr$) (F. a. L., *l.c.* p. 179). V.D. 104·7 at c. 130° (F. a. L., *l.c.*). Reacts with NH_3 to form an amorphous compound, $2SiBrCl_3.11NH_3$, easily decomposed by water (Besson, *C. R.* 112, 788).

SILICON DIBROMO-DICHLORIDE $SiBr_2Cl_2$. A colourless liquid, boiling at 103°–105°, and not solidifying at −60°. Prepared by heating $SiHCl_3$ and Br above 100° (F. a. L., *l.c.*). Also by passing the vapour of HBr and $SiCl_4$ through a red-hot porcelain tube (Besson, *l.c.*). Combines with NH_3 to form $SiBr_2Cl_2.5NH_3$, decomposed by water.

SILICON TRIBROMO-CHLORIDE $SiBr_3Cl$. Mol. w. 302·92. A colourless liquid, fuming in air, boiling at 140°–141°, not solidifying at −40°; S.G. 2·432. V.D. 150·5 at c. 185° (Reynolds, *C. J.* 51, 590). Obtained, along with SBr_4, by passing Br vapour over a mixture of SiO_2 and C heated in a wind-furnace, passing dry H through the warm product, shaking with Hg, and fractionating (R., *l.c.*). Besson (*C. R.* 112, 788) seems to haye obtained the same compound, along with $SiBr_2Cl_2$, by passing the vapours of HBr and $SiCl_4$ through a red-hot porcelain tube. B. gives the b.p. 126°–128°, and m.p. −39°; he says a compound $SiBr_3Cl.11NH_3$ is formed by interaction with NH_3.

Silicon, bromo-iodides of, *v.* SILICON IODOBROMIDES, p. 461.

Silicon, chlorides of. Two chlorides of Si have been isolated with certainty, Si_2Cl_6 and $SiCl_4$; these formulæ are molecular. There are indications of the existence of another chloride, $SiCl_2$.

SILICON HEXACHLORIDE Si_2Cl_6. (*Silicon trichloride* $SiCl_3$.) Mol. w. 268·22.

Preparation.—1. By heating $HgCl_2$ with Si_2I_6, fractionating, and distilling the portion boiling at 146°–148° from $HgCl_2$ (Friedel a. Ladenburg, *A.* 203, 253).—2. Vapour of $SiCl_4$ is passed over Si kept molten in a porcelain tube ($3SiCl_4+Si=2Si_2Cl_6$); the product is rapidly cooled, and fractionated from $SiCl_4$, Si oxychlorides (and ? $SiCl_2$) (Troost a. Hautefeuille, *A. Ch.* [5] 7, 459).

Properties.—A colourless, mobile liquid, boiling at 146°–148°; S.G. 1·58 at 0°; solidifies at −14° to large leaflets, which melt at 1° (F. a. L., *l.c.*). V.D. 140 at c. 240° (T. a. H., *l.c.*). Fumes in air, decomposed by water; vapour takes fire when Si_2Cl_6 is heated in air.

Reactions and Combinations.—1. Decomposed to $SiCl_4$ and Si by *heat* in a closed tube; decomposition is extremely slow at 350°, nearly complete at 800°; heated rapidly above 1000° the dissociation-pressure falls; the compound is stable below 350° and above 1000° (T. a. H., *l.c.*).—2. Decomposed by *water*. At ordinary temperatures products remain in solution, and are ppd. by NH_3Aq; at 0° $Si_2H_2O_4$ is formed (*v.* SILICO-OXALIC ACID, p. 463) (F. a. L., *l.c.*).—3. *Caustic potash* forms SiO_2 and gives off H (F. a. L., *A.* 203, 254).—4. *Phosphorus hydride* is changed to the solid hydride at −10° (Besson, *C. R.* 110, 516).—5. Combines with *ammonia* to form $Si_2Cl_6.5NH_3$ (B., *l.c.*).

SILICON TETRACHLORIDE $SiCl_4$. Mol. w. 169·78. Boils at 57·57° at 760 mm. pressure (Thorpe, *C. J.* 37, 327). S.G. $\frac{0°}{4°}$ 1·52408 (T., *l.c.*). V.D. 85·5 at 100° (Dumas, *A. Ch.* [2] 33, 368). S.H. of $SiCl_4$ vapour, at 90° to 234°, =·1322, at constant pressure, referred to equal weight of water; ·12, at constant volume, referred to equal weight of water (Regnault, *Acad.* 26, 1). Regnault (*l.c.*) gives the vapour-pressures of $SiCl_4$ as follows:—

Temp.	Vapour-pressure.
−20°	26·49 mm. mercury
−10	46·46 ,, ,,
0	78·02 ,, ,,
+10	125·90 ,, ,,
20	195·86 ,, ,,
30	294·49 ,, ,,
40	429·08 ,, ,,
50	607·46 ,, ,,
60	837·23 ,, ,,

H.F. $[Si,Cl^4]=157,640$ (Troost a. Hautefeuille, *A. Ch.* [5] 9, 70).

Formation.—1. By passing dry Cl, or HCl gas, over a mixture of SiO_2 and C at full red heat (Oerstedt, *B. J.* 6, 119; Deville, *A. Ch.* [3] 43, 23). According to Weber (*P.* 112, 649) C is not necessary if the temperature is high enough. 2. By heating crystalline Si, or Si containing H, in Cl (Berzelius, *C. J.* 4, 91).—3. Favre (*C. R.* 107, 339) heats impure Si, and passes HCl and vapour of naphthalene over it.—4. By heating iron containing c. 15 p.c. Si in Cl (Warren, *C. N.* 60, 158).—5. By passing vapour of BCl_3 over SiO_2 heated to dull redness ($4BCl_3+3SiO_2=3SiCl_4+2B_2O_3$; Troost a. Hautefeuille, *A. Ch.* [5] 7, 476).

Preparation.—1. Amorphous SiO_2 is mixed with an equal weight of lampblack, and the mixture is made into a paste with oil. Small pellets are made of this paste; these are imbedded in charcoal powder, and strongly heated. The dry pellets are placed in a porcelain tube, which is heated to very bright redness in a furnace while a stream of Cl (dried by H_2SO_4 and then by $CaCl_2$) is passed through. The exit end of the porcelain tube is connected with a U-tube, from the bottom of the bend of which a short tube passes down into a small flask; the U-tube and small flask are surrounded by a freezing mixture. The $SiCl_4$ which condenses in the flask is shaken in a dry flask with Hg and a few pieces of K, and then distilled with sodium.

L. Meyer (*A.* 270, 238) recommends the use of charcoal-powder in place of lampblack, and starch-paste rather than oil.—2. Gattermann (*B.* 22, 186) places impure amorphous Si (containing some Mg, &c.), prepared as described under SILICON, *Preparation*, No. 1, in a tube a

2 cms. wide, leaving a space of c. 1 cm. above the Si along the tube; he bends this tube at right angles, and connects it with a U-tube placed in a freezing mixture; he then passes dry Cl through the apparatus, while he heats the tube, laid in an iron trough in a gas-furnace so that the tips of the flames just touch the iron trough. The temperature must not get too high, else the Si glows, and $MgCl_2$ and O are formed, and the O oxidises the Si to SiO_2.

Properties.—A colourless, very clear, and very mobile liquid, with a disagreeable odour resembling that of cyanides; reddens litmus; fumes in moist air. Does not become viscid at −75° (Haase, *B.* 26, 1052).

Reactions and Combinations.—1. Heated to redness with *hydrogen* a little $SiHCl_3$ is formed (Friedel a. Ladenburg, *Bl.* [2] 12, 92).—2. Oxychlorides are produced by the action of *oxygen* under the influence of induction sparks (Troost a. Hautefeuille, *A. Ch.* [5] 7, 465).—3. $SiCl_4$ is decomposed by passing the vapour with dry *air* through a white-hot tube, giving Si_2OCl_6 and Cl (F. a. L., *l.c.*). Berthelot (*A. Ch.* [5] 15, 185) says that SiO_2 is also produced.—4. *Water* produces H_2SiO_3 and HClAq.—5. *Hydrogen sulphide* forms $SiCl_3.SH$, when $SiCl_4$ and H_2S are passed through a red-hot tube (F. a. L., *A.* 145, 179; Pierre, *A. Ch.* [3] 24, 300).—6. Many *metals*—*e.g.* K, Na, Zn, Ag—withdraw all Cl from $SiCl_4$ when heated to redness in vapour of $SiCl_4$ (F. a. L.; *cf.* Rauter, *A.* 270, 235).—7. Most *metallic oxides* form SiO_2 and metallic chlorides when heated with $SiCl_4$ (R., *l.c.*); CaO, MgO, Al_2O_3, and BeO form silicates and crystalline SiO_2 (Daubrée, *C. R.* 39, 135); TiO_2 is not changed (T. a. H., *A. Ch.* [5] 7, 476).—8. Decomposed by heating with *alkali carbonates*, *potassium chlorate* or *nitrate*, and various oxidising salts (R., *l.c.*).—9. SiO_2 and HCl are produced by reaction with *sulphuric acid.*—10. *Ammonia* forms $SiCl_4.6NH_3$ (Persoz, *A. Ch.* [2] 44, 315); also, according to Gattermann (*B.* 22, 194), $Si.NH_2.N$.—11. *Phosphoretted hydrogen* does not react at ordinary temperatures; but at −40° c. 40 vols. of PH_3 are absorbed by $SiCl_4$, forming a solution which does not solidify at −60° (Besson, *C. R.* 110, 240). A colourless crystalline compound is produced by compressing PH_3 and $SiCl_4$ and then decreasing pressure to 20 atmospheres at 10° (B., *l.c.*).—12. Heated with *sodium silicate*, NaCl is formed. If $SiCl_4$ vapour is passed through a tube containing fragments of *felspar*, at a white heat, KCl, SiO_2, and Si_2OCl_6 are formed (F. a. L., *l.c.*).

For the compound $SiHCl_3$ *v.* Silico-chloroform, p. 453.

? Silicon dichloride $SiCl_2$. In the preparation of Si_2Cl_6 by the reaction of $SiCl_4$ with Si, Troost a. Hautefeuille (*A. Ch.* [5] 7, 463) obtained a liquid which took fire when heated in air, and reacted with ice-cold water to form a hydroxide of Si having reducing properties.

Silicon, chlorobromides of, *v.* Silicon bromochlorides, p. 458.

Silicon, chlorohydrosulphide of, $SiCl_3.SH$. (*Trichloro-silico-mercaptan.*) Mol. w. 167·39. This compound may be looked on as a derivative of hypothetical ortho-thio-silicic acid $Si(SH)_4$, obtained by replacing 3SH by 3Cl.

Prepared by passing dry H_2S into $SiCl_4$ in a retort, and then passing the mixed vapours of H_2S and $SiCl_4$ through a red-hot porcelain tube connected with a receiver surrounded by a freezing mixture, and fractionating the liquid that condenses (Friedel a. Ladenburg, *A.* 145, 179). Colourless liquid, with sharp, disgusting smell; boils at 96°; S.G. 1·45. V.D. 83·5 at c. 167°. Decomposed by *moist air*, more rapidly by *water*, to H_2S, S, HClAq, and $SiO_2.xH_2O$; *bromine* produces $SiBrCl_3$ and HBr. *Alcohol* in excess forms $Si(OEt)_4$, H_2S, and HCl; by reacting in the ratio $3EtOH : SiCl_3.SH$, F. a. L. (*l.c.*) obtained a liquid boiling at 164°–167°, probably $Si(OEt)_3.SH$; this liquid could not be obtained pure, as it changed to $Si(OEt)_4$, HCl, and H_2S.

Silicon, chloro-iodides of, *v.* Silicon iodochlorides, p. 461.

Silicon, compounds of, with carbon and oxygen. According to Colson (*Bl.* [2] 38, 56), the compound $SiCO_3$ is formed by heating Si with benzene vapour, the compound $Si_2C_3O_2$ by heating Si to whiteness in a carbon crucible, and the compound Si_2C_2O by heating Si in CO_2.

Silicon, compound of, with carbon and sulphur. Colson (*Bl.* [2] 38, 56) says that a compound, to which he gives the formula Si_4C_4S, is produced by heating Si to a white heat in CS_2 vapour.

Silicon, compounds of, with hydrogen and oxygen. The compounds of the form $SiO_2.xH_2O$ are described under Silica, hydrates of (p. 447); the compounds $Si_2H_2O_3$ and $Si_2H_2O_4$ are described as *silico-formic anhydride* and *silico-oxalic acid* respectively (pp. 455, 463). Wöhler (*A.* 127, 257) obtained a substance, by the decomposition of impure Ca silicide by HClAq, to which he gave the name *silicone*, and either the composition $Si_4H_4O_3$ or $Si_3H_3O_2$. On account of the yellow colour of this body, Miller proposed to call it *chryseone.* Silicone is described as orange-yellow leaflets, insol. water, alcohol, CS_2, $SiCl_4$, or PCl_3; when heated below redness it takes fire, burning to SiO_2 and amorphous Si; heated out of air, H is given off and SiO_2 and amorphous Si remain; not acted on by Cl, fuming HNO_3, or conc. H_2SO_4; caustic alkali solutions, even dilute NH_3Aq, produce SiO_2 with rapid evolution of H; acts as an energetic reducer towards solutions of many metallic salts.

Silicon, fluorides of. The existence of any compound of Si and F except SiF_4 is doubtful. Troost a. Hautefeuille (*A. Ch.* [5] 7, 464) obtained a fine dust by passing SiF_4 over molten Si and suddenly cooling, which was probably a lower fluoride than SiF_4.

Silicon tetrafluoride SiF_4. Mol. w. 104·3.

Formation.—1. By passing BF_3 vapour through a red-hot porcelain tube (Troost a. Hautefeuille (*A. Ch.* [5] 7, 464).—2. By the interaction of HFAq and SiO_2 or silicates.

Preparation.—A fair-sized flask is one-third filled with a mixture of equal parts of powdered CaF_2 and quartz or white sand; sufficient conc. H_2SO_4 is added to thoroughly moisten the mixture; the flask is gently warmed, and the gas that comes off is collected over Hg ($2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4$).

Properties.—A colourless gas, with a disagreeable odour and sour taste; reddens dry litmus paper; fumes strongly in air. V.D. 51·9

(Dumas, *A. Ch.* [2] 33, 368). Condensed to a colourless mobile liquid at −106·5° and 9 atmos. pressure (Faraday, *T.* 1845. 155). According to Olszewski (*M.* 5, 127) SiF_4 solidifies at −102°. Acts as a powerful poison (*v.* Cameron, *Dublin J. of Med. Sci.* Jan. 1887).

Reactions.—1. Decomposed by *electric sparks* with separation of Si (T. a. H., *C. R.* 43, 443).—2. *Potassium* and *iron*, when hot, burn in SiF_4, forming fluorides and Si.—3. *Moist air* forms $Si_2O_3F.OH$ (Landolt, *A. Suppl.* 4, 27, and *v.* DIMETASILICIC FLUORHYDRIN, *infra*).—4. *Water* absorbs SiF_4, forming $SiO_2.xH_2O$ and H_2SiF_6Aq (*v.* SILICOFLUORHYDRIC ACID, p. 454).—5. *Ammonia* forms $SiF_4.2NH_3$ (J. Davy, *T.* 1812. 352); also, according to Harris (*C. C.* 1889 (ii.) 283), $SiNH_2.N$ (*v.* SILICON AMIDONITRIDE, p. 457).

Combinations.—1. Combines with dry *phosphoretted hydrogen*, when the gases are strongly compressed at −22° and 50 atmospheres in the ratio $2PH_3:3SiF_4$, to form lustrous crystals (Besson, *C. R.* 110, 80).—2. *Alcohol* absorbs SiF_4 freely, forming an acid liquid which gives off SiF_4 in the air (Knop, *J.* 1858. 146).—3. SiF_4 is absorbed by many *metallic oxides*.

Dimetasilicic fluorhydrin $Si_2O_3.OH.F$. Landolt (*A. Suppl.* 4, 27) obtained this compound as a white crystalline solid (*v.* also Schiff, *J.* 1865. 196).

Silicon, haloid compounds of. The compounds of Si with halogens belong to the forms Si_2X_6 and SiX_4; the compounds SiX_4, where X is a single halogen, have been gasified, and the compound Si_2Cl_6 has also been gasified. The formulæ are probably all molecular. There are also indications of the existence of some compounds of the type SiX_2. Besides the compounds where X is a single halogen, there exist the compounds $SiXX'_3$, $SiX_2X'_2$, and $SiX'X_3$, where X and X′ are Br and Cl, I and Cl, and I and Br respectively; the only one of these compounds that has been gasified is $SiBr_3Cl$.

Silicon, hydrides of. The compound SiH_4 has been isolated and examined. The existence of another hydride, probably Si_2H_3, is likely.

SILICON TETRAHYDRIDE SiH_4. (*Siliciuretted hydrogen.*) Mol. w. 32·3. Si and H do not combine directly, even in the electric arc (Friedel, *C. R.* 73, 497).

Formation.—1. Al containing Si is made the positive pole in NaClAq (Buff a. Wöhler, *A.* 103, 218).—2. Crude Mg silicide is decomposed by dilute HClAq (*v. Preparation*). These processes yield mixtures of SiH_4 and H.—3. By the reaction of Na with $SiH(OEt)_3$ (*v. Preparation*).

Preparation.—1. Small pieces of Na are dropped into $SiH(OEt)_3$ (*v. infra*), and the liquid is gently warmed; the escaping gas is allowed to drive out the air (if the Na or $SiH(OEt)_3$ was moist H comes off, and the gas takes fire), and is then collected over Hg (Friedel a. Ladenburg, 143, 123). The $SiH(OEt)_3$ is prepared by adding dry absolute alcohol to pure $SiHCl_3$, in a long-necked flask, in the ratio $3EtOH : SiHCl_3$, distilling after some time, and collecting the liquid that boils from 134° to 137°.—2. Impure SiH_4, mixed with considerable quantities of H, is prepared by placing coarsely-pulverised crude Mg silicide (for preparation, *v. infra*) in a small two-necked flask, fitted with a funnel tube and a short *wide* delivery tube; the flask and delivery tube are quite filled with water from which all air has been driven out by boiling, the delivery tube is made to dip under boiled water, and the bell-jar to receive the gas is filled with boiled water; conc. HClAq is added, little by little, by the funnel tube. The gas, which comes off very rapidly, is collected in a bell-jar fitted with a stop-cock; this jar is then connected with a U-tube containing $CaCl_2$ and carrying a short, narrow piece of glass tubing, which is made to dip under a dry vessel full of Hg. By depressing the bell-jar, the gas is forced out; it burns in the tubes till the air is exhausted, when it passes into the vessel full of Hg, where it is collected.

Preparation of the crude Mg silicide. A mixture of 1 part finely-powdered, dry, white sand and 1½ parts Mg powder is heated in a stout glass tube; reduction takes place with production of much light, and a blue-grey, semi-molten mass is obtained (Gattermann, *B.* 22, 186). For other methods of preparing the Mg silicide required, *v.* Wöhler (*A.* 137, 369), Warren (*C. N.* 58, 215), and Mermet (*Bl.* [2] 47, 306).

Properties.—A colourless gas; insol. water; liquefied at −11° and 50 atmos., −7 and 70 atmos., or −1° and 100 atmos. pressure (Ogier, *A. Ch.* [5] 20, 5). V.D. 15·9 (F. a. L., *A.* 143, 123). H.F. $[Si,H^4]$ = 32,900 (O., *l.c.*). Does not react with N, NO, NH_3, H_2SO_4Aq, or HClAq.

Reactions.—1. Decomposed completely to Si and H by *heating* to above 400° (O., *l.c.*).—2. *Induction sparks* cause increase of volume from 100 to 121–129; H is produced, and yellow solid separates, probably Si_2H_3 (*v.* DISILICON TRIHYDRIDE, *infra*).—3. SiH_4 takes fire in *air* when slightly heated, or when the pressure is decreased; if the pure gas is passed into a tube filled with Hg, the pressure is lowered to 100–150 mm., and air is admitted, the gas takes fire (F. a. L., *l.c.*). The gas as prepared from Mg silicide is mixed with H, and takes fire in air at ordinary temperature and pressure.—4. Burns in *chlorine* with violent explosion.—5. Conc. *potash solution* forms K_2SiO_3 and H; the volume of H is four times that of the SiH_4 ($SiH_4 + 2KOHAq + H_2O = K_2SiO_3 + 8H$) (F. a. L., *l.c.*).—6. Reduces solutions of many *metallic salts*; ppts. Ag and Si from $AgNO_3Aq$, Pd from Pd salts, Cu silicide from $CuSO_4Aq$, &c. Does not react with $PtCl_4Aq$ or $Pb(C_2H_3O_2)_2Aq$.—7. The action of *electric discharges* on SiH_4 *mixed with nitrogen* produces NH_3, and (?) Si_2H_3 which combines with some of the N (Ogier, *A. Ch.* [5] 20, 31).

DISILICON TRIHYDRIDE Si_2H_3. This formula is given by Ogier (*A. Ch.* [5] 20, 31) to a yellow solid obtained by the action of induction sparks on SiH_4. The composition of the substance is somewhat doubtful. It takes fire when rubbed or heated in air; heated in H or N, inflammable SiH_4 is produced, or at higher temperatures Si and H are formed.

Silicon hydrogen bromides *v.* SILICO-BROMOFORM, p. 453, and SILICO-ETHANE, PENTABROMO-DERIVATIVE OF (Si_2HBr_5), p. 454.

Silicon hydrogen chloride *v.* SILICO-CHLOROFORM, p. 453.

Silicon hydrogen iodide *v.* Silico-iodoform, p. 455.

Silicon, hydroxides of, *v.* Silica, hydrates of, p. 447; Silico-formic acid, p. 455; Silico-formic anhydride, p. 455; Silico-oxalic acid, p. 463; and *Silicone*, under Silicon, compounds of, with hydrogen and oxygen, p. 459.

Silicon, iodides of. Two compounds have been isolated, SiI_4 and Si_2I_6, and a third, which is probably SiI_2, seems also to exist.

Silicon tetra-iodide SiI_4. Mol. w. 534·42. Melts at 120·5°; boils at 290°. V.D. at 360° = 268·5. H.F. $[Si,F^4] = 58,000$ (Berthelot).

Preparation.—1. The crude product obtained by reducing a mixture of 4 parts fine white sand by heating with 1 part Mg powder (*v.* Silicon, *Preparation of*, No. 1, p. 456) is strongly heated in a mixture of dry CO_2 and I vapour, in a tube which projects c. 20 cm. from the furnace; SiI_4 collects in the cold part of the tube, it is dissolved in CS_2 (1 part CS_2 dissolves c. 2·2 parts SiI_4), shaken with Hg till colourless, and the CS_2 is evaporated by passing dry CO_2 through it at the lowest possible temperature (Gattermann, *B.* 22, 190).—2. A mixture of CO_2 and I vapour is passed over Si strongly heated in a porcelain tube; the SiI_4 that collects in the cold part of the tube is purified as in 1 (Friedel, *A.* 149, 96).

Properties and Reactions.—Colourless, transparent, regular octahedra; isomorphous with CI_4. (For M.P., &c., *v. supra.*) The vapour burns when *heated in air*, with separation of I. *Water* produces $SiO_2.xH_2O$ and HIAq. *Alcohol* forms EtI, HI, and SiO_2. *Ether*, at 100°, produces $Si(OEt)_4$ and EtI (F., *l.c.*).

Silicon hexa-iodide Si_2I_6. Formula probably molecular, from analogy of Si_2Cl_6. Prepared by heating SiI_4 with finely-divided Ag (formed by reducing AgCl) to 290°–300° for some hours, removing SiI_4 by washing with a little dry CS_2 (1 part CS_2 dissolves c. ·26 parts Si_2I_6 and c. 2·2 parts SiI_4), dissolving in much hot CS_2, and crystallising (Friedel a. Ladenburg, *A.* 203, 254). Colourless, six-sided, double refractive plates. Melts at 250° *in vacuo*, with partial decomposition. When heated, decomposes to SiI_4, and a substance that is probably SiI_2. Fumes in air; with water gives $H_2Si_2O_4$ and HIAq.

Silicon di-iodide. The yellow solid that is formed by heating SiI_4 is probably SiI_2; it is insol. in the ordinary solvents; with water becomes grey, perhaps forming H_2SiO_2 (*v.* Silico-formic acid, p. 455) (Friedel a. Ladenburg, *A.* 203, 247).

For the compound $SiHI_3$ *v.* Silico-iodoform, p. 455.

Silicon, iodobromides of. Three compounds, corresponding with the three bromochlorides and the three iodochlorides, are formed by passing IBr (alone or mixed with H) over crystalline Si heated to dull redness; also by passing the vapour of a solution of I in $SiBr_4$ over crystalline Si at a low red heat (Besson, *C. R.* 112, 1447). The compounds are solids which decompose in air with separation of I; they all combine with NH_3 to form white compounds that are decomposed by water.

Silicon iodotribromide $SiIBr_3$. Melts at 14° and boils at 192°. Prepared as described above, also (probably) by the interaction of I and $SiHBr_3$ at 200°–250°, also by passing HI over $SiBr_4$ heated to low redness (B., *l.c.*).

Silicon di-iododibromide SiI_2Br_2. Melts at c. 38° and boils at 230°–231°.

Silicon tri-iodobromide SiI_3Br. Melts at c. 55° and boils at c. 255°.

Silicon, iodochlorides of. Three compounds have been isolated, corresponding with the three bromochlorides, and the three iodobromides. The V.D. of none has been determined, but from the analogy with the bromochlorides the simplest formulæ are probably molecular.

Silicon iodotrichloride $SiICl_3$. Obtained by passing HI mixed with $SiCl_4$ vapour through a red-hot tube, also by the interaction of HI and $SiHCl_3$ at 200°–250°, also by distilling ICl over crystallised Si heated to redness (Besson, *C. R.* 112, 60, 1314). A colourless liquid, boiling at 113°–114°; fumes in air; decomposed by water; I separates on standing, especially in sunlight. With NH_3 forms white amorphous $2SiICl_3.11NH_3$.

Silicon di-iododichloride SiI_2Cl_2. Formed from HI and $SiCl_4$, also from ICl and Si; also by heating HI with SiI_3Cl at 250°. Colourless liquid, boiling at 172°. With NH_3 forms amorphous $SiI_2Cl_2.5NH_3$ (B., *l.c.*).

Silicon tri-iodochloride SiI_3Cl. A solid obtained in preparation of the two former compounds; melts at 2°. Fumes in air, with separation of I.

Silicon, nitrides of. Schutzenberger (*C. R.* 114, 1089) obtained small quantities of a compound to which he gave the formula Si_3N_4, along with a carbide of Si, by heating 1 part Si and 2 parts SiO_2 in a covered carbon crucible, imbedded in lampblack in an outer crucible, to bright redness for some hours. By passing NH_3 through a porcelain tube kept at a white heat, Colson (*C. R.* 94, 1710) found a black layer in the hottest part of the tube, which was probably a mixture of Si and nitride of Si. A compound of Si, N, and H, probably $Si.NH_2.N$, was obtained by Harris (*C. C.* 1889 (ii.) 283) by the reaction of NH_3 with $SiCl_4$ or SiF_4.

Silicon, oxide of, SiO_2; *v.* Silica, p. 446.

Silicon, oxychlorides of. The compound Si_2OCl_6 is formed by heating $SiCl_4$ vapour in air or O. According to Troost a. Hautefeuille (*Bl.* [2] 35, 360) several oxychlorides are formed by passing a mixture of $SiCl_4$ vapour and O through a red-hot tube, or, better, by passing a mixture of 1 vol. Cl and $\frac{1}{5}$ to $\frac{1}{2}$ vol. O over crystalline Si heated to not above 800°. T. a. H. isolated the following oxychlorides:—

$Si_4O_3Cl_{10}$; liquid, b.p. 152°–154°.
$Si_4O_4Cl_8$; liquid, b.p. 198°–202°.
$Si_2O_3Cl_2$; oily liquid, b.p. above 400°.
$Si_4O_7Cl_2$; solid, m.p. above 400°.

Silicon oxychloride Si_2OCl_6. (*Perchloro-silico-methyl ether* $(SiCl_3)_2O$.) Mol. w. 284·78. Prepared by passing vapour of $SiCl_4$ through a porcelain tube heated in a wind furnace burning coke, condensing the product, repeating the operation with the portion which boils above 70°, fractionating, and separating the liquid boiling at 137°–138° (Friedel a. Ladenburg, *A.* 147, 355). A colourless liquid, boiling at 137°–138°. V.D. 144 at c. 200°. Fumes in air, decomposed by water to HClAq and $SiO_2.xH_2O$. Miscible in all proportions with $CHCl_3$, CCl_4, CS_2,

$SiCl_4$, and Et_2O. Alcohol produces $Si_2O_7(Et)_6$; zinc-ethide at 180° forms $SiEt_4$ and Si_2OEt_6 (F. a. L., *l.c.*).

The compound $SiP_2O_8Cl_2$ is described as SILICOPHOSPHORIC OXYCHLORIDE (p. 461).

Silicon, oxysulphide of. According to Colson (*Bl.* [2] 38, 56), a compound SiOS is formed, along with SiS and Si_4SC_4, by heating Si to white heat in CS_2.

Silicon, sulphides of. The only compound of Si and S certainly isolated is SiS_2. Colson (*Bl.* [2] 38, 56) says that *silicon monosulphide*, SiS, is produced, along with SiOS and Si_4SC_4, by heating Si to white heat in CS_2; he describes SiS as a yellow solid, decomposed by water giving off H_2S, sol. in very dilute KOHAq with evolution of H. SiS is also said to be formed, along with SiS_2, by heating Si to redness in H_2S (Sabatier, *Bl.* [2] 38, 153).

SILICON DISULPHIDE SiS_2. Mol. w. not determined. Sabatier (*Bl.* [2] 38, 153) gives H.F. $[Si,S^2]=19,900$. *Amorphous* Si and S combine when strongly heated (Berzelius). Prepared by heating Si to redness in a stream of dry H_2S; the other products are a yellow solid, probably SiS, and a brown substance that is likely a mixture of SiS_2 and SiS, or of SiS_2 and Si (S., *l.c.*; *v.* also Fremy, *A. Ch.* [3] 38, 324). Also prepared by strongly heating dried pellets of oil and SiO_2 (separated from SiF_4) in a slow stream of dry CS_2, quickly separating the white needles that form on the cooler part of the tube, and keeping in a closed tube (Fremy, *l.c.*). The residue that remains on distilling the products of the interaction of $SiCl_4$ and H_2S (*v.* SILICON CHLOROHYDROSULPHIDE, p. 459) contains SiS_2 and S; S may be removed by carefully heating in a stream of N (Gay-Lussac a. Thénard, *A. Ch.* [2] 69, 204). Long, lustrous, white needles; volatilised at very high temperatures (Fremy, *l.c.*). Unchanged in dry air at ordinary temperatures; decomposed by moist air to H_2S, and crystalline SiO_2 pseudomorphous with SiS_2; burns to SO_2 and SiO_2 when heated in air. Decomposed rapidly by water to $SiO_2.xH_2O$ and H_2S; also decomposed by alcohol and ether (Fremy, *l.c.*). HNO_3 oxidises rapidly, producing H_2SO_4. M. M. P. M.

Silicon, sulphocyanide of; *v.* p. 463.

SILICON, ORGANIC COMPOUNDS OF.

Silicic ethers are described elsewhere—*v.* AMYL, AMYLPHENYL, ETHYL, METHYL, PHENYL, THYMYL, TOLYL, and XYLYL SILICATES.

Tetra-methyl-silicane $SiMe_4$. Mol. w. 88. (31°). V.D. 3·08 (calc. 3·04). Formed by heating $SiCl_4$ with $ZnMe_2$ at 120° (Friedel a. Crafts, *A.* 136, 203). Light oil, burning with bright flame emitting SiO_2. Not attacked by potash or HNO_3 (S.G. 1·4).

Tetra-ethyl-silicane $SiEt_4$. Mol. w. 144. (153°). V.D. 5·13 (calc. 4·99). S.G. $\frac{0}{0}$ ·834. Prepared by heating $SiCl_4$ with $ZnEt_2$ at 160°. Formed also by the action of $ZnEt_2$ and Na on ethyl silicate (Friedel a. Crafts, *Bl.* 1863, 468; 1865, 358; *A.* 127, 31; 138, 19). Oil, insol. H_2SO_4. Chlorine forms liquid $Et_3SiC_2H_4Cl$ (185°), converted by alcoholic KOAc at 180° into $Et_3SiC_2H_4OAc$ (208°–214°), whence alcoholic potash at 120° forms oily $Et_3SiC_2H_4OH$ (190°).

Hexa-ethyl di-silicane Si_2Et_6. (252°). S.G. $\frac{0}{0}$ ·851; $\frac{20}{20}$ ·840. V.D. 8·6 (calc. 7·96). Formed by distilling Si_2I_6 with $ZnEt_2$ (Friedel a. Ladenburg, *A.* 203, 251). Oil, burning with bright flame.

'Silicopropionic acid' EtSiO.OH. Got by heating its ortho- ether with HIAq (Ladenburg, *A.* 159, 271; 164, 305). Amorphous powder, insol. water and Na_2CO_3Aq, sol. conc. KOHAq.

Methyl ortho- ether $EtSi(OMe)_3$. (126°). S.G. $\frac{0}{0}$ ·9747. Formed from $Si(OMe)_4$, sodium, and $ZnEt_2$ (Ladenburg, *B.* 5, 1081). Oil.

Ethyl ortho- ether $EtSi(OEt)_3$. (159°). S.G. $\frac{0}{0}$ ·927. Formed by the action of Na and $ZnEt_2$ on $ClSi(OEt)_3$ or $Si(OEt)_4$. Oil. Converted by BzCl into EtOBz and $EtSiCl_3$ (100°), which fumes in the air and is converted by water into silicopropionic ether.

'Silicodiethyl ether' $Et_2Si(OEt)_2$. (156°). S.G. $\frac{0}{0}$ ·875. V.D. (H=1) 87 (calc. 88). Formed from Na, $ZnEt_2$, and silicic ether. Oil, sol. alcohol and ether. AcCl (1 mol.) at 200° forms EtOAc and $Et_2SiCl(OEt)$ (147°). A larger quantity (2 mols.) of AcCl at 250° forms Et_2SiCl_2 (129°), which is decomposed by water, forming syrupy $SiEt_2O$ (above 360°), which may also be got by boiling $SiEt_2(OEt)_2$ with HIAq.

'Silicoheptyl ether' $SiEt_3.OEt$. Mol. w. 160. (153°). S.G. $\frac{0}{0}$ ·840. V.D. (H=1) 80·8 (calc. 80). Formed from $SiEt_2(OEt)_2$, Na, and $ZnEt_2$. Oil, sol. alcohol and ether. Sol. conc. H_2SO_4. AcCl at 180° forms $SiEt_3Cl$ (144°), S.G. $\frac{0}{0}$ ·925, a fuming liquid converted by NH_3Aq into $SiEt_3OH$.

Tri-ethyl-silicol $SiEt_3OH$. Mol. w. 132. (154°). S.G. $\frac{0}{0}$ ·871. Formed by dropping $SiEt_3.OEt$ into NH_3Aq, or by heating it with Ac_2O at 250° and decomposing the resulting $SiEt_3.OAc$ with Na_2CO_3Aq. Thick liquid, smelling like camphor. Insol. water, miscible with alcohol and ether. Burns with bright flame. Sodium forms $SiEt_3.ONa$, which, in ethereal solution, combines with CO_2, forming $SiEt_3.CO_2Na$, an amorphous deliquescent solid, decomposed at a red heat into Si_2Et_6O and Na_2CO_3. AcCl forms HOAc and $SiEt_3Cl$. HIAq at 200° forms ethane and $SiEt_2O$. Oxidising agents have no action. Fuming H_2SO_4 forms $EtSiO_2H$, ethane, H, and SO_4.

Acetyl derivative $SiEt_3OAc$. (168°). S.G. $\frac{0}{0}$ ·903. Formed by heating $SiEt_3.OEt$ with Ac_2O at 250°. Liquid with ethereal odour.

'Silicoheptyl oxide' $(SiEt_3)_2O$. Mol. w. 246. (231°). S.G. $\frac{0}{0}$ ·859. Formed as above, and also by the action of P_2O_5 on tri-ethyl-silicol. Got also from $SiEt_3Cl$ and KOHAq. Colourless syrup, sol. H_2SO_4 and separated unchanged on dilution, if heating be avoided.

Tri-ethyl-silicane $SiEt_3H$. (107°). S.G. $\frac{0}{0}$ ·751. V.D. (H=1) 59 (calc. 58). Formed, together with $SiEt_4$, by the action of excess of $ZnEt_2$ and Na on Et_4SiO_4. Liquid, insol. water and H_2SO_4, sol. alcohol and ether. Fuming H_2SO_4 converts it into $(SiEt_3)_2O$. HNO_3 attacks it vigorously. Bromine added slowly to the cooled liquid forms $SiEt_3Br$ (161°), which is converted by NaOHAq into $(SiEt_3)_2O$, and by NH_3Aq into $SiEt_3.OH$.

Silicoformic acid. ***Ethyl ortho- ether*** $SiH(OEt)_3$. (134°). Formed from $SiHCl_3$ and absolute alcohol (Friedel a. Ladenburg, *A.* 143, 123; *Bl.* [2] 7, 322; Gattermann, *B.* 22, 190). Hygroscopic liquid, decomposed by alkalis with

evolution of H. Sodium decomposes it into SiH_4 and Et_4SiO_4.

Chloro-silicoformic ether *v.* Ethyl silicate.

'Silicoacetic acid.' *Ethyl ortho- ether* $CH_3.Si(OEt)_3$. (145°–151°). S.G. $^{\underline{0}}$ ·928. Formed by heating silicic ether with $ZnMe_2$. Oil, sol. alcohol. Converted by HIAq into amorphous silico-acetic acid $CH_3.SiO_2H$, which is insol. water and ether (Ladenburg, *B.* 6, 1029).

The term silicoacetic acid is also sometimes used to denote $H_2Si_2O_4$, which is got by decomposing Si_2I_6 by water at 0° (Friedel a. Ladenburg, *A.* 203, 249; *v.* Silico-oxalic acid, *infra*). A compound $Si_2C_3O_2$ is formed, as a bottle-green powder, by heating silicon to whiteness in a crucible lined with lampblack. It is insol. KOHAq and HFAq (Colson, *C. R.* 94, 1316).

Tetra-propyl-silicane $Si(C_3H_7)_4$. (213°). S.G. $\frac{0}{4}$ ·7979; $\frac{15}{4}$ ·7883. V.D. 99·7· (obs.). Formed, together with $SiHPr_3$, by heating $ZnPr_2$ (2 pts.) with $SiHCl_3$ (1 pt.) at 150° (Pape, *B.* 14, 1872; *A.* 222, 370). Colourless oil, sol. alcohol. and ether, insol. H_2SO_4. Br has no action in the cold, but on warming it forms oily $SiC_{12}H_{27}Br$, converted by alcoholic potash into oily $SiC_{12}H_{26}$ (206°–210°).

Tri-propyl-silicane $SiHPr_3$. (170°). S.G. $\frac{0}{4}$ ·7723; $\frac{15}{4}$ ·7621. V.D. 82 (obs.). Formed as above. Oil, v. sol. alcohol and ether, insol. conc. H_2SO_4. Burns with bright flame, forming SiO_2. Br acts violently, forming $SiPr_3Br$ (213°), a fuming liquid, which is slowly converted by water into $SiPr_3.OH$.

Tri-propyl-silicol $SiPr_3.OH$. (205°–208°). Formed by the action of NH_3Aq on $SiPr_3Br$, or of Na_2CO_3Aq on $SiPr_3.OAc$ (Pape). Oil.

Acetyl derivative $SiPr_3.OAc$. (212°–216°). Formed from $SiPr_3Br$ and AgOAc. Oil.

Hexa-propyl-di-silicyl oxide $(SiPr_3)_2O$. (280°–290°). Formed by warming $SiHPr_3$ with H_2SO_4 and, together with $SiPr_3.OH$, by boiling $SiHPr_3$ with Na_2CO_3Aq (Pape, *A.* 222, 369). Liquid, sol. alcohol, ether, and H_2SO_4.

Silicon sulphocyanide $Si(CNS)_4$. [142°]. (c. 300°). Formed by distilling lead sulphocyanide with $SiCl_4$ (Miguel, *A. Ch.* [5] 11, 343). Colourless prisms, insol. ether and CS_2, soluble in a solution of HCNS in benzene. Burns with violet flame. Dyes the skin red. Decomposed by water into HCNS and SiO_2.

Tetra-phenyl-silicane $SiPh_4$. [233°]. (above 360°). S.G. $\frac{20}{20}$ 1·0780. Formed from chlorobenzene, $SiCl_4$, and Na in presence of a little EtOAc (Polis, *B.* 18, 1540; 19, 1012; 20, 3331). Dimetric crystals; $a{:}c = 1{:}·440$, sol. hot benzene, sl. sol. alcohol and ether. May be sublimed. Sulphonated by fuming H_2SO_4. HNO_3 forms $Si(C_6H_4.NO_2)_4$ [105°], a yellow powder, v. sol. benzene. Converted by PCl_5 into liquid $SiPh_2Cl_2$ (234° at 90 mm.) and $SiPh_3Cl$ [89°], from which water produces tri-phenyl-silicol $SiPh_3.OH$ [141°], which separates from ether in colourless crystals.

Phenyl-tri-chloro-silicane $SiPhCl_3$. (197°). Formed by heating $SiCl_4$ with $HgPh_2$ at 300° (Ladenburg, *B.* 6, 379). Oil. Decomposed by hot water, or by NH_3Aq, yielding 'silicobenzoic acid' $SiPh(OH)_3$ [92°]. Absolute alcohol forms 'silicobenzoic' ethyl ortho- ether $SiPh(OEt)_3$ (237°). S.G. $^{\underline{0}}$ 1·018; $^{\underline{10}}$ 1·006. Silicobenzoic acid is converted at 100° into amorphous 'silicobenzoic anhydride' $(SiPhO)_2O$.

Phenyltriethyl-silicane $SiPhEt_3$. (230°). S.G. $^{\underline{0}}$ ·904. Formed, together with $SiEt_4$ and $SiPh_2Et_2$ (c. 310°), by heating $SiPhCl_3$ with $ZnEt_2$ at 150°. Oil, smelling like cloves. Yields a bromo- derivative (270°–280°). Cl forms $SiC_{12}H_{19}Cl$ (260°–265°), S.G. $^{\underline{0}}$ 1·0185.

Tetra-*m*-tolyl-silicane $Si(C_7H_7)_4$. [151°]. (above 550°). S.G. $^{\underline{20}}$ 1·119. Formed from *m*-bromo-toluene, $SiCl_4$, and Na (Polis, *B.* 19, 1021). Pale-yellow needles (from ether), v. sol. benzene and chloroform, insol. alcohol.

Tetra-*p*-tolyl-silicane $Si(C_7H_7)_4$. [228°]. (above 360°). S.G. $^{\underline{20}}$ 1·079. Formed from *p*-bromo-toluene, $SiCl_4$, and Na (Polis, *B.* 18, 1542). Colourless crystals, sol. benzene.

***p*-Tolyl-tri-chloro-silicane** $C_7H_7SiCl_3$. (219°). Formed from $Hg(C_7H_7)_2$ and $SiCl_4$ at 310° (Ladenburg, *A.* 173, 165). Fuming liquid, decomposed by water. Converted by NH_3Aq into viscid $C_7H_7SiO_2H$, which is converted at 200° into the solid anhydride $(C_7H_7SiO)_2O$, which is not melted at 200°.

Tetra-benzyl-silicane *v.* vol. i. p. 502.

Silicon tetra-phenyl-tetra-amide $Si(NHPh)_4$. [138°]. Formed from $SiBr_4$ and excess of aniline diluted with benzene, the product being distilled in a current of H at 105° (Reynolds, *C. J.* 55, 477). Colourless monoclinic crystals; $a{:}b{:}c = ·985{:}1{:}1·043$; $\beta = 110° 20'$. V. sol. benzene, sol. CS_2, insol. ligroïn. Decomposed by water and alcohol. Not decomposed by heating at 210°. HCl forms $SiCl_4$ and aniline.

Silicon di-chloro-di-phenyl-di-amide $SiCl_2(NHPh)_2$. Formed from $SiCl_4$ and aniline (Harden, *C. J.* 51, 40). Amorphous solid. Decomposed by water into aniline hydrochloride and silica.

Silicon tetra-*o*-tolyl-tetra-amide $Si(NHC_7H_7)_4$. Formed from $SiCl_4$, *o*-toluidine, and benzene (Reynolds). Prisms, v. sol. benzene and CS_2. The compound $SiCl_2(NHC_7H_7)_2$, which is also formed from $SiCl_4$ and *o*-toluidine, is a white granular powder (Harden).

Silicon tetra-*p*-tolyl-tetra-amide $Si(NHC_7H_7)_4$. [132°]. Formed from $SiCl_4$ and *p*-toluidine in benzene (Reynolds). Botryoidal aggregate of needles, v. sol. benzene and ether, decomposed by water and alcohol.

Silicon tetra-naphthyl-tetra-amide $Si(NHC_{10}H_7)_4$. Formed from (β)-naphthylamine and $SiCl_4$ (R.). Nodules, decomposed by water. Sl. sol. ligroïn, sol. benzene.

SILICO-NITRATES. SiO_2 seems to form some compounds with N_2O_5 and basic oxides· the salt $3SiO_2.N_2O_5.7Ag_2O$ ($= 3Ag_4SiO_4.2AgNO_3$) was obtained, in ruby-coloured prisms, by Rousseau a. Tite (*C. R.* 114, 294), by heating $AgNO_3$ with a little water and fragments of marble in a sealed tube at 180°–300° for several hours; heated to dull redness, it gave off N oxides, and Ag and Ag_2SiO_3 remained.

M. M. P. M.

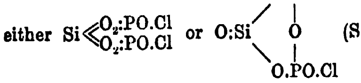
SILICO-OXALIC ACID $H_2Si_2O_4 = \begin{matrix} O{:}Si.OH \\ O{:}Si.OH \end{matrix}$. This compound is obtained, as a white amorphous powder, by the interaction of water and Si_2Cl_6 or Si_2I_6 at 0°; the gelatinous pp. is washed with ice-cold water, dried *in vacuo* and then at 100° (Friedel a. Ladenburg, *A.* 203, 118). It is also produced by the interaction of Si_2I_6 with

absolute alcohol. The compound is decomposed even by weak bases, with evolution of H.
M. M. P. M.

SILICO-PHOSPHORIC OXIDES. (*Silico-phosphoric acids.*) $SiO_2.P_2O_5$ and $SiO_2.2P_2O_5.4H_2O$. The compound $SiO_2.P_2O_5 = SiP_2O_7$ is formed by dropping SiO_2, prepared by decomposing SiF_4 by water and drying the pp., into molten HPO_3, and washing with water (Hautefeuille a. Margottet, *C. R.* 96, 1052; *v.* also Skey, *C. N.* 16, 187). Large, hard, transparent crystals; S.G. 3·1 at 14°; melts when strongly heated to a glass-like mass. The crystals are polymorphous; they are hexagonal under 300°; at c. 300° they form leaflets resembling *tridymite*, between 700° and 800° they are regular octahedra, and between 800° and 1000° they assume the form of clinorhombic prisms. Water attacks the hexagonal, but not the octahedral or prismatic, crystals. Molten $AgNO_3$ forms Ag_3PO_4 and SiO_2 with all the forms (H. a. M., *C. R.* 99, 789).

The compound $SiO_2.2P_2O_5.4H_2O$ was obtained (H. a. M., *C. R.* 104, 56) by one-fourth saturating H_3PO_4Aq with $SiO_2.xH_2O$, heating the solution in a Pt dish to 125° for 7-8 hours, and drying the solid which separated. The compound is a crystalline powder; decomposed by moist air; sol. water at 0°, but decomposed by water at the ordinary temperature to H_3PO_4Aq and gelatinous $SiO_2.xH_2O$. M. M. P. M.

SILICOPHOSPHORIC OXYCHLORIDE $SiP_2O_6Cl_2$. (*Silicopyrophosphoryl chloride.*) Prepared by heating $SiCl_3.OEt$, or $Si(OEt)_4$, with excess of $POCl_3$ to 180° for 2 hours, distilling off EtCl, and $SiCl_4$ if prepared from $SiCl_3.OEt$, and heating the solid that remains to 150°-200° in a stream of dry air to remove adhering $POCl_3$. A white, loose, very hygroscopic, amorphous powder. Very sol. water, but with separation of $SiO_2.xH_2O$; easily sol. alcohol, insol. ether. Decomposed very slowly below 200°, more rapidly above 200°, giving off $POCl_3$; at a red heat P_2O_5 comes off, and a glassy mass remains, probably consisting of SiO_2 and $SiO_2.P_2O_5$. Addition of excess $AgNO_3Aq$ to solution in water (with a little alcohol to prevent separation of silica), followed by HNO_3Aq, ppts. AgCl, and on filtering this off and adding NH_3Aq drop by drop $Ag_4P_2O_7$ is ppd. mixed with some Ag_3PO_4. Heated to 100° with PCl_5 the equation $SiP_2O_6Cl_2 + 4PCl_5 = SiCl_4 + 6POCl_3$ is realised. The constitution of the compound is probably



either $Si\begin{cases}O_2{:}PO.Cl\\O_2{:}PO.Cl\end{cases}$ or $O{:}Si\begin{cases}O.PO.Cl\\ \quad\; | \\ \quad\; O \\ \quad\; | \\ O.PO.Cl\end{cases}$ (Stokes, *Bulletin U.S. Geolog. Survey*, No. 90 [1892] 47; also in *B.* 24, 933). M. M. P. M.

SILICOTITANATES. Compounds of silicates and titanates are found in certain minerals; *sphene*, for instance $(CaO.3SiO_2.2CaTiO_3)$, may be called a silicotitanate. M. M. P. M.

SILICOTUNGSTATES. Compounds containing SiO_2, WO_3, and basic radicles; *v.* TUNGSTO-SILICATES.

SILICOVANADATES *v.* VANADO-SILICATES.

SILK *v.* PROTEÏDS.

SILVER. Ag. At. w. 107·66. Mol. w. not known (*v. infra, Properties*). Melts at c. 950°; Person (*A. Ch.* [3] 27, 250) gave 1000°, Daniell (*T.* 1830. 237) 1024°, Violle (*C. R.* 85, 543) 954°, Becquerel (*J.* 1863.) 916°, Deville (*B.* 12, 791) 916°. B.p. not known; Meyer (*B.* 12, 1428) says that Ag does not appreciably evaporate at c. 1570°. S.G. c. 10·5; Playfair a. Joule (*C. S. Mem.* 3, 66) gave 10·53, and 9·13 to 9·28 for molten Ag, Dumas (*C. N.* 37, 82) gave 10·512 for Ag heated *in vacuo*, Roberts-Austen gave 10·57, and 9·46 to 9·5 for liquid Ag (*Pr.* 23, 495); for further data *v.* Clarke's *Table of Specific Gravities* [new ed.] 14. S.H. 0°-100° = ·0557 (Dulong a. Petit, *A. Ch.* [2] 7, 113); ·0559 (Bunsen, *P.* 141, 1); ·05722 (Louguinine, *A. Ch.* [5] 27, 398). C.E. ·00002 between 0° and 100° (*v.* Matthiessen, *P.* 130, 50; Fizeau, *C. R.* 68, 1125); ·00003721 from 0° to the m.p. (Roberts-Austen, *Pr.* 23, 495). T.C. 100 (that of copper = 73·6, and of Au = 53·2, Wiedermann a. Franz, *A.* 88, 191); heat sufficient to raise 109·6 mgm. water from 0° to 1° passes in 1 second through each sq. mm. of a plate of Ag 1 mm. thick, the two sides of which differ in temperature by 1° (Weber, *B. B.* 1880. 467). E.C. (Hg at 0° = 1) 57·226 for soft Ag, 63·845 for hard Ag (Siemens, *P.* 110, 1); 62·12 (Benoit, *C. R.* 76, 382). H.C. $[Ag^2,O] = 5.900$ (*Th.* 3, 381). Heat of fusion (for 108 g.) 2·275 (Person, *A. Ch.* [3] 24, 275); 2·67 (Pionchon, *A. Ch.* [6] 11, 100). S.V.S. c. 10·3. Emission spectrum gives a line 5464 in the yellow, 5209·9 in the green, and many lines in the orange, green, blue and violet (*v. B. A.* 1884. 442); for absorption-spectrum of Ag vapour *v.* Lockyer a. Roberts-Austen (*Pr.* 23, 344). Refraction equiv. $= \frac{\mu - 1}{d}$. At. w. = 12·62 (Kanonnikoff, *J. R.* 1884. [1] 119); 13·2 (Gladstone, *Pr.* 18, 49).

Occurrence.—Found native, generally alloyed with Au, Cu, &c. The chief compounds found in ores are Ag_2S (frequently in combination with Cu_2S, Fe_2S_3, Sb_2S_3, As_2S_3, Bi_2S_3, PbS, &c.), AgCl, AgBr, AgI, compounds of Ag with Se, Te, As, Sb, Bi, &c. Ag is also found in small quantities in most lead ores. According to Malaguti (*J. pr.* 42, 422; *cf.* Field, *D. P. J.* 143, 397), traces of salts of Ag (c. 1 mgm. Ag in 100 litres) are found in sea-water. Small quantities of Ag, probably as AgCl, have been found in volcanic dust (Mallet, *Pr.* 47, 277). Silver has been known and used from the earliest times (for a full historical account of silver, including the derivation of the name, *v.* SILBER in Ladenburg's *Handwörterbuch der Chemie*, 10, 635).

Formation.—1. By heating Ag_2S with PbO or $PbSO_4$, SO_2 and a compound or alloy of Ag and Pb are formed; the Pb may be separated from this alloy by cupellation.—2. By shaking AgCl with Hg and water, HgCl and an amalgam of Ag and Hg are formed; Ag remains when the Hg is removed from this amalgam by heating.—3. Ag is ppd. from solutions of its salts by Zn, Cu, Fe, &c.—4. AgCl is reduced to Ag by treatment with many reducing agents, such as Zn and H_2SO_4Aq, also by fusion with Na_2CO_3 and C.—5. Most easily-oxidised metals ppt. Ag from solutions of its salts. For an account of the extraction of Ag from its ores *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 386.

Preparation.—Silver coins are dissolved in pure dilute boiling HNO_3Aq, the solution is evaporated to dryness, the residue is heated till it melts, after cooling it is dissolved in NH_3Aq, after standing forty-eight hours the liquid is passed through a filter made of specially good paper, and the filtrate is diluted till it contains not more than 2 p.c. of Ag. This ammoniacal solution contains $AgNO_3$ and $Cu(NO_3)_2$; the whole of the Ag is ppd. by ammoniacal solution of $(NH_4)_2SO_3$ at 60°. A solution of $(NH_4)_2SO_3$ is prepared by saturating pure NH_3Aq with SO_2 (made by heating pure Cu with pure H_2SO_4 diluted with $\frac{1}{2}$ to $\frac{2}{3}$ its volume of water); a measured quantity of this solution is mixed with excess of pure NH_3Aq, heated to boiling, and the ammoniacal solution containing $AgNO_3$ and $Cu(NO_3)_2$ is run from a burette into the boiling liquid until there is the faintest trace of blue colour in the liquid above the ppd. Ag. Cuprous sulphite is formed, and this reduces the $AgNO_3$ in the ammoniacal liquid; when all the $AgNO_3$ is reduced, the blue colour of the ammoniacal copper nitrate appears. The whole of the ammoniacal solution of $AgNO_3$ and $Cu(NO_3)_2$ is now mixed with the proper quantity of ammoniacal $(NH_4)_2SO_3Aq$ required for complete reduction of the $AgNO_3$, the mixed liquids are set aside in a closed vessel for forty-eight hours, when c. $\frac{1}{3}$ of the Ag is ppd.; the blue liquid is decanted off and heated on a water-bath to 60°-70°, whereby the whole of the Ag in solution is ppd. The two quantities of ppd. Ag are washed with ammoniacal water, by decantation, until the washings show no trace of blue colour on standing (or until $BaCl_2Aq$ gives no trace of pp.), the Ag is kept in contact with conc. NH_3Aq for some days, and is then washed with water until every trace of NH_3 is removed. If it is desired to have the Ag in bars, the finely-divided metal obtained by ppn. is mixed with 5 p.c. of its weight of pure borax which has been strongly heated, and ·5 p.c. pure $NaNO_3$, fused in a porcelain crucible and poured into kaolin moulds lined with a paste made of a mixture of kaolin that has been strongly heated and unignited kaolin; when cold the bars are cleaned with fine sand, then strongly heated with pure KOHAq (to remove traces of kaolin) and washed with water. The bars may be cut with a chisel of very hard steel; if this is done the pieces must be warmed for some time with pure conc. HClAq, washed with NH_3Aq, and then with water (*Stas. Rech.* 88 *et seq.*). The Ag may be freed from traces of absorbed gases by distilling it; this is done by placing the Ag in a hole in a block of strongly-heated marble; this hole communicates, by a slit in the marble, with another hole from which an opening passes upwards to the surface of the marble; another opening admits the nozzle of an O-H blowpipe, so that the flame plays on the surface of the Ag. (For details *v.* Stas, *l.c.*) Dumas (*A. Ch.* [5] 15, 289) found that 1 kilo. of Ag considered pure gave from 59 to 174 c.c. O when heated in a Sprengel vacuum; it was supposed by some chemists (*v.* Mallet, *T.* 1880. 1003; Clarke, *Recalculations of the Atomic Weights*, 262) that this result proved that Ag made by Stas' process was not quite pure; but Brauner has proved experimentally (*C. J.* 55, 399) that Ag prepared by Stas's method described above, and distilled by the O-H flame in a block of burnt marble, gives off no O when heated *in vacuo* (*v.* also Stas, *Bull. Acad. roy. Belg.* [3] 18, 23; abstract in *C. J.* 58, 561).

Properties.—A white, very lustrous metal. Crystallises in forms in the regular system, chiefly cubes, octahedra, and rhombododecahedra; these crystals are obtained by slowly cooling molten Ag, or by the electrolytic deposition of the metal; they are also sometimes found native. Finely divided Ag—as obtained, for instance, by reduction of AgCl—is a grey powder, which becomes white and lustrous when compressed with a flat iron. A thin deposit of Ag on glass transmits bluish light.

Ag is harder than Au and softer than Cu. Ag reflects light and heat strongly; its absorptive power is very small. It is very malleable; Ag foil has been obtained ·003 mm. thick. Ag is very ductile; ·06 gram may be drawn to a wire 130 metres long; it is so tenacious that a cold-drawn wire of 2 mm. diameter does not break till it is loaded with 80-85 kilos (Baudrimont, *A. Ch.* [3] 30, 304). Ag is slightly volatile at a low-red heat *in vacuo*, but not at the ordinary pressure at this temperature, nor *in vacuo* at 440°-450° (Stas, *Bull. Acad. roy. Belg.* [3] 18, 23). It may be distilled, by heating, by the O-H flame, Ag placed in a block of burnt marble. Stas distilled 50 g. Ag in c. 15 mins.; part of the Ag appeared as a blue vapour during the distillation. When an alloy of Ag with a more volatile metal, such as Hg, Pb, or Sn, is heated, part of the Ag volatilises with the other metal. Molten pure Ag absorbs c. 20 times its volume of O from the air (*v.* Lucas, *A. Ch.* [2] 12, 402; Gay-Lussac, *A. Ch.* [2] 45, 221; Graham, *P. M.* [4] 32, 503; Neumann, *M.* 13, 40; Levol, *J. pr.* 57, 192); as the Ag cools it 'spits' and gives off the O it has absorbed; Dumas' experiments (*A. Ch.* [5] 15, 289) show that a little O is retained, but Brauner (*C. J.* 55, 399) has proved that no O remains if the Ag is distilled in a block of burnt marble. (For the chemical action of O on Ag *v. Reactions*, No. 1.) Pure Ag suffers no change when heated in air, H, or CO (van der Plaats, *Mundblad voor Natuurwetenschappen*, 1886. No. 2). Molten Ag absorbs P, but the whole of the P, except c. ·002 p.c., separates on cooling (Warren, *C. N.* 56, 113).

The at. wt. of Ag has been determined (1) by finding the ratio of Ag to Cl in AgCl (Berzelius, *P.* 8, 17 [1826]; Turner, *T.* 1829. 297 [1829]; Marignac, *A.* 44, 23 [1842]; *ibid. Bibl. univ. Genève*, 46, 354 [1843]; Maumené, *A. Ch.* [3] 18, 41 [1846]; Dumas, *A. Ch.* [3] 55, 134 [1859]; Stas, *Stas. Rech.* 38 *et seq.* [1860]); (2) by finding the ratio of Ag to Br in AgBr, and of Ag to I in AgI (Marignac, *l.c.* 46, 360 [1843]; Stas, *Stas. Nouv. R.* 158 *et seq.* [1865]); (3) by determining the ratio of Ag to Ag_2S formed therefrom (Dumas, *A. Ch.* [3] 55, 147 [1859], Stas, *Stas. Rech.* 53 [1860]); (4) by reducing Ag_2SO_4 to Ag (Struve, *A.* 80, 203 [1851]; Stas, *Stas. Rech.* 125 [1860]); (5) by converting Ag_2SeO_3 into Ag (Pettersson a. Ekman, *Bl.* [2] 27, 205 [1876]); (6) by converting Ag into $AgNO_3$ (Marignac, *A.* 59, 289 [1843]; Stas, *Stas. Rech.* 50 *et seq.* [1860]); (7) by determining

S.H. of Ag; (6) by finding V.D. of AgCl at white heat (Biltz a. Meyer, *B.* 22, 725). The classical work of Stas has placed the value for the at. wt. on a very sure foundation.

Ramsay (*C. J.* 55, 521) measured the depression of the vapour-pressure of Hg by dissolving Ag therein; assuming that the mol. w. of liquid Hg is 200, and that equal volumes of dilute solutions of metals in Hg contain equal numbers of molecules, the results led to the conclusion that the mol. w. of Ag is the same as the at. wt.

AgCl is the only compound of Ag the vapour-density of which has been determined; the value found shows that the atom of Ag is monovalent in the gaseous molecule AgCl.

Ag is fairly closely related chemically to Cu and Au (*v.* Copper group of elements, vol. ii. p. 250).

Allotropic forms of silver. According to Schneider (*B.* 25, 1281, 1440), an aqueous solution of Ag, containing c. 20 g. Ag per litre, is obtained by mixing 150 g. $FeSO_4.7aq$ in 500 c.c. water and 280 g. Na citrate in 700 c.c. water, pouring the mixture into 500 c.c. of 10 p.c. $AgNO_3Aq$ (it is best to divide the mixture into five parts, as small quantities are more easily dealt with), removing liquid from ppd. Ag after half an hour (by a pipette), filtering through a good filter under decreased pressure, and dissolving the ppd. Ag in as little water as possible; by adding absolute alcohol, and filtering, after some days, with help of a good water-pump, colloidal Ag containing from ·3 to ·5 p.c. of Fe salts is obtained. A very little HClAq ppts. Ag with a little AgCl and Ag_2Cl(?) from solution of colloidal Ag. Carey Lea has carried out a series of researches on the properties of Ag ppd. from solutions of its salts by ferrous citrate, ferrous tartrate, and dextrin in presence of alkali (*Am. S.* [3] 37, 476; 38, 47, 129, 237; 41, 179, 259; *P. M.* [5] 31, 238, 320, 497; 32, 337). The pps. of Ag show almost every shade of colour, such as blue, red, green, purple, golden; some of the pps. are soluble in water, and some are not; most of the pps. are very sensitive to light, but they vary much in this respect; some of the pps. yield ordinary Ag when heated; ordinary Ag is also ppd. from solutions of soluble colloidal Ag by a little very dilute HClAq. In no case does any so called allotropic Ag seem to have been obtained quite free from organic compounds; the percentage of Ag in the pps. varied from c. 90 to c. 98. For accounts of the properties of the various coloured pps. the memoirs of Carey Lea must be consulted; *v.* also Schneider, *B.* 24, 3370; Barus a. Schneider, *Z. P. C.* 8, 278; Prange, *R. T. C.* 9, 121; Muthmann, *P.* 20, 983. B. a. S. determined many of the physical properties of a solution of colloidal Ag, and concluded that the colloidal variety consists of extremely minute particles of ordinary Ag that remain suspended in the liquid for a considerable time.

Reactions and Combinations.—1. According to Debray (*C. R.* 66, 735), Ag is partially oxidised by very strongly *heating* in the O-H flame, using *excess of oxygen.* According to Le Chatelier (*Bl.* [2] 48, 342) pure ppd. Ag is oxidised by heating in *oxygen* at 300° under 15 atmos. pressure; after 50 p.c. of the Ag was oxidised the change stopped.—2. *Ozonised oxygen* acts on moist, finely-divided Ag at the ordinary temperature, forming a peroxide (*v.* Silver peroxide, p. 471).—3. Ag combines easily with *chlorine, bromine, iodine,* and *sulphur* (*v.* Silver chloride &c.); also, by heating, with *selenion, arsenic,* and *phosphorus* (*v.* Silver selenide &c.).—4. Finely-divided Ag is said to dissolve, with oxidation, in ammonia solution in presence of air (Carey Lea, *Zeit. für anorg. Chem.* 3, 180).—5. Ag reacts with *steam* at a white heat, absorbing O while H is given off.—6. Finely-divided Ag is oxidised by *hydrogen peroxide* (Berthelot, *A. Ch.* [5] 21, 164).—7. Finely-divided Ag is said to be oxidised by *heating with oxides and salts that readily give up oxygen—e.g.* MnO_2, Pb_3O_4, $Pb(NO_3)_2$, &c.—8. *Hydrogen sulphide* forms Ag_2S. *Alkali sulphides* also produce Ag_2S.—9. *Molten sodium chloride* forms AgCl, some Na vapour being given off; *solution of sodium chloride,* as also of *potassium or ammonium chloride,* dissolves some Ag as AgCl.—10. *Potassium iodide solution,* in air, forms soluble AgI.KI.—11. Hot *solution of potassium cyanide* dissolves Ag, forming $AgK(CN)_2$ (*v.* Christomanos, *Fr.* 7, 301).—12. *Fusion with silicates,* such as glass, forms Ag_2O, which dissolves in the molten silicate.—13. Ag dissolves in *solution of ferric sulphate* on warming; as the solution cools the Ag_2SO_4 is again decomposed, with formation of $Fe_2(SO_4)_3$ and ppn. of finely-divided Ag.—14. A compound of Ag and Si is said to be formed by strongly heating Ag with *potassium silicofluoride and potassium* (Warren, *C. N.* 60, 5).—15. Ag dissolves in moderately dilute *nitric acid,* forming $AgNO_3$, and giving off N oxides; the gaseous products are N_2O and NO, according to Montemartini (*G.* 22, 384, 397, 426).—16. Conc. *hydrobromic* and *hydriodic acids* dissolve Ag on warming, with evolution of H; the dissolved AgBr or AgI is ppd. on dilution.—17. Hot conc. *sulphuric acid* dissolves Ag, giving off SO_2; if a little $Fe_2(SO_4)_3$ solution is added the Ag goes into solution without heating. Very finely-divided Ag, obtained by reduction of Ag salts by milk-sugar and alkali, is dissolved by very dilute H_2SO_4Aq (Carey Lea, *Zeit. für anorg. Chem.* 3, 180). Friedheim (*B.* 19, 2554; 20, 307) says that Ag dissolves in dilute H_2SO_4Aq containing $KMnO_4Aq$.—18. *Chromic acid* (*i.e.* solution of CrO_3 in water) produces red Ag_2CrO_4; HNO_3Aq, S.G. 1·2, in which K_2CrO_4 is dissolved, gives a red deposit on the surface of Ag; this test is used to distinguish Ag from other white metals, such as Sn.—19. Ag in pieces is scarcely acted on by *hydrochloric acid,* even when hot and conc.; very finely-divided Ag is said to form a little AgCl, with evolution of H. *Hydrofluoric acid* is without reaction.—20. Ag is not acted on by *molten alkalis or alkaline carbonates*; hence KOH, &c., may be fused in dishes of Ag.—21. Ag alloys with many *metals* (*v.* Silver, alloys of).

Silver, alloys of. Ag forms alloys with many metals. They are generally formed by heating the metals together; in a few cases—*e.g.* alloy with Ba or Mn—they are formed by heating Ag with metallic oxides and C.

With aluminium. An alloy of 100 parts Al with 5 parts Ag is harder and more easily polished than Al, but otherwise has most of the properties of Al; it is used for making the pans, &c., of balances. Hirzel (*J.* 1858. 137) obtained alloys corresponding in composition with the formulæ Ag_4Al, Ag_2Al, and AgAl (*v.* also Tissier, *C. R.* 43, 885; 52, 931; Debray, *C. R.* 43, 925).

With antimony, and *with arsenic*; *v.* SILVER ANTIMONIDE and ARSENIDE, *infra.*

With copper. Ag becomes harder, more elastic, more capable of being polished, and more slowly worn away when alloyed with Cu without losing much in malleability and ductility. Alloys with less than 50 p.c. Cu are white, with more than 50 p.c. Cu the colour becomes reddish. The S.G. of a Ag-Cu alloy is rather smaller than the mean of those of the constituent elements (*v.* Karmarsch, *D. P. J.* 108, 278). The composition of these alloys is rarely identical throughout a mass (*v.* Levol, *A. Ch.* [3] 36, 193). Alloys of Ag and Cu are used for making silver vessels and ornaments, and for coinage; the standard silver coinage alloy of the United Kingdom contains 925 parts Ag and 75 parts Cu per 1,000.

With mercury. The amalgams of Ag are formed (1) by the action of Hg on $AgNO_3Aq$, (2) by the action of finely-divided Ag on $HgCl_2Aq$, (3) by dissolving Ag in Hg. The compositions of many of these amalgams can be represented by formulæ, but it is very doubtful whether any of them are definite compounds. For accounts of these amalgams *v.* Campani, *J.* 1870. 373; Joule, *C. J.* [2] 1, 378; Crookewitt, *J.* 1847-48. 393; Malaguti a. Durocher, *Ann. M.* 17, 336; Gay-Lussac, *A. Ch.* 58, 218.

Alloys of Ag with the following metals have been described:—Ba (Clarke, *G. A.* 62, 373; Lampadius, *S.* 15, 146); Cd (Wood, *C. N.* 6, 135); Au (G. Rose, *P.* 23, 181; Levol, *A. Ch.* [3] 15, 55; 27, 310); Ir; Fe; Pb (Levol, *A. Ch.* [3] 39, 173); Mg; Mo; Ni; Pd (Graham, *J.* 1868. 144); Pt; K; Rh; Na; Sn; Zn (*v.* Wright a. Thompson, *Pr.* 48, 25).

Silver, antimonide of. The mineral *dyskrasite* has approximately the composition Ag_6Sb; when heated to dull redness in H, the compound Ag_3Sb is said to remain (von Bonsdorff, *S.* 34, 225). The compound Ag_3Sb is also obtained by ppg. $AgNO_3Aq$ by Sb hydride; using conc. $AgNO_3Aq$ the compound $Ag_3Sb.3AgNO_3$ was formed (Poleck a. Thümmel, *B.* 16, 2435).

Silver, arsenide of. No definite compound of Ag and As has been obtained. By heating Ag powder with As about 16 p.c. of As is absorbed by the Ag to form a grey, brittle solid (Gehlen). By passing As hydride into conc. $AgNO_3Aq$ the compound $Ag_3As.3AgNO_3$ was obtained (P. a. T., *l.c.*).

Silver, bromide of, AgBr. (*Argentic bromide.*) Formula probably molecular, from analogy of AgCl. Occurs native in Chili and Mexico.

Preparation.—HBrAq or alkali bromide solution is added to $AgNO_3Aq$ till ppn. is complete; the pp. is washed with water in the dark and dried.

Properties.—A pale-yellow solid; melts at c. 434° (Carnelley, *C. J.* 29, 489). S.G. 6·245 at 0°, 5·595 at m.p. (Rodwell, *Pr.* 31, 291). S.H. (15° to 98°) ·07391 (Regnault, *A. Ch.* [3] 1, 129). For effects of heat on AgBr *v.* Rodwell (*Pr.* 25, 280). Obtained in octahedra by crystallising from HBrAq. Solubility of AgBr dried at 100° in NH_3Aq S.G. ·986, = ·051 (Pohl, *J. pr.* 82, 52). Granular AgBr is slightly sol. water above 50°; flocculent AgBr is slightly sol. water above 33° (Stas, *A. Ch.* [5] 3, 289). Sol. hot $Hg(NO_3)_2Aq$; AgBr crystallises out on cooling (Debray, *C. R.* 70, 995). Sol. solutions of alkali bromides. H.F. [Ag,Br] = 22,700 (*Th.* 3, 381). According to Berthelot (*Bl.* [2] 39, 19), the reaction [Ag,Br] has the value 23,700 when crystalline AgBr is formed, and the value 20,000 when the AgBr is amorphous (in both cases using liquid Br). B. also says that in the formation of AgBr by adding KBrAq to $AgNO_3Aq$ 20,700 cals. are produced, and that when $AgNO_3Aq$ is added to KBrAq only 17,600 cals. are produced at first, but that temperature then rises until 20,600 cals. are evolved; B. thinks that two forms of AgBr are formed, one more stable than the other. Vogel (*B.* 16, 1160) distinguishes two modifications of AgBr, one ppd. from aqueous solutions and very sensitive to blue rays, the other ppd. from solutions in absolute alcohol and sensitive to the violet rays. Stas (*A. Ch.* [5] 3, 289) distinguishes six forms of AgBr:—(1) flocculent, white, by adding dilute alkali bromide solution to excess of cold $AgNO_3Aq$; (2) flocculent, yellow, by using excess of bromide as pptant.; (3) powdery, white, by shaking (1) or (2) with water; (4) intense yellow, by heating (4); (5) granular, white-yellow, by pouring the flocculent or powdery variety, shaken with water, into boiling water, also by adding very dilute NH_4BrAq to boiling $AgNO_3Aq$ (1:1000); (6) pure yellow, crystalline variety.

Reactions and Combinations. — 1. AgBr darkens rapidly when exposed to *sunlight.* Carey Lea says that the dark product of the action of light on AgBr reacts with HNO_3Aq to re-form AgBr, and Ag which dissolves in the acid (*Am. S.* [3] 15, 189). The action of light on the Ag haloids is treated more fully under *Silver chloride* (*q. v.*).—2. Heated in *chlorine*, AgCl and Br are produced. — 3. Dissolves slowly in hot *silver nitrate* solution; the salt $AgBr.AgNO_3$ separates on cooling (Risse, *A.* 111, 43; Riche, *A.* 111, 39).—4. Combines with silver chloride and iodide to form compounds $Ag_aBr_bI_cCl_d$ (*v.* SILVER IODOBROMOCHLORIDES, p. 470).

AgBr resembles AgCl in most of its reactions; NH_3 is not absorbed by dry AgBr (Rammelsberg, *P.* 55, 248).

Silver, bromo-iodochlorides of, *v.* SILVER IODOBROMOCHLORIDES (p. 470).

Silver, carbides of. Gay-Lussac noticed that Ag absorbed c. 3 p.c. C when heated with lampblack (*A. Ch.* [2] 58, 222); Ag_4C requires 2·7 p.c. C. A yellow powder, approximately agreeing with the composition Ag_2C, was obtained by Gerhardt and Cahours (*A. Ch.* [3] 1, 76) by heating Ag cuminate; the same compound was probably produced by Liebig by heating AgCN (*A.* 38, 21). By heating an aqueous solution of Ag pyrotartrate, filtering from the brown pp. produced, and boiling the pp., Berzelius obtained a dark-brown, metal-like pp., probably AgC (*P.* 36, 28; *cf.* Regnault, *A.* 19, 153).

Silver, chlorides of. The isolation of a chloride of Ag containing less Cl than AgCl is not yet certain. Cl is given off when AgCl darkens in sunlight, but whether the darkened product is a chloride or an oxychloride is not finally determined (*v. Action of light on silver chloride, infra*).

Silver subchloride ? Ag_2Cl. (*Argentous chloride.*) According to Güntz (*C. R.* 112, 861), Ag_2Cl is formed by passing dry HCl over Ag_2F (*v.* Silver subfluoride, p. 469) as long as darkening occurs and the solid continues to gain in weight. The compound is also said to be formed by passing vapour of CCl_4, $SiCl_4$, or PCl_3 over dry Ag_2F. A subchloride is formed, according to von Bibra (*J. pr.* [2] 12, 55), by digesting with conc. HClAq the product of the reduction of Ag citrate by H at 100°; after drying, the black solid is said to have the composition Ag_4Cl_3, and with NH_3Aq to give Ag and $AgCl.3NH_3$. Newbury (*Am.* 8, 196) failed to obtain any subchloride by this method; he also found that the reduction of Ag citrate by H at 100° does not yield any definite compound, but probably a mixture of unchanged citrate and Ag.

Silver chloride AgCl. (*Argentic chloride.*) Mol. w. 143·03. V.D. 80 at c. 1700° (Biltz a. Meyer, *B.* 22, 725). Melts at c. 457° (Carnelley, *C. J.* 29, 489). S.G. at 0° = 5·505; at m.p. = 4·919 (Rodwell, *Pr.* 31, 291). S.H. (13° to 98°) ·09109 (Regnault, *A. Ch.* [3] 1, 129). For expansion of AgCl by heat *v.* Rodwell (*Pr.* 25, 280). H.F. [Ag,Cl] = 22,700 (*Th.* 3, 381); 29,200 (Berthelot, *Bl.* [2] 39, 19). For solubilities in various liquids *v. Properties.*

Occurrence.—Native, as *hornsilver*, in Siberia, Mexico, Peru, the Harz, Alsace, &c.

Preparation.—1. By adding dilute HClAq, or solution of a chloride, to solution of any salt of Ag except $Ag_2S_2O_3$, washing the white curdy pp., drying, and heating to incipient fusion. Obtained in octahedral crystals by dissolving in large quantity of conc. HClAq and evaporating.—2. By heating Ag to redness in a stream of Cl or HCl gas.—3. By fusing NaCl with finely-divided Ag, washing, and drying.—4. Very slowly by the action of HClAq on Ag in the presence of air.

Properties.—A white solid. According to Cooke (*Am. S.* [3] 21, 220) AgCl is very slightly sol. cold water, and very distinctly sol. boiling water; he found that 1·4561 g. AgCl washed with 60 litres boiling water lost ·2241 g. = 15·39 p.c.; the solvent action was entirely prevented by the addition of ·05 g. $AgNO_3$ per litre of water. Stas (*C. R.* 73, 998) distinguished four forms of AgCl: (1) gelatinous; (2) curdy, flocculent; (3) powdery; (4) granular, crystalline, or fused. The curdy, flocculent form is the most sol. in water; it is formed by ppg. cold dilute $AgNO_3Aq$ by a chloride solution; on shaking it changes to the less sol. powdery variety. The granular, crystalline, or fused form is insol. cold water (10 million parts cold water dissolve 1 part) but it begins to dissolve at 30° (*cf.* Berthelot, *A. Ch.* [5] 29, 241, for the heats of solution in KCNAq of different preparations of AgCl). AgCl is sol. conc. HClAq and in saturated solutions of various metallic chlorides; Vogel (*C. C.* 5, 578) gives the following table:—

100 c.c.	cold HClAq S.G. 1·165	dissolve	·298	g.	AgCl
”	boiling ” ”	”	·560	”	”
”	conc. HClAq diluted with 1 pt. H_2O	”	·056	”	”
”	conc. HClAq diluted with 2 pts. H_2O	”	·018	”	”
”	conc. HClAq diluted with 3 pts. H_2O	”	·0089	”	”
”	conc. HClAq diluted with 5 pts. H_2O	”	·0035	”	”
”	saturated $BaCl_2Aq$	”	·0143	”	”
”	” $SrCl_2Aq$	”	·0884	”	”
”	” $CaCl_2Aq$	”	·0930	”	”
”	” $MgCl_2Aq$	”	·171	”	”
”	” NaClAq	”	·095	”	”
”	” KClAq	”	·0472	”	”
”	” NH_4ClAq	”	·1575	”	”

One part AgCl dissolves in 50,000 parts boiling conc. HNO_3Aq (Thorpe, *C. N.* 25, 198). NH_3Aq dissolves AgCl; 1 litre NH_3Aq S.G. ·924 dissolves 69·5 g. freshly ppd. AgCl, according to Millon and Comaille (*C. R.* 56, 309). AgCl crystallises from solutions in NH_3Aq, on evaporation; explosive silver is obtained from boiling solutions (*v.* Silver nitrides, p. 470). According to Terreil (*Bl.* [2] 51, 598), crystals of $AgCl.2NH_3$ separate from a hot solution of AgCl in NH_3Aq; these crystals lose NH_3 in the air. AgCl dissolves easily in $Na_2S_2O_3Aq$, forming $Ag_2Na_4(S_2O_3)_3Aq$; AgCl also dissolves readily in KCNAq forming $AgK(CN)_2$, and in NH_4HSO_3Aq forming double Ag-NH_4 sulphites (*v.* Svensson, *B.* 4, 714). A hot solution of $AgNO_3Aq$ dissolves AgCl; Risse says that a double compound of $AgNO_3$ and AgCl separates on cooling (*A.* 111, 39), but Debray asserts that simple solution occurs (*C. R.* 70, 995). $Hg(NO_3)_2Aq$ also dissolves AgCl; Wackenroder (*A.* 91, 317) and Field (*J.* 1857. 255) say that AgCl separates on cooling a hot saturated solution; Stas (*A. Ch.* [5] 3, 180) found that a little $AgNO_3$ is formed.

Reactions.—1. AgCl is reduced to Ag by many *metals*, *e.g.* Zn or Fe, in presence of dilute acid; Cu reduces AgCl in presence of NH_3Aq, with formation of Ag and $CuO.H_2O$.—2. Heated in *hydrogen*, or with *carbon*, or with several *organic compounds*, AgCl is reduced to Ag.—3. Solution of *hydriodic acid* forms AgI and HClAq.—4. *Caustic alkali solutions* produce Ag_2O.

Action of light on silver chloride. AgCl darkens when exposed to sunlight in ordinary air. During the darkening Cl is given off (Scheele; von Bibra, *J. pr.* 122, 39; Hitchcock, *Am.* 11, 474; Béchamp, *Bl.* [3] 6, 836; Richardson, *C. J.* 59, 536; Baker, *C. J.* 61, 728). Only a small portion of the AgCl is changed to the dark compound (*v.* R., *l.c.*; B., *l.c.*, got ·09 g. of the dark body from 51 g. AgCl). AgCl does not darken in thoroughly dried oxygen (B., *l.c.*; nor in dried air according to Carey Lea, *Zeit. für anorg. Chem.* 3, 184). AgCl does not darken *in vacuo*, when thoroughly dry (Abney; B., *l.c.*). Carey Lea (*l.c.*) found that AgCl darkened under dry petroleum; Baker noticed darkening under benzene in absence of air, and he showed that the dark substance was Ag. B. (*l.c.*) noticed darkening, with formation of Ag, under CCl_4, but he proved that if the CCl_4 contained no trace of free Cl darkening did not occur. For the influence of HCl and chlorides in water upon the rate of darkening of AgCl in the water *v.* Richardson (*l.c.*). The dark substance was supposed by some to be a subchloride, but Baker has shown that it contains O (Hodgkinson had formerly arrived at this conclusion; *v.* Meldola's *Chemistry of Photography* [1889], p. 856). B. kept pure AgCl, dried at 150°, in sunshine, in a current of air freed from CO_2 and dried by H_2SO_4, until it darkened; he measured the O obtained from the darkened product, by decomposing by Cl, and also determined the Ag and Cl; the results agreed approximately with the formula Ag_2OCl; the atomic ratio of Ag to Cl found in various experiments was almost exactly 2:1, and of Ag to O was nearly 5:2; the darkened product dissolved in conc. KClAq, on dilution AgCl was ppd. and the solution had a slightly alkaline reaction, as would be expected if an oxychloride were present in the dark-coloured substance. B. also found that a little H_2O was obtained by heating the dark substance in dry H; Richardson (*C. J.* 59, 536) failed to obtain any water by treating darkened AgCl in this way; R. also failed to get O from the darkened AgCl by heating it to the m.p. in connection with a Sprengel pump. B. (*l.c.*) found that the dark-coloured product became white when left in the dark for some days, and that a small quantity of O was absorbed during this change; he, therefore, concludes that two oxychlorides of Ag are formed, one of which is dark-coloured and absorbs a little O to form another, white, oxychloride. Carey Lea (*Am. S.* [3] 38, 356) thinks that the darkening action of light on AgCl is preceded by the formation of what he calls a *photochloride*. The photochloride is supposed to contain less Cl than the normal chloride, and probably to be a compound of AgCl with a subchloride or oxychloride; it is extremely sensitive to the action of light, and undergoes many changes of colour when exposed to light (*Am. S.* [3] 33, 349, 480, 489; 34, 33; and full abstract in *C. J.* 54, 1). For the application of the effects of light on AgCl to photography *v.* PHOTOGRAPHIC CHEMISTRY, this vol. p. 154; and PHOTOGRAPHY, in DICTIONARY OF APPLIED CHEMISTRY, vol. iii.

Combinations.—1. With several *metallic chlorides*, especially the alkaline chlorides; generally forming compounds of the type AgCl.MCl. Wells and Wheeler (*Am. S.* [3] 44, 155) obtained the compound AgCl.2CsCl.—2. With *ammonia gas*. According to H. Rose (*P.* 20, 157), $2AgCl.3NH_3$ is formed. Isambert (*C. R.* 64, 1259; *v.* also Horstmann, *B.* 9, 749) studied the vapour-pressures of the NH_3 given off, and concluded that two compounds are formed when NH_3 is absorbed by AgCl—viz. $2AgCl.3NH_3$ and $AgCl.3NH_3$ (*v.* curves given in DISSOCIATION, vol. ii. p. 397). Bodländer (*Z.P.C.* 9, 730) measured the reduction of the freezing-point of water produced by the compound $2AgCl.3NH_3$; as this reduction was much larger than the normal, he concluded that the compound is dissociated in aqueous solution; a similar conclusion was come to by measuring the electrical conductivities of aqueous solutions. The dissociation cannot have been into NH_3 and AgCl, says B., else AgCl would have separated out; hence the dissociation must be electrolytic, and the solution must contain Ag and Cl as free ions. This conclusion was confirmed by finding that $PbAc_2Aq$ ppd. $PbCl_2$ from $2AgCl.3NH_3$ in NH_3Aq, KIAq ppd. AgI, and $(NH_4)_2SAq$ ppd. Ag_2S; confirmatory evidence was also found in the fact that addition of NH_4Cl or $AgNO_3$ reduced the solubility in water of $2AgCl.3NH_3$, in keeping with the law regarding the effect on the solubility of an electrolyte of the presence of one of its ions. B. concludes that $2AgCl.3NH_3$ is a definite compound, which is electrolytically dissociated in aqueous solution.—3. With *silver iodide and bromide*; *v.* SILVER IODOBROMOCHLORIDES, p. 470.

Silver, chloro-iodobromides of; *v.* SILVER IODOBROMOCHLORIDES, p. 470.

Silver, cyanide of; *v.* vol. ii. p. 346.

Silver, ferricyanide of; *v.* vol. ii. p. 340.

Silver, ferrocyanide of; *v.* vol. ii. p. 337.

Silver, fluorides of. Two fluorides of Ag probably exist, Ag_2F and AgF, although there is still some doubt as to the isolation of the first of these.

SILVER SUBFLUORIDE (? Ag_2F). (*Argentous fluoride.*) By electrolysing saturated AgFAq, using Ag electrodes, and a current so strong that the liquid became hot, Güntz (*C. R.* 110, 1337) noticed the separation of brass-coloured crystalline plates at the negative pole (if a weaker current was used, Ag was deposited). Treatment of these crystals with water gave AgFAq and Ag, the ratio of Ag separating to Ag going into solution being practically unity; hence G. gives the formula Ag_2F to the yellow crystals. G. says that the same compound is obtained by heating finely-divided Ag with AgFAq in a sealed tube to nearly 90°. Ag_2F does not change in dry air; it decomposes slowly in moist air, and rapidly in water. Heated in dry HCl, CCl_4, PCl_3, &c., Ag_2Cl is said to be formed (G., *C. R.* 112, 861).

SILVER FLUORIDE AgF. (*Argentic fluoride.*) Formula probably molecular, from analogy of AgCl. Prepared by dissolving Ag_2CO_3 that has been freshly ppd. and well washed, in HFAq, evaporating to dryness in a Pt dish, with constant stirring, dissolving the black residue in water, filtering, and evaporating *in vacuo* over H_2SO_4, in the dark (Moissan, *Bl.* [3] 5, 456; *cf.* Güntz, *A. Ch.* [6] 3, 42). A yellow, transparent, elastic solid; sol. water; melts at c. 435° (M., *l.c.*). S.G. 5·852 at 15·5° (Gore, *Pr.* 18, 157). Fremy (*A. Ch.* [3] 47, 39) obtained large colourless prisms, to which he gave the formula AgF.2aq, by evaporating a solution of Ag_2CO_3 or Ag_2O in HFAq; these crystals lost 2aq *in vacuo*, but some oxyfluoride was always formed (*cf.* Marignac, *Ann. M.* [5] 15, 270). Heated in air, AgF is decomposed, by the moisture present, to Ag, O, and HF, according to Gore (*l.c.*). AgF interacts violently with $POCl_3$, PCl_3, $SiCl_4$, and BCl_3, giving AgCl and fluoride of P, Si, or B (Moissan, *l.c.*). Molten AgF attacks vessels of Ag or Pt. The dry salt is said to absorb c. 800 times its volume of NH_3 (Gore, *l.c.*). Heating with I produces AgI and IF_5 (Gore, *Pr.* 30, 70; where a few other reactions of compounds with AgF are given).

Silver, fulminating; *v.* SILVER NITRIDES, p. 470; *Silver fulminate* (*q. v.*, vol. ii. p. 317) is sometimes called fulminating silver.

Silver, hydroxides of; *v.* SILVER OXIDES AND HYDRATED OXIDES, p. 470.

Silver, iodides of. The isolation of an iodide other than AgI is very doubtful.

Silver subiodide (? Ag_2I). Güntz (*C. R.* 112, 861) states that this compound is formed by the interaction of HI and Ag_2F; but no analyses are given.

Silver iodide AgI. (*Argentic iodide.*) Formula probably molecular, from analogy of AgCl. Melts at c. 530° (Carnelley, *C. J.* 29, 489); at 527° (Rodwell, *Pr.* 25, 280). S.G. at 0° = 5·675, at 527° = 5·522; maximum density at 142° (R., *l.c.*). V.D. said to be 214 (Dewar a. Scott, *B. A.* 1881. 597). S.H. (15° to 98°) ·06159 (Regnault, *A. Ch.* [3] 1, 129; *v.* also Bellati a. Romanese, *Pr.* 34, 104). H.F. [Ag,I] = 13,800 (*Th.* 3, 381); 14,300 for crystalline AgI (Berthelot, *Bl.* [2] 39, 18).

Occurrence.—As *iodite* in Peru, Mexico, the Harz, Spain, &c.; forms hexagonal tablets; also in combination with AgBr as *iodobromite* in small quantities in Nassau.

Preparation.—1. By adding HIAq, or solution of an iodide, to $AgNO_3Aq$, washing, and drying.—2. By the interaction of finely-divided Ag with HIAg, H is evolved at ordinary temperatures and AgI formed; a solution saturated by heating HIAq with Ag deposits crystals of $AgI.xHI$ on cooling (*v. infra, Combinations*, No. 2), and the liquid decanted from these deposits hexagonal crystals of AgI on standing in air.—3. Crystals of AgI are also obtained by boiling saturated $AgNO_3Aq$ with HgI_2, and allowing to cool (Field, *J.* 1857. 255).—4. The interaction of a mixture of HClAq and HIAq with Ag produces only AgI, according to Deville (*A.* 101, 197).

Properties.—As obtained by adding alkali iodide to excess of $AgNO_3Aq$, AgI is a curdy pp., yellow, with a slight orange tint; by adding $AgNO_3Aq$ to excess of alkali iodide, a pure yellow, powdery pp. of AgI is formed; the former pp. is sensitive to light, the latter, after washing in the dark, is not discoloured by light. AgI melts to a yellow liquid, which becomes red and then dark-red as temperature rises; the liquid solidifies to a yellow, horny, crystalline mass. Rodwell (*Pr.* 25, 280) found that AgI contracted considerably at the moment of solidification; regular contraction then took place to 142°, whereat there was sudden and considerable expansion accompanied by change from the amorphous to the crystalline form; this was followed, as temperature fell, by slight expansion (for measurements *v.* R., *l.c.*). AgI exists in two forms: above 142° up to the m.p. it is yellow, transparent, and flexible; below 142° it is pale green, crystalline, opaque, and brittle (R., *l.c.*). AgI is nearly insol. NH_3Aq; according to Martini (*S.* 56, 153) 1 part AgI requires 2560 parts NH_3Aq, S.G. ·96, for solution. AgI dissolves in $Na_2S_2O_3Aq$, in KCNAq, and in NaClAq; it dissolves readily in hot $Hg(NO_3)_2Aq$, and crystallises therefrom on cooling (*v.* also *Combinations*).

Reactions.—1. Heated in *chlorine*, AgCl is formed.—2. Reduced by contact with *metals*, such as Zn or Fe, in presence of acids. Most of the reactions of AgI closely resemble those of AgCl.

Combinations.—1. Dry AgI absorbs *ammonia*; Rammelsberg (*P.* 48, 170) says that $2AgI.NH_3$ is formed (for dissociation-pressures of this compound *v.* Isambert, *C. R.* 64, 1259). By heating AgI with excess of NH_3Aq in a sealed tube at 100°, Terreil obtained crystals of $AgI.2NH_3$ (*Bl.* [2] 41, 598).—2. AgI dissolves in hot conc. *hydriodic acid* solution; the liquid deposits large, colourless, unstable crystals of AgI.HI (?) (Deville, *C. R.* 42, 895); Berthelot obtained transparent crystals of $3AgI.HI.7H_2O$ (*A. Ch.* [5] 23, 89).—3. According to Preuss (*A.* 29, 328) a solution of AgI in a hot solution of *mercuric nitrate* deposits crystals of $4AgI.2Hg(NO_3)_2.aq$ on cooling.—4. AgI dissolves in *silver nitrate* solution containing more than 3 p.c. $AgNO_3$ (Vogel); water re-ppts. AgI. For accounts of different compounds obtained *v.* Kremers (*J. pr.* 71, 54), Stürenberg (*Ar. Ph.* [2] 143, 112), Weltzien (*A.* 95, 127), Riche (*A.* 111, 39), Risse (*A.* 111, 43). AgI also combines with *silver nitrate and lead nitrate*, and with *antimonide, arsenide, phosphide*, and *sulphide of silver* (*v.* Poleck a. Thümmel, *Ar. Ph.* [3] 22, 1).—5. With *alkali iodides* and *alkaline earth iodides* (*v.* Boullay, *A. Ch.* [2] 34, 377; Berthelot, *Bl.* [2] 39, 24; Johnson, *C. N.* 37, 110; Maxwell Simpson, *Pr.* 27, 120).

Silver, iodobromochlorides of. Rodwell (*Pr* 25, 292) prepared various compounds of AgI AgBr, and AgCl by melting the constituents together. R. studied especially the effects of heat on the S.G., change of volume, and m.p. of these bodies. The formula $xAgI.yAgBr.zAgCl$ expresses the composition of the compounds examined; x varied from 1 to 4, y was always 1, and z varied from 1 to 2.

Silver, nitrides of. Raschig (*A.* 233, 93) has shown that the explosive substance first prepared by Berthollet, by the action of conc. cold NH_3Aq on Ag_2O, and supposed by B. to be a compound of Ag_2O and NH_3, is a nitride of Ag, Ag_3N, mixed with finely-divided Ag. Ag_3N is best prepared by allowing a conc. solution of Ag_2O in NH_3Aq to stand in air, or by adding alcohol. Ag_3N dissolves in KCNAq, forming AgCN, KHOAq, and NH_3.

The Ag salt of HN_3 may be called silver nitride; *v.* Hydrazoïc acid, vol. iii. p. 559.

Silver, nitroprusside of, *v.* vol. ii. p. 341.

Silver, oxides and hydrated oxides of. Only one oxide of Ag has been certainly isolated; the existence of any hydrated oxide is doubtful.

Silver oxide Ag_2O. (*Argentic oxide.*) Mol. w. not known.

Formation.—1. By heating Ag much above the temperature of volatilisation in the O-H flame, using excess of O (Debray, *C. R.* 66, 735).—2. By passing an electric current through KNO_3Aq, using a plate of Ag as positive electrode (Wöhler, *A.* 146, 264).—3. By boiling freshly-ppd. AgCl with KOHAq, S.G. 1·25 to 1·3 (Mohr, *A.* 66, 65).

Preparation.—KOHAq is added in slight excess to $AgNO_3Aq$, the pp. is thoroughly washed with hot water, best in air freed from CO_2, and dried at c. 80°.

Properties.—A black powder (brownish when ppd.), with an unpleasant, metallic taste. S.G. 7·52 (Schröder, *B.* 9, 1888); 7·15 (Playfair a. Joule, *C. S. Mem.* 3, 84); 7·25 (Boullay, *A. Ch.* [2] 43, 266). H.F. $[Ag^2,O]$ = 5,900 (*Th.* 3, 381). Slightly sol. water; 1 part dissolves in 3,000 parts water according to Bineau (*C. R.* 41, 509), but according to Abl in 96 parts water at 18·5°

(*Oester. Zeit. f. Pharm.* 8, 201 [1884]). Sol. NH_3Aq (for so-called *explosive silver*, formed by dissolving in conc. NH_3Aq, *v.* SILVER NITRIDES, p. 470). Also sol. aqueous solutions of alkali thiosulphates, chlorides, and cyanides. Sol. aqueous $MeNH_2$ and $EtNH_2$ (Wurtz, *A. Ch.* [3] 30, 453). Moist Ag_2O absorbs CO_2 from the air, forming Ag_2CO_3, and reacts with many salts like the alkalis (*v. Reactions*). Ag_2O is decomposed to Ag and O by heat (*v. Reactions*).

Reactions and Combinations.—1. Decomposed to Ag and O by *heat*; Carnelley and Walker (*C. J.* 53, 79) say that O begins to come off at c. 100°, rapid decomposition occurs at c. 270°, and reduction is complete at 300°–340° (*v.* also H. Rose, *P.* 85, 317; Joulin, *Bl.* [2] 19, 349; *cf.* HYDRATED SILVER OXIDE, *infra*).—2. *Antimony sulphide*, *arsenic sulphide*, finely-powdered *sulphur* and *selenion*, amorphous *phosphorus*, and some *organic compounds*, are ignited by rubbing with Ag_2O (Böttger, *J.* 1863. 284).—3. Reduced to Ag by heating to 100° in *hydrogen* (Wöhler, *A.* 30, 4).—4. Finely-divided Ag_2O under water is reduced to Ag by *cadmium*, *copper*, *tin*, and *zinc* (not reduced by Fe or Hg) (Fischer, *P.* 10, 605).—5. AgI and HIO_3 are formed by the reaction of *iodine* with Ag_2O suspended in water (Naquet, *Bl.* 1860. 123); with *chlorine* the products are AgCl, HClOAq, AgClO, and $AgClO_3$ (Stas).—6. Moist Ag_2O decomposes many *metallic salts* in solution, ppg. metallic hydroxides, *e.g.* salts of Bi, Cr, Co, Cu, Fe, Hg (*v.* H. Rose, *B. B.* 1857. 245).—7. The moist oxide removes halogens from many *halogen-containing organic compounds*, replacing the halogen by OH (*e.g.* $2NMe_4I + Ag_2O.H_2O = 2NMe_4OH + 2AgI$).—8. Ag_2O reacts with *acids* as a decidedly basic oxide, forming salts Ag_2X, where $X = SO_4$, $2NO_3$, &c.—9. A little $AgNO_2$ is said to be formed when *nitric oxide* is passed into water with Ag_2O suspended therein (Sabatier a. Senderens, *C. R.* 114, 1476).—10. Ag_2O combines with *lead monoxide*; by allowing a mixture of $PbO.xH_2O$ and freshly ppd. Ag_2O to stand in contact with NaOHAq, a compound was obtained, probably $2Ag_2O.PbO$ (E. Aston, *C. J.* 59, 1093).

HYDRATED SILVER OXIDE (? AgOH). According to H. Rose (*P.* 85, 904), no compound of Ag_2O and H_2O exists. By ppg. an alcoholic solution of $AgNO_3$ by KOHAq at −40°, Bruce obtained a white flocculent pp. which he supposed to be a hydroxide of Ag (no analyses are given); the pp. darkened on heating, forming Ag_2O and H_2O according to B. (*C. N.* 50, 208). Carey Lea (*Am. S.* 1892. 249) found that ppd. Ag_2O retained some water after drying at 100° for 40 hours, and that all water was removed at 160°-165° but some O went off also. Carnelley and Walker (*C. J.* 53, 79) say that the product of drying ppd. silver oxide in air for 6 months had the composition AgOH, and that this was scarcely decomposed at 100°, but that above this temperature it gave off water and a little O, and was gradually changed to Ag_2O mixed with a little Ag. Some reactions of moist Ag_2O point to the existence of such a compound as AgOH (*v.* SILVER OXIDE, *Reactions*, Nos. 6 and 7).

OXIDE OF SILVER WITH LESS OXYGEN THAN Ag_2O. (*Silver suboxide.*) Many experiments are recorded on the interactions of reducing agents and Ag salts whereby salts of a lower oxide than Ag_2O were supposed to be formed, and the corresponding oxide was supposed to be ppd. from these salts by alkali. Wöhler (*A.* 30, 1) reduced Ag citrate by heating in H; W. a. Rautenberg reduced ammoniacal solutions of chromate, molybdate, and tungstate of Ag (*A.* 114, 119); W. reduced arsenate and phosphate of Ag by $FeSO_4$ (*A.* 146, 263); H. Rose reduced $AgNO_3$ in NH_3Aq by ferrous and manganous salts (*P.* 101, 264, 321, 497; *v.* also Weltzien, *A.* 142, 105). More recent experiments have shown that the products of such reductions in presence of alkali are mixtures containing Ag (*v.* Pillitz, *Fr.* 27, 496; Newbury, *Am.* 8, 196; Muthmann, *B.* 20, 983; Bailey a. Fowler, *C. J.* 51, 416).

Faraday (*Q. J. S.* 4, 268) supposed that a suboxide of Ag was formed by the action of air on an ammoniacal solution of Ag_2O; but Bailey and Fowler (*l.c.*) have shown that the substance is a mixture of Ag_2O with a little explosive silver.

The result of a long series of experiments by O. v. d. Pfordten (*B.* 18, 1407; 20, 1458; 21 2288, 3375) on reducing $AgNO_3Aq$ by H_3PO_3Aq, alkali bisulphites, and tartaric acid, is that the black pp. thus obtained is not a suboxide of Ag (for some time it was asserted to be Ag_4O); the accuracy of this result has been strengthened by the critical experimental work of Bailey (*C. N.* 55, 263; *C. J.* 51, 466), and especially of Friedheim (*B.* 20, 2554; 21, 307). F. regards the supposed Ag_4O as a mixture of finely-divided Ag with more or less Ag_2O, or with some organic compounds. V. d. P. (*B.* 21, 2288, 3375) thinks his latest work points to the black substance being a compound of Ag, H, and O in the ratio 4Ag:2H:O; he gives it the formula $Ag_4.H_2O$, or $Ag_4.OH.H$, and calls it *silver hydrate*. According to Güntz (*C. R.* 112, 861) Ag_4O is produced by the action of steam on Ag_2F at 160°.

The question of the existence and isolation of a compound with less O than Ag_2O cannot be regarded as settled.

OXIDES OF SILVER WITH MORE OXYGEN THAN Ag_2O. By electrolysing conc. $AgNO_3Aq$, using Pt as positive and Ag as negative electrode, Ritter obtained a black deposit on the Pt; to this black substance R. gave the formula Ag_2O_2, and described it as crystallising in octahedra, S.G. 5·474, giving up half its O when carefully heated, with NH_3Aq evolving N, and with H_2O_2Aq producing Ag, H_2O, and O. A similar production of what seemed to be a peroxide of Ag was noticed by Fischer (*J. pr.* 33, 237) and by Wöhler (*A.* 146, 264). Böttger (*B.* 6, 1398) noticed that the peroxide produced by electrolysis formed explosive Ag and rapidly evolved N, with NH_3Aq. Ag peroxide is formed by the action of ozone on Ag, according to Schönbein (*J. pr.* 41, 321); and of ozone on Ag_2O according to Schiel (*J.* 1864. 118). Ag peroxide is an energetic oxidiser; it sets fire to H_2S, and Au sulphide when rubbed therewith (*v.* Böttger, *l.c.*).

The analyses made by Fischer (*J. pr.* 33, 237), Mahla (*A.* 82, 289), and Gmelin (*J.* 6, 105) of the peroxide showed the presence of H_2O and $AgNO_3$; their preparations were probably impure. The analyses of Wallquist (*J. pr.* 31, 179) agreed well with the formula AgO (or Ag_2O_2).

The supposed peroxide of Ag, prepared by electrolysing $AgNO_3Aq$, is regarded by Berthelot (*Bl.* [2] 34, 138) as a compound of $AgNO_3$ with an oxide to which he gives the formula Ag_4O_3. By the interaction of H_2O_2Aq with Ag_2O, Berthelot (*l.c.*) obtained black flocks, which were separated from Ag by washing; to this substance B. gives the formula Ag_4O_3 as the result of a not very complete analysis; he looks on it as probably identical with the product of the interaction of moist ozone and Ag or Ag_2O. This substance loses O when dried over H_2SO_4; with acids it gives salts of Ag_2O and evolves O.

Silver, oxychlorides of. The action of light on AgCl probably produces two oxychlorides of Ag; *v.* SILVER CHLORIDE, *Action of light on*, p. 468.

Silver, oxyfluoride of. To the yellow crystals obtained by evaporating an aqueous solution of AgF, Pfaundler gives the composition AgF.AgOH (*W. A. B.* 46 [2] 259).

Silver, phosphides of. Molten Ag absorbs P; according to Pelletier (*A. Ch.* 13, 101), some of the P remains in combination on cooling, but Warren (*C. N.* 56, 113) says that all except c. ·002 p.c. separates as the Ag cools. According to Emmerling (*B.* 12, 152), a compound AgP is formed by heating Ag and P in a sealed tube to a dark-red heat; on heating the compound P is given off and Ag remains (*v.* also Landgrebe, *S.* 60, 128). By heating powdered Ag in vapour of P, Schrötter obtained a grey solid, S.G. 4·63, to which he gave the composition Ag_2P_3 (*J.* 1869. 247).

Fresenius and Neubauer (*Fr.* 1, 340) obtained a pp. said to contain Ag phosphide and Ag, by leading PH_3, or CO_2 laden with vapour of P, into $AgNO_3Aq$; using PH_3 diluted with CO_2, Poleck and Thümmel (*B.* 16, 2435) obtained a compound, probably $Ag_3P.3AgNO_3$.

Silver, photosalts of. Carey Lea (*Am. S.* [3] 33, 349, 480, 489; 34, 33; abstract in *C. J.* 54, 1) gives the name of photosalts to variously-coloured compounds of Ag with the halogens which are very sensitive to light. These bodies are regarded by C. L. as identical with the substances that form the latent images on exposed photographic plates. The photosalts are obtained by the action of reducers, such as $FeSO_4Aq$ or $FeCl_2Aq$, on the normal Ag haloids, by reducing Ag salts by such bodies as dextrose or tannin in presence of alkali and treating the products with HClAq, or by treating finely-divided Ag with the haloid salts of Cu or Fe and certain other halogenating reagents. The photosalts are regarded by C. L. as compounds of the normal haloids with sub-haloids; from the methods of preparation it seems fairly certain that the coloured bodies called photosalts contained various substances besides Ag and halogen.

Silver, platinocyanide of, *v.* vol. ii. p. 344.

Silver, platinosulphocyanide of, *v.* vol. ii. p. 351.

Silver, salts of. Compounds derived from acids by replacing H by Ag. These salts belong to the type AgX, where $X=NO_3$, $\frac{1}{2}SO_4$, $\frac{1}{2}CO_3$, $\frac{1}{3}PO_4$, &c. Subsalts of the type Ag_2X possibly exist, where X is a halogen. The principal silver salts of oxyacids are: *arsenate* and *arsenite*, *borate*, *bromate*, *carbonates*, *chlorate*, *chlorite*, *perchlorate* and *hypochlorite*, *chromate* and *dichromate*, *iodate* and *periodates*, *molybdates*, *nitrate*, *nitrite* and *hyponitrite*, *phosphates*, *selenate* and *selenite*, *sulphates*, *sulphite* and *thionates*, *tellurates* and *tellurite*. Several salts derived from sulphur-containing acids also exist, the chief of which are: *thio-antimonates* and *antimonites*, *thio-arsenates* and *arsenites*, *thio-carbonate*, *thio-molybdates*, *thio-phosphates* and *phosphites*, and *thio-tellurite*.

Silver, selenide of, Ag_2Se. Occurs native, also in combination with selenides of Cu and Pb. Obtained by heating Ag with Se, SeO_2, or H_2Se; also by passing H_2Se into solution of a Ag salt; and by heating $AgNO_3Aq$ with Se (Senderens, *C. R.* 104, 175). A grey solid, melting at red heat to silver-white regulus. A little Se is lost by roasting in air; sol. conc. hot HNO_3Aq, crystals of Ag_2SeO_4 separating as liquid cools.

Silver, selenocyanide of, *v.* vol. ii. p. 348.

Silver, silicides of. Berzelius found that Ag after fusion with SiO_2 and C gave a residue of SiO_2 when dissolved in HNO_3Aq. Percy (*Silver and Gold*, 1, 131) failed to obtain any compound of Ag and Si. Warren (*C. N.* 60, 5) obtained compounds or alloys of Ag and Si by heating Ag with K_2SiF_6 and Na.

Silver, silico-fluoride of, $Ag_2SiF_6.2H_2O$. White, deliquescent crystals, melting below 100°; when strongly heated gives a residue of Ag with some SiO_2. Obtained by evaporating a solution of Ag_2O in H_2SiF_6Aq (Marignac, *Ann. M.* [5] 15, 270).

Silver, sulphides of. The isolation of any sulphide other than Ag_2S is very doubtful.

SILVER SULPHIDE Ag_2S. (*Argentic sulphide.*) Mol. w. not known. Occurs native as *argentite* or *silver glance*. Prepared by heating Ag in vapour of S, or in H_2S, or by the action of H_2S on red-hot AgCl (Durocher, *C. R.* 32, 823). H_2S quite free from admixed O is said not to react with Ag. Also prepared by passing H_2S into a solution of a salt of Ag; by boiling Ag_2SO_4Aq or $AgNO_3Aq$ with S (Filhol a. Senderens, *C. R.* 104, 175); and by the contact of H_2SAq with moist Ag_2O. Spring formed Ag_2S by subjecting a mixture of Ag powder and amorphous S to a pressure of several thousand atmospheres, powdering, and compressing again, and repeating this treatment seven or eight times (*Bl.* [2] 39, 641; 41, 488, 492; *cf.* Friedel, *Bl.* [2] 40, 526). Thomsen (*Th.* 3, 381) gives $[Ag^2,S]=5,340$. Winssinger (*Bl.* [2] 49, 452) obtained a dilute aqueous solution of colloidal Ag_2S by ppg. from a very dilute solution of a Ag salt, by H_2S, and dialysing; the solution was reddish brown, and did not change after keeping for more than two months.

Ag_2S obtained by ppn. is a black solid; when melted, out of air, it solidifies to a grey-black, lustrous, malleable mass, that can be cut with a knife; S.G. 6·85 (Karsten, *S.* 65, 394). S.G. of *argentite* 7·27 to 7·32 (Dauber, *J.* 13, 748). Heated in air slowly goes to Ag, giving off SO_2. With conc. boiling HClAq gives AgCl and H_2S; hot HNO_3Aq forms $AgNO_3Aq$ and H_2S; conc. H_2SO_4 produces Ag_2SO_4 and SO_2. Heated in Cl, AgCl and S_2Cl_2 are formed. Reduced to Ag by action of metals and dilute acid; also reduced by heating with PbO, CuO, Fe powder, or Hg (*cf.* Rammelsberg, *C. J.* 39, 874).

Many compounds of Ag_2S with metallic sulphides occur in minerals, *e.g.* with Cu_2S, Sb_2S_3, As_2S_3, Bi_2S_3, &c. Schneider (*J. pr.* 41, 414) obtained a compound of Ag_2S and Bi_2S_3 by fusing the two sulphides together in a covered crucible. Poleck and Thümmel (*Ar. Ph.* [3] 22, 1) obtained $Ag_2S.AgNO_3$ by passing H_2S into conc. $AgNO_3Aq$ so long as it was completely absorbed, washing the greenish pp. with HNO_3Aq, and drying; a black amorphous powder, decomposed by water to Ag_2S and $AgNO_3Aq$.

SILVER SUBSULPHIDE. According to Güntz (*C. R.* 112, 861), Ag_4S is obtained by the action of H_2S on Ag_2Cl.

Silver, sulphocyanide of, *v.* vol. ii. p. 352.

Silver, telluride of, Ag_2Te. Occurs native as *hessite.* Prepared by melting together Ag and Te, by passing vapour of Te diluted with much N over red-hot Ag (Margottet, *C. R.* 85, 1142), and by heating $AgNO_3Aq$ with Te in a sealed tube (Senderens, *C. R.* 104, 175). Grey, lustrous solid; obtained in needles (octahedral) by the second method given above. M. M. P. M.

SINALBIN $C_{30}H_{44}N_2S_2O_{16}$. A glucoside occurring in the seed of white mustard (Will, *Z.* [2] 7, 89; *A.* 199, 150). Prepared by washing the seeds with CS_2 and extracting the residue with alcohol. Concentric groups of pale-yellow needles (from alcohol), v. sol. water, insol. CS_2 and ether. Reduces Fehling's solution, with formation of Cu_2S. Split up by the ferment myrosin into glucose, sinapine sulphate $C_{16}H_{23}NO_5H_2SO_4$, and C_7H_7OCNS, a pungent oil. Aqueous $AgNO_3$ produces a similar decomposition, forming a pp. whence H_2S removes Ag, leaving in solution sulphate of sinapine and C_8H_7NO [69°]. Coloured yellow by alkalis, and yields Na_2SO_4 and sodium sulphocyanide on boiling with NaOHAq. $HgCl_2$ gives a white pp.

SINAMINE *v.* ALLYL CYANAMIDE.

SINAPIC ACID $C_{11}H_{12}O_5$. [192° cor.]. Formed, together with neurine, by boiling sinapine sulphocyanide with alkalis (Von Babo a. Hirschbrünn, *A.* 84, 19; Remsen a. Coale, *Am.* 6, 50). Small yellow prisms (from alcohol), sl. sol. cold water, insol. ether. The ammoniacal solution turns brown in air. Salt.—BaA'' (dried at 110°). Pp.

Acetyl derivative $C_{11}H_{11}AcO_5$. [281°]. Got by boiling the acid with Ac_2O. White crystals, sol. hot water.

SINAPINE $C_{16}H_{23}NO_5$. Occurs as sulphocyanide in seeds of white mustard (O. Henry a. Garot, *J. Ph.* 17, 1; 20, 63; Pelouze, *A. Ch.* [2] 44, 214; *J. Ph.* 17, 271; Boutron a. Robiquet, *J. Ph.* 17, 279; O. Henry a. Plisson, *A. Ch.* [2] 46, 198; Winckler, *Rep. Pharm.* 41, 169; 67, 257; Simon, *P.* 43, 651; 44, 593; Boutron a. Fremy, *J. Ph.* 26, 50; Von Babo a. Hirschbrünn, *A.* 84, 10; Remsen a. Coale, *Am.* 6, 50). Formed also by the action of myrosin on sinalbine (Will a. Laubenheimer, *A.* 199, 162). The free base is known only in solution, and is decomposed on evaporation, leaving a resin. Boiling baryta-water splits it up into neurine $C_5H_{13}NO_2$ and sinapic acid.

Salts.—$B'H_2SO_4$ 2aq: rectangular plates, v. sol. water and hot alcohol, nearly insol. ether.—$B'HHgCl_3$: thin prisms.—B'HCNS. [176°].

SINAPOLINE *v.* DI-ALLYL UREA.

SINCALINE *v.* NEURINE.

SINISTRIN *v.* INULIN.

SIPERINE. An amorphous, resinous, alkaloid occurring, together with bebirine, in the greenheart tree (*Nectandra Rodiæi* or *Bebeeru Sipceri*). It is v. sl. sol. water, m. sol. alcohol, insol. ether (Maclagan, *A.* 48, 106).

SKATOLE *v.* METHYL-INDOLE.

SKELETINS *v.* PROTEÏDS, *Appendix* C.

SKIMMIN $C_{15}H_{16}O_8$. [210°]. A glucoside extracted by alcohol from *Skimmia japonica* (Eijkman, *R. T. C.* 3, 204). White needles, sl. sol. cold water. Its alkaline solutions show blue fluorescence. It is not poisonous, and does not reduce Fehling's solution.

Skimmetin $C_9H_6O_3$. [223°]. Formed, together with glucose, by boiling skimmin with dilute mineral acids. Colourless crystals, sol. alcohol and ether. Its solutions exhibit blue fluorescence. Does not reduce Fehling's solution. $FeCl_3$ gives a blue colour. Gold chloride gives a rose colour, turning blue and violet.

SMILACIN $C_{18}H_{30}O_6$ (?). Occurs in sarsaparilla root (*Smilax Sarsaparilla*) (Reinsch, *Rep. Pharm.* 82, 145; Thubeuf, *A.* 5, 204; 14, 76; Batka, *A.* 11, 305; Poggiale, *A.* 13, 84; Henry, *A.* 14, 77; Petersen, *A.* 15, 74; 17, 166; Wright a. Rennie, *C. J.* 39, 237). Nodular groups of leaflets, m. sol. hot water and alcohol, sol. alkalis.

Reference.—PARILLIN.

SNAKE POISON *v.* PROTEÏDS.

SOAP *v.* DICTIONARY OF APPLIED CHEMISTRY.

SOBREROL $C_{10}H_{18}O_2$. [150°]. $[\alpha]_D = \pm 150°$. A product of atmospheric oxidation of turpentine in sunlight (Armstrong a. Pope, *C. J.* 59, 316). Long tables (from alcohol) or monoclinic prisms (from water); $a:b:c = 2{\cdot}411:1:{\cdot}853$; $\beta = 83°38'$. Tastes bitter. Converted by boiling dilute H_2SO_4 into an oily isomeride of camphor. By crystallising a solution of equal quantities of dextro- and lævorotatory sobrerol there is obtained an inactive sobrerol [131°] crystallising from alcohol in trimetric tables; $a:b:c = 2{\cdot}424:1:{\cdot}827$.

SOCALOÏN *v.* ALOÏN.

SODA; *v.* SODIUM HYDROXIDE, p. 479.

SODIUM Na. At. w. 22·995. Mol. w. very probably same as at. w. (*v. infra*). Melts at 95·6° (Bunsen, *A.* 125, 367), 97·6° (Hagen, *W.* 19, 436); solidifies at 97·6° (Regnault, *J.* 1856. 43). Boils between 860° and 950°, according to Carnelley and Williams (*C. J.* 35, 565); at 742° (Perman, *C. J.* 55, 326). S.G. ·985 $^{0°}_{4°}$ (Schröder, *P.* 106, 226); ·9743 at 10° (Baumhauer, *B.* 6, 655); c. ·74 at b.p. (Ramsay, *C. J.* 39, 49). V.D. 12·7 at 1200°–1500° (Scott, *Pr. E.* 14, 410; *v. infra*). S.H. ·2734 from −28° to 6° (Regnault, *A. Ch.* [3] 46, 257); ·21 when liquid (Joannis, *A. Ch.* [6] 12, 358). C.E. (0° to 50°) ·00007105 (Hagen, *W.* 19, 436). E.C. (Hg at 0° = 1) 18·3 solid at 0°, 8·3 liquid at 120° (Matthiessen, *P. M.* [4] 12, 199; 13, 81). T.C. (Ag = 100) = 36·5 (Calvert a. Johnson, *P. M.* [4] 16, 381). H.C. $[Na^2,O] = 99{,}760$ (*Th.* [3] 232). Refraction-equivalent $\frac{\mu-1}{d} \times$ at. w. $= 4{\cdot}4$ (Gladstone, *Pr.* 18, 49);

4·03 (Kanonnikoff, *J. R.* 1884 [i.] 119). Emission spectrum characterised by a double line D, the components of which have the wave-lengths 5895 and 5889 (for detailed measurements of lines *v.* B., *A.* 1884. 443). For absorption spectrum *v.* Roscoe a. Schuster (*Pr.* 22, 362). S.V.S. solid 23·3; at b.p. 31 (Ramsay, *C. J.* 39, 49).

Occurrence.—Compounds of Na occur widely distributed in large quantities. NaCl is found abundantly as *rock-salt*, also in sea-water and many mineral springs. Large quantities of $NaNO_3$ or *Chili saltpetre* occur in S. America. Carbonate, sulphate, and borate of Na are found, in comparatively small quantities, in rocks, and in lake and spring waters. *Cryolite* is a double fluoride of Na and Al. Many silicates contain Na silicate—*e.g. natrolite, albite, labradorite*, &c. The ashes of many plants contain Na salts, especially NaCl, NaI, and Na_2SO_4; some plant ashes are free from Na salts, even when the plants grow near the sea; the ashes of *algæ* and some other sea plants are richer in salts of K than in those of Na. NaCl, Na_2CO_3, Na_2HPO_4, and some other compounds of Na, are found in animal organisms.

Historical.—Caustic soda was decomposed by Davy in 1807 (*T.* 1808. 1) by electrolysis; Gay-Lussac a. Thénard heated NaOH with Fe filings and obtained Na (*A. Ch.* 65, 325 [1808]). Brunner (*S.* 71, 201) reduced Na_2CO_3 by heating with charcoal; this process was made applicable on the large scale by Deville (*A. Ch.* [3] 43, 5 [1855]).

The word *neter* is used by the older Hebrew writers to denote a substance employed for washing clothes; the same, or a similar, substance seems to have been known as *νίτρον* or *nitrum*, and by the fifteenth century this name was given to saltpetre; when the existence of two similar but distinct substances having detergent properties was recognised, the name *nitrum* was given to one, and the other was called *natrum* or *natron*. The metal obtained from natron was called *natrium*; this name is retained in German, but in English and French the metal is named from *soda*, a word applied in the Middle Ages to designate alkaline substances, and used as synonymous with *nitrum* and *natron*. The symbol Na is universally employed for the metal.

Formation.—1. By electrolysing NaOH (*cf.* Potassium, *Formation*, No. 1, p. 298).—2. By reducing Na_2CO_3 by heating it with charcoal, or with charcoal and very finely-divided iron (Castner, *C. N.* 54, 218).—3. By electrolysing fused NaCl, or conc. NaClAq, using Hg as the negative electrode.

Preparation.—1. An intimate mixture of 30 parts calcined Na_2CO_3, 13 parts coal, and 5 parts chalk is heated in an iron bottle with a short exit tube, in a furnace, until vapours of Na appear at the mouth of the tube, when a small flat receiver, made of sheet iron, is adapted to the tube; when the receiver is full of Na it is removed, and the metal is taken out under mineral oil (*cf.* Potassium, *Preparation*, p. 298). As Na does not combine with CO, the difficulty which attends the preparation of K because of the formation of KCO, does not occur with Na.—2. A mixture of NaOH, C, and Fe is heated in egg-shaped iron retorts, connected with cast-iron condensers about 3 ft. long and 5 in. diameter, and having small openings near the nozzles through which the molten Na runs into pots placed beneath. The mixture of C and Fe is made by heating a mixture of very finely divided iron and pitch; this is heated with NaOH in approximately the proportion 6NaOH:2C:4Fe. (For details *v.* Dictionary of Applied Chemistry, vol. iii. p. 422.)

The metal is purified by pressing through linen under rock oil kept at c. 100°; it must be kept under oil free from O. Rosenfeld (*B.* 24, 1658) recommends to soak the metal in a mixture of 1 part amyl alcohol and 3 parts petroleum, and to rub it with a rag soaked in the same mixture, till the surface is bright; then to let it remain under petroleum with 5 p.c. amyl alcohol; to wash it with pure petroleum, and to keep it under petroleum containing from ½ to 1 p.c. amyl alcohol. The film of sodium-amyl oxide which forms is easily rubbed off with filter paper.

Properties.—A silver-white, lustrous metal; usually described as whiter than K, but according to Long (*C. J.* 13, 122) a clean surface has a pale rose colour. By melting Na in a glass tube, narrowed at one place, and filled with coal-gas or H, and allowing the semi-solidified metal to flow slowly through the narrowed part of the tube, Na is obtained in lustrous, white, quadratic octahedra, with a rosy sheen (Long, *l.c.*; *cf.* Böttger, *B.* 7, 1536). According to Linnemann (*J. pr.* 75, 128), the surface of a freshly-cut piece of Na shows green phosphorescence that soon disappears, but returns again at 60°–70° (*cf.* Baumhauer, *J. pr.* 102, 123, 361). A sublimate, in a very thin film on glass, shows a greenish blue colour in transmitted light (Dudley, *C. N.* 66, 163; Newth, *N.* 47, 55). The vapour obtained by boiling Na in an atmosphere of H is colourless in thin layers, and violet to purple when seen in thick layers (Roscoe a. Schuster, *Pr.* 22, 362; Carnelley a. Williams, *C. J.* 35, 565). At the ordinary temperature Na is as soft as wax; it is ductile at 0°, and fairly hard at −20°; at c. 50° it is pasty; it melts at c. 96°, and boils at c. 750° (*v.* beginning of this article). Na dissolves in liquid NH_3, forming a blue liquid (*v.* Sodium-ammonium, p. 475). A freshly-cut surface of Na exposed to air becomes rapidly covered with a film of oxide; Na is said to be unchanged at the ordinary temperature in perfectly dry air. It decomposes cold water rapidly, but the H evolved does not generally take fire. Na must be kept under a liquid free from O, such as mineral oil or naphtha (*v. Preparation, supra*).

The *atomic weight* of Na has been determined (1) by converting NaCl into AgCl (Berzelius, *P.* 8, 189 [1826]; Pelouze, *C. R.* 20, 1047 [1845]; Dumas, *A. Ch.* [3] 55, 182 [1859]; Stas, *Stas. Rech.* 78); (2) by reducing $NaClO_3$ to NaCl (Penny, *T.* 129 [1] 25 [1839]); (3) by converting NaCl into $NaNO_3$ (Stas, *Nouv. R.* 248 [1865]); (4) by determining S.H. of Na.

The *molecular weight* of Na is not known with certainty. Dewar a. Dittmar (*C. N.* 27, 121) and D. a. Scott (*Pr.* 29, 206 [1879]) obtained numbers that indicated a mol. w. of 23; but the values varied considerably. D. a. S. used a vessel of wrought iron. Scott (*Pr. E.* 14, 410 [1888]) obtained fairly concordant results, giving values for V.D. varying from 11·8 to 15, using a Pt vessel heated above the m.p. of cast iron; but V. Meyer's experiments (*B.* 13, 391 [1880]) seemed to indicate that Na vapour attacks vessels of Ag or Pt. Mitscherlich (*A.* 12, 173 [1834]) found that vessels of hard glass were also attacked; and Rieth (*B.* 4, 807 [1871]) got no constant results by using a vessel of Cu. The values obtained by Scott were so constant that there is a large probability in favour of the monatomicity of the molecule of gaseous Na. Ramsay (*C. J.* 55, 521) dissolved Na in Hg and measured the decrease of vapour-pressure of the Hg thereby produced; assuming the mol. w. of liquid Hg to be 200, and assuming that equal vols. of dilute solutions in Hg contain equal numbers of molecules, the results gave values for mol. w. of Na varying from 15 to 21·5.

The V.D. of no compound of Na has been determined; from the analogy of K, Rb, Cs, and Ag, the atom of Na is probably monovalent in gaseous molecules.

Sodium is a strongly positive element; it comes after Rb, Cs, and K in order of decreasing electropositiveness (Bunsen). In all its compounds Na reacts as a metal; it does not enter into the composition of any negative radicles. Na forms few basic salts and no oxyhaloid compounds; its haloid compounds are very stable towards heat. Na is closely related to Li, K, Cs, and Rb (*v.* ALKALIS, METALS OF THE, vol. i. p. 114), and less closely to Cu, Ag, and Au (*v.* COPPER GROUP OF ELEMENTS, vol. ii. p. 250).

Reactions and Combinations.—1. Heated in *air* or *oxygen*, Na_2O and Na_2O_2 are formed (*v. Oxides*, p. 482). According to von Bonsdorff (*P.* 41, 296), Na is unchanged in quite dry air at the ordinary temperature.—2. Na absorbs *hydrogen* at c. 300°, probably forming a compound (*v. Hydride*, p. 479).—3. Combines with *chlorine*, *bromine*, and *iodine* when heated with these elements (*v. Chloride, bromide,* and *iodide*).—4. Forms sulphides, by reacting with *sulphur* at the ordinary temperature; combines, when heated, with *selenion* and *tellurium*, also with *arsenic* and *phosphorus* (*v. Sulphide*, p. 483, *Selenide*, p. 482, *Telluride*, p. 483, *Arsenide*, p. 476, and *Phosphide*, p. 482).—5. Alloys with several *metals* (*v. Alloys, infra*).—6. Na decomposes *water* at the ordinary temperature, forming NaOHAq and H; much heat is produced, but the H does not generally take fire unless the reaction is slackened, and friction is increased, by thickening the water by gum &c., or placing the Na on moist filter paper (*v.* Ducatel, *Am. S.* 25, 90; Serullas, *A. Ch.* [3] 40, 329). If Na is allowed to react with water in a cylinder standing over water, the H collecting in the cylinder, a violent explosion sometimes occurs, probably due to formation of a peroxide that is then decomposed with evolution of O, which mixes with the H (Böttger, *J. pr.* 85, 397; Griffin, *J.* 1856. 320).—7. Na reduces many *oxides* at high temperatures, *e.g.* CO, N_2O, B_2O_3, P_2O_5, As_2O_3, HgO, CuO, Ag_2O, PbO, ZnO, Fe_2O_3, &c.—8. Many *carbonates*, *sulphates*, *nitrates*, *phosphates*, and *silicates* are reduced when strongly heated with Na.—9. Many *metallic chlorides* are reduced by heating with Na, *e.g.* $MgCl_2$, $AlCl_3$ &c.—10. By heating with solid *caustic potash* to c. 170°, an alloy of Na and K is formed (*v.* Williams, *C. N.* 3, 21; Wanklyn, *C. N.* 3, 66).—11. Heated in *ammonia gas*, $NaNH_2$ is formed (*v. Amide, infra*), and when this is more strongly heated Na_3N is formed (*v. Nitride*, p. 482).—12. Na reacts with aqueous solutions of *acids* to form salts NaX, where X is a monovalent acidic radicle.

Sodium, alloys of. Na forms alloys with many metals; these alloys are generally formed by directly melting the metals together, or by reducing the chlorides by Na. By the action of sodammonium (*v. infra*) on Sb, Bi, Pb, Joannis (*C. R.* 114, 585) says that alloys of Na with these metals are obtained agreeing in composition with the formulæ Na_3Sb, Na_3Bi, and NaPb. Schumann (*W.* 43, 101) obtained a definite alloy of Na and Hg corresponding with the formula $NaHg_5$ (*v.* also SODAMMONIUM, *infra*).

Sodium, aluminates of, *v.* vol. i. p. 141.

Sodium, amide of, $NaNH_2$. (*Sodamide.*) Mol. w. not determined. First prepared by Gay-Lussac and Thénard (*Recherches physico-chimique*, 1, 354) by heating Na in NH_3; the Na absorbed 142 to 163 vols. NH_3 and 100 vols. H were produced. Prepared by Beilstein and Geuther (*A.* 108, 88) by driving out the air from several flasks, connected by tubes, by a stream of dry H, then placing a few grams Na in each flask, replacing the H by dry NH_3, free from CO_2 (Drechsel, *J. pr.* [2] 16, 203), and heating the flasks on sand-trays; the Na melts and swims on the blue-green liquid that forms. When the Na has all disappeared the liquid is allowed to cool; the solid that forms is at first brown, but when quite cold it forms a crystalline, olive-green mass. Also obtained by the gradual decomposition at the ordinary temperature (hastened by light) of sodammonium; as the liquid decomposes, crystals of $NaNH_2$, 1 mm. long, are formed; these crystals are said to be white (Joannis, *C. R.* 112, 392).

Heating in CO produces NaCN and H_2O, along with NaOH and NH_3. When heated in CO_2 much NH_3 is given off, and the final products are H_2O and $CN.NNa_2$ (disodium salt of cyanamide; *v.* vol. ii. pp. 313, 314); B. a. G. (*l.c.*); Drechsel (*l.c.*). CS_2 reacts to form NaSCN and H_2S, then NH_3 is given off, and NaSH remains. Dilute HClAq reacts violently, producing NaCl and NH_4Cl. EtCl forms NaCl, NH_3, and C_2H_4, but no $EtNH_2$. Heated with C the products are NaCN and H (Drechsel, *J. pr.* [2] 21, 91). When strongly heated $NaNH_2$ gives off NH_3 and leaves NaN_3 (*v.* SODIUM NITRIDE, p. 482).

Sodium-ammonium or **Sodammonium.** Weyl (*P.* 121, 611; 123, 350) obtained a blue liquid, by the action of liquid NH_3 on Na, which he regarded as a compound or alloy of Na and NH_4. As Na remained when the NH_3 was allowed to evaporate, Seeley (*C. N.* 23, 169) looked on the blue liquid as a solution of Na in liquid NH_3. Joannis (*C. R.* 109, 900, 965; 110, 238) found that the vapour-pressure of a solution of Na in liquid NH_3 decreased to a limit whereat it became constant if temperature remained unchanged; that on then removing more NH_3 a copper-red solid separated, and that NH_3 was then given off at constant pressure till only Na remained. When the last part of the change commenced, the copper-red substance contained

Na and NH_3 in the ratio $Na:NH_3$; the evolution of NH_3 at constant pressure was regarded by J. as due to the dissociation of a compound $NaNH_3$. The heat of formation of NH_3Na from gaseous NH_3 and solid Na was determined by J. to be 5,200, and from liquid NH_3 and solid Na to be 800, cals. J. determined the lowering in the freezing-point of liquid NH_3 by solution in it of $NaNH_3$, and so calculated the mol. formula of this body to be $Na_2N_2H_6$ (*C. R.* 115, 820). The solution of $Na_2N_2H_6$ in liquid NH_3 is decomposed by Sb, Pb, and Hg, but not by Al, Cu, Ag, or Zn; the final product of the action of Pb is $Pb_4Na.2NH_3$; by dropping the liquid on to Hg, and washing the product with liquid NH_3, the crystalline amalgam $NaHg_8$ was obtained (J., *C. R.* 113, 795). According to J. (*C. R.* 112, 392), $Na_2N_2H_6$ decomposes slowly at the ordinary temperature to $NaNH_2$ and H. With excess of NaCl the blue liquid becomes colourless and $NaNH_2$ separates; the compound NH_2Na_2Cl is first formed, and is then decomposed by the liquid NH_3 to $NaNH_2$ and NaCl. By passing dry O into $Na_2N_2H_6$ in liquid NH_3 at −50°, J. (*C. R.* 116, 1370) obtained NH_2Na_2OH; by the prolonged action of O he obtained Na_2O_2.

Sodium, arsenates of, *v.* vol. i. p. 309.

Sodium, arsenide of. Gay-Lussac and Thénard found that Na combined directly with As. According to Landolt (*A.* 89, 210) Na_3As is formed, as a silver-white solid, by heating the elements in the ratio 3Na:As. A compound of Na and As is also formed when Na is heated in AsH_3. Decomposed by water, giving off AsH_3.

Sodium, arsenites of, *v.* vol. i. p. 307.

Sodium, aurobromate of, $NaAuBr_4$. Orange-red prisms, by dissolving NaBr in $AuBr_3Aq$ (*cf.* vol. ii. p. 649).

Sodium, aurochlorate of, $NaAuCl_4$. By dissolving NaCl in $AuCl_3Aq$ (*cf.* vol. ii. p. 650).

Sodium, borates of, *v.* vol. i. p. 529.

Sodium, boride of. The product of the reduction of B_2O_3 by Na may contain a compound of B and Na.

Sodium borofluoride *v.* vol. i. p. 526.

Sodium, bromide of, NaBr. Mol. w. not certainly known, but probably 102·745 (= NaBr). Melts at 708° (Carnelley, *C. J.* 33, 279); at 727° (*v.* Meyer a. Riddle, *B.* 26, 2443). S.G. 3·079 at 17·5° (Kremers, *P.* 99, 443); 3·198 at 17·3° (Favre a. Valson, *C. R.* 77, 579); 2·448 when molten (Quincke, *P.* 138, 141). Kremers (*P.* 99, 443) gives solubilities as follows:—

Temp.	S.	Temp.	S.
0°	77·5	60°	111·1
20	88·4	80	112·5
40	104·2	100	114·9

Coppet (*A. Ch.* [4] 25, 506; [5] 30, 411) gives the following:—

Temp.	S.	Temp.	S.
44·1°	115·6	86°	118·8
51·5	116·2	90·5	119·7
55·1	116·8	100·3	120·6
60·8	117	110·6	122·7
64·5	117·8	114·3	124
74·5	118·4		

C. represents S. of NaBr as 110·34 + ·1075*t* when *t* varies from 44° to 114°. S. in alcohol 90 p.c. = 6. B.P. of saturated NaBrAq = 121°. S.G. of NaBrAq given by Kremers a. Gerlach (*Fr.* 8, 279) at 15° as follows:—

S.G. NaBrAq	P.C. NaBr	S.G. NaBrAq	P.C. NaBr
1·04	5	1·281	30
1·08	10	1·344	35
1·125	15	1·410	40
1·174	20	1·483	45
1·226	25	1·565	50

H.F. [Na,Br] = 85,770; [Na,Br,Aq] = 85,580 (*Th.* 3, 232).

Formation.—1. By passing Br vapour over Na. According to Merz and Weith (*B.* 6, 1518), Na remains unchanged for months in liquid Br at the ordinary temperature, and even at 100° or 200° the formation of NaBr proceeds very slowly.—2. By treating BrAq with iron filings, boiling the solution of $FeBr_2Aq$ with NaOHAq, filtering, and evaporating (Henry, *J. Ph.* 15, 54).—3. By neutralising HBrAq by NaOHAq or Na_2CO_3Aq, and evaporating.—4. By decomposing $CaBr_2Aq$ by Na_2SO_4, filtering after some time, adding Na_2CO_3 as long as turbidity is produced, filtering, and evaporating (Klein, *A.* 128, 237).—5. By decomposing pure NH_4Br by NaOHAq or Na_2CO_3Aq, and evaporating (Castelhaz, *C. R.* 70, 1050).

Preparation.—Br is added, little by little, to moderately conc. pure NaOHAq (*v.* Sodium hydroxide, p. 479) till the liquid is slightly yellow; the liquid is evaporated to dryness; the residue of $NaBrO_3$ and NaBr is strongly heated, in a porcelain dish, till traces of Br are given off, the residue is dissolved in water, evaporated, and allowed to crystallise at a temperature not under 30° (NaBr. 2aq separates below 30°).

Properties.—Lustrous, white cubes; strong alkaline taste; reaction in water is neutral. Dissolves easily in water, with slight fall of temperature [NaBr,Aq] = −190 (*Th.* 3, 232); NaBr separates from this solution at c. 30°, but at the ordinary temperature crystals of NaBr. 2aq are formed.

Reactions.—1. *Chlorine* reacts with NaBrAq to give NaClAq and Br.—2. Heated with *potassium chromate and sulphuric acid*, Br is given off; NaCl under similar conditions gives CrO_2Cl_2.—3. *Conc. sulphuric acid* forms HBr, Br, and SO_2; by using dilute H_2SO_4Aq (c. 30 p.c.) a mere trace of Br is obtained (*v.* Addyman, *C. J.* 61, 94).—4. *Potassium permanganate* does not react with NaBrAq even when boiled, but addition of a little H_2SO_4Aq causes evolution of Br (Hempel, *A.* 107, 160).

Combinations.— 1. With *water* to form $NaBr.2H_2O$. This hydrate separates from solutions of NaBr saturated when hot and cooled to under 30°; it crystallises in monoclinic prisms, which melt at 50°, leaving NaBr.—2. With many *bromides of less positive metals*, *e.g.* with $PbBr_2$ to form $PbBr_2.2NaBr$, and $CdBr_2$ to form $CdBr_2.5NaBr.5aq$ (*v.* the various metallic bromides).—3. With *arsenious oxide* to form $NaBr.As_4O_6$ (Rüdorff, *B.* 21, 3051).

Sodium, chloride of, NaCl. (*Common salt.*) Mol. weight not known with certainty, but probably 58·365 (= NaCl). Melts at 772° (Carnelley, *C. J.* 33, 280); at 851° (Meyer a. Riddle, *B.* 26, 2443). S.G. 2·16 at 0° (Quincke, *P.* 138, 141); 2·157 at 4° (Schröder, *P.* 106, 220);

(?) 1·612 at m.p. (Braun, *B.* 7, 958); 2·04 after fusion (Quincke, *P.* 135, 642); for other values *v.* Clarke's *Table of Specific Gravities* [2nd ed.] 20. S.H. 15° to 98° ·21401 (Regnault, *A. Ch.* [3] 1, 129; *v.* also Kopp, *T.* 155 [i.] 71). Vol. at 40° = vol. at 0° (1 + ·00012117 × 40) (Fizeau, *C. R.* 64, 314). H.F. [Na,Cl] = 97,690 (*Th.* 3, 232). Poggiale (*A. Ch.* [3] 8, 469) gives following data for solubility in water:—

Temp.	S.	Temp.	S.
−15°	32·73	40°	36·64
−10	33·49	50	36·98
− 5	34·22	60	37·25
0	35·52	70	37·88
+ 5	35·63	80	38·22
9	35·74	90	38·87
14	35·87	100	39·61
25	36·13	109·7	40·35

Coppet (*A. Ch.* [5] 30, 411) gives S. above 20° to 109° = 34·359 + ·0527*t*. Gerlach (*Fr.* 8, 281) gives the following data:—

S.G. NaClAq at 15°

1 p.c.	1·00725	10 p.c.	1·14315
2 „	1·01450	11 „	1·15107
3 „	1·02174	12 „	1·15931
4 „	1·02809	13 „	1·16755
5 „	1·03624	14 „	1·17580
6 „	1·04366	15 „	1·18404
7 „	1·05108	16 „	1·19228
8 „	1·05851	17 „	1·20098
9 „	1·06593	18 „	1·20433

1000 c.c. of NaClAq saturated at 15° contain 318·479 g. NaCl and 888·669 g. water (Michel a. Kraft, *J.* 1854. 296). NaClAq containing 29·4 to 29·5 p.c. NaCl boils at 109·25° (at 760 mm. pressure) and freezes at −21·3° (Karsten, *Salinenkunde* [Berlin, 1847] 2,38). The following freezing-points are given by Karsten (*l.c.*) for NaClAq (*cf.* Rüdorff, *P.* 114, 63; and de Coppet, *A. Ch.* [4] 25, 509):—

P.C. NaCl	F.P.	P.C. NaCl	F.P.
2	−1·32°	16	−11·69
4	−3·024	20	−14·44
6	−4·52	22	−15·78
8	−5·99	24	−17·11
10	−7·44	26	−18·42
12	−8·88		

For freezing-points of dilute NaClAq, containing from c. ·006 to c. 2·6 p.c. NaCl, *v.* Jones (*Z. P. C.* 11, 210).

Solution of NaCl in water is accompanied by lowering of temperature and contraction; 36 parts NaCl in dissolving in 100 parts water at 12·6° lower the temperature to 10·1° (Rüdorff, *B.* 2, 68); Thomsen gives [NaCl,Aq] = −1180 (*Th.* 3, 232). By mixing 36 parts NaCl with 100 parts snow, temperature falls to −21·3° (Rüdorff, *P.* 114, 79; 122, 337).

NaCl is insol. absolute alcohol; Girardin (*A. Ch.* [4] 5, 146) gives the following data for S. in aqueous alcohol S.G. ·9282; 10·9 at 4°, 11·1 at 10°, 11·43 at 13°, 11·9 at 23°, 12·3 at 32°, 13·1 at 44°, 13·8 at 51°, 14·1 at 60°. Schiff (*A.* 118, 365) gives S. in alcohol at 15° as follows; 28·33 in 10 p.c. alcohol, 13·25 in 40 p.c., 5·93 in 60 p.c., 1·22 in 80 p.c. NaCl crystallises in the regular system, generally in cubes, sometimes in octahedra.

Occurrence.—As *rock salt*, or *halite*, in very large quantities very widely distributed; in sea-water, many salt lakes, brine springs, and most mineral springs.

Formation.—1. By burning Na in moist Cl. According to Wanklyn (*C. N.* 20, 271), dry Cl does not combine with Na even at the M.P. of the metal; Donny a. Mareska (*C. R.* 20, 817) state that Na is unacted on by liquid Cl at −80°.—2. By neutralising NaOHAq or Na_2CO_3Aq by HClAq, and evaporating.—3. By the reaction of excess of conc. HClAq with several salts of Na, *e.g.* Na_2SO_4.—4. By strongly heating Na_2SO_4 with excess of NH_4Cl; also by decomposing Na_2SO_4Aq by several chlorides, *e.g.* $MgCl_2$ or $CaCl_2$.—5. As a by-product in making KNO_3 by the reaction of KCl with $NaNO_3$. 6. By the reduction of many chlorides by Na.

Preparation.—Pure $NaHCO_3$ is prepared by washing a large quantity of the ordinary 'pure' salt, in fine powder, with cold water till the washings cease to be clouded on addition of a salt of Ag or Ba; after boiling with slight excess of HNO_3Aq, the residue is dried and heated to dull redness in a Pt dish; a boiling saturated solution of the Na_2CO_3 thus obtained is prepared, filtered, and shaken while crystallising to insure the formation of small crystals; the crystals are dried by suction by a water-pump, they are then twice moistened with cold water to remove all mother-liquor, and crystallised three times from water. The pure Na_2CO_3 is dissolved, and NaCl is formed by passing in a stream of pure HCl gas (obtained by heating pure conc. HClAq); a little pure NH_4Cl is added to the solution (for preparation of pure NH_4Cl *v.* vol. i. p. 197, under AMMONIA, *Preparation*, No. 3), which is then evaporated to dryness in a Pt retort; the residue is very strongly heated, and then dissolved in water; after standing for 24 hours the solution is poured off (from any $Al_2O_3.xH_2O$ and SiO_2 that settle), a little pure NH_4Cl is added, the solution is evaporated to dryness in a Pt retort, the residue is strongly heated for some time, and after partial cooling the still liquid NaCl is poured off (from Pt, SiO_2, and Al_2O_3) into a Pt dish; when cold, the NaCl is dissolved in water, the solution is poured off after 2 days and evaporated to dryness in a Pt retort, and the residue is fused in a Pt vessel (Stas, *Chem. Proport.* 275).

For preparation of NaCl from rock salt, brine, and sea-water, *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 429.

Properties.—A pure, white, lustrous solid; crystallises in the regular system, generally in cubes. Decrepitates when heated. NaCl is diathermanous. Solution in water is neutral to indicators, and has a bitter taste. Pure NaCl is very slightly hygroscopic, taking up c. ½ p.c. water from moist air (Stas, Karsten). Melts at c. 772°; vapourises markedly at white heat in a stream of N (*v.* Stas, *l.c.*). NaCl is almost wholly ppd. from an aqueous solution by leading in HCl (Margueritte, *C. R.* 4?, 50); also ppd. from a conc. solution by cold conc. NaOHAq (Berthelot *C. R.* 76, 111); also by warming a conc. solution with excess of NaBr or NaI and cooling (von Hauer, *J. pr.* 98, 137). Saturated NaClAq deposits the hydrate NaCl.2aq at −7° to c. −22°, and at c. −23° NaCl.10aq separates (*v. Hydrates* under *Combinations*, p. 478).

Reactions.—1. **According to de Sanderval (*C. R.* 116, 641), when NaCl is *vapourised around a porous tube* Cl collects in the inside of the tube.**—2. *Electrolysis* of NaClAq produces Cl and NaOHAq, but NaClOAq and $NaClO_3$ are soon formed by secondary reactions; if a diaphragm of asbestos is used, the cathode being on one side and the anode on the other, and CO_2 is passed into the NaClAq, Cl is given off and Na_2CO_3 is formed (*v.* Hempel, *B.* 22, 2475).—3. Fusion with *potassium* produces KCl and Na. 4. Fusion with *sulphur* is said to form Na_2S and S_2Cl_2, but this is denied by Karsten; NaCl is not decomposed by *hydrogen*, or *oxygen*, at a red heat.—5. Superheated *steam* has no reaction, according to Kunheim (*J.* 1861. 149); there is a slight reaction, according to Lunge (*Soda-industrie*, 2, 288).—6. *Sulphuric anhydride vapour* is absorbed, without heating, giving S_2O_6NaCl (Na salt of $SO_2(Cl).O.SO_2.OH$); according to Schultz-Sellack (*B.* 4, 112) more SO_3 is then absorbed, and a compound approximately $NaCl.4SO_3$ is formed; on heating Na_2SO_4, SO_2 and Cl are produced. By heating with *liquid sulphuric anhydride* $S_2O_5Cl_2$ is formed (Rosenstiehl, *C. R.* 53, 658).—7. Decomposed by heating to c. 500° in a mixture of *air, sulphur dioxide, and water vapour*, giving Na_2SO_4 and HCl (Hargreaves and Robinson's process for making Na_2SO_4; *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 444).—8. NaCl is decomposed, with formation of oxychlorides or chlorides, by heating with *phosphoric*, *chromic*, or *molybdic anhydride*, or with *antimonic oxide*; decomposition occurs with *silica*, *boric oxide*, *alumina*, and *tungstic oxide* only in presence of air or water vapour, forming silicate, borate, aluminate, or tungstate of Na, and HCl; in presence of water vapour Cl is evolved in some of these reactions (*v.* Schulze, *J. pr.* [2] 21, 407; Delalande a. Prudhomme, *Bl.* 20, 74; Gorgeu, *A. Ch.* [5] 10, 145). *Lead oxide* decomposes NaClAq, forming $PbCl_2$ and NaOHAq (Scheele); but molten NaCl is said not to interact with PbO. Moist NaCl mixed with *caustic lime* and exposed to air becomes covered with an efflorescence of Na_2CO_3 crystals. *Magnesia* interacts with NaClAq, in presence of CO_2, to form $NaHCO_3$ and $MgCl_2$ (Weldon; Wagner, *J.* 1873. 256).—9. *Sulphuretted hydrogen* partially decomposes hot NaCl to Na_2S, more completely in presence of steam (Kingzett, *C. J.* [2] 11, 456).—10. Many *metallic sulphides, e.g.* Cu_2S, produce Na_2SO_4 and metallic chlorides (sometimes Cl is set free) when roasted in air with NaCl.—11. Several *metallic sulphates* when fused with NaCl produce Na_2SO_4 and metallic chlorides—*e.g.* $PbSO_4$, $ZnSO_4$, $CuSO_4$; some of these sulphates react also with NaClAq. Some sulphates form Na_2SO_4, and give off Cl when heated with NaCl, *e.g.* $FeSO_4$ (*v.* Barreswil, *J. Ph.* [3] 12, 456).—12. Fusion with *potassium chlorate* only decomposes a trace of NaCl (Schulze, *J. pr.* [2] 21, 407).—13. *Ammonium oxalate* heated with NaCl forms Na_2CO_3 and distinct quantities of NaCN (Fresenius); addition of $(NH_4)_2C_2O_4$ to hot saturated NaClAq ppts. $Na_2C_2O_4$.—14. *Potassium carbonate* reacts with NaClAq to form Na_2CO_3Aq and KClAq; if CO_2 is passed in $NaHCO_3$ ppts.—15. *Ammonium bicarbonate* and NaClAq produce $NaHCO_3$ and NH_4ClAq. Passage of CO_2 into NaClAq saturated with NH_3 ppts. $NaHCO_3$ (*v. Ammonia-soda process*, in DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 494).—16. *Sulphuric acid* decomposes NaCl, forming HCl, and $NaHSO_4$ or Na_2SO_4 according to the temperature. The Leblanc process for making sodium carbonate takes advantage of this reaction (*v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 459).—17. Evaporation with excess of *nitric acid* produces $NaNO_3$ and HCl.—18. NaCl is readily decomposed by *hydrofluoric acid*, also by *hydrofluosilicic acid*.—19. *Carbonic acid* is said to set free some HCl from NaClAq (*v.* H. Müller, *B.* 3, 40; Funk, *Chem. Zeitung*, 1879. 660).—20. Repeated evaporation with excess of *oxalic acid* completely decomposes NaCl to $Na_2C_2O_4$.

Combinations.—1. With *water* to form hydrates. The *dihydrate* NaCl.2aq separates from saturated NaClAq cooled to −7° to −22°, in large clear monoclinic crystals (*v.* Hankel, *P.* 53, 623; Mitscherlich, *J. pr.* 83, 485). The crystals effloresce at −10°, and deliquesce at 0°. Ehrenberg (*P.* 36, 240) and Frankenheim (*P.* 37, 638) obtained this hydrate by evaporating dilute NaClAq at a moderate temperature. The crystals that separate from hot NaClAq containing HCl are hydrated, according to Bevan (*C. N.* 35, 17), and contain 5·48 p.c. water, but after a time they change to the ordinary crystals of NaCl. According to Naumann (*Thermochemie*, 106), crystals of the *decahydrate*, NaCl.10aq, separate from NaClAq at −23°.—2. NaCl absorbs considerable quantities of *ammonia*, under pressure. Joannis dissolved NaCl in liquid NH_3 at −10°; on cooling to −30° and letting NH_3 escape at the ordinary pressure, he obtained slender white needles, probably $NaCl.5NH_3$ (*C. R.* 112, 337).—3. *Sulphuric anhydride* is absorbed by NaCl, forming $NaCl.2SO_3$, and then perhaps $NaCl.4SO_3$ (*v. Reactions*, No. 6).—4. Compounds with *sodium iodate* are formed, by adding excess of NaCl to $NaIO_3Aq$, and by boiling $NaIO_3$ with HClAq; the compound $NaCl.NaIO_3.4aq$ was obtained by Ditte, and $3NaCl.2NaIO_3.18aq$ by Rammelsberg (*P.* 44, 548; 115, 584).—5. With many *chlorides of less positive metals, e.g.* $AlCl_3$, $CdCl_2$, $CrCl_3$, $PbCl_2$, $MgCl_2$ (*v. Chlorides of various metals*).

SODIUM SUBCHLORIDE. H. Rose (*P.* 120, 15) noticed that a grey-blue solid was produced by fusing NaCl with Na in H; he thought this might be a subchloride of Na. Bunsen and Kirchhoff (*P.* 113, 339) noticed the formation of a deep-blue substance during the electrolysis of molten RbCl; this substance dissolved in water, giving off H and producing a colourless, strongly alkaline solution; a similar reaction was obtained on electrolysing KCl; these blue substances were regarded by B. a. K. as probably subchlorides, but no analyses or proofs of composition were given.

Sodium, chromisulphocyanide of, *v.* vol. ii. p. 349.

Sodium, cyanide of, *v.* vol. ii. p. 347.

Sodium, ferrate of, *v.* vol. ii. p. 547.

Sodium, ferricyanide of, *v.* vol. ii. **p. 340.**

Sodium, ferrite of, *v.* vol. ii. p. 547.

Sodium, ferrocyanide of, *v.* vol. ii. p. 337.

Sodium, fluoboride of, *v.* vol. i. p. 526.

Sodium, fluoride of, NaF. Mol. w. not known with certainty, but the formula NaF is probably molecular.

Formation.—1. By neutralising HFAq by NaOHAq and evaporating.—2. Formed along with $NaHSO_4$ by the reaction of HFAq with Na_2SO_4 (Weldon, *D. P. J.* 182, 228).—3. By fusing together CaF_2, Na_2SO_4, and charcoal, and extracting with water (Jean, *C. R.* 66, 801, 918).—4. By boiling powdered *cryolite* with NaOHAq of at least 1·35 S.G. till a little taken out is entirely sol. boiling water, decanting the alkaline liquid from NaF, pressing the NaF, dissolving in boiling water, separating any Al_2O_3 in solution by Na_2SiO_3Aq, removing silica by CO_2, filtering, evaporating, and recrystallising the NaF that separates (Schuch, *A.* 126, 108).—5. Berzelius (*Lehrbuch* [5th ed.] 3, 216) prepared NaF by adding to 100 parts Na_2SiF_6 and 112 parts Na_3CO_3 water enough to make the whole pasty, boiling as long as CO_2 was given off, extracting the solid thus formed with boiling water, evaporating the solution to dryness, heating the residue gently, again extracting with hot water, filtering from SiO_2, and crystallising.

Preparation.—Pure Na_2CO_3 (for preparation *v.* Sodium chloride, *Preparation*, p. 477) is dissolved in pure HFAq, till the acid is just saturated, in a Pt dish, the solution is evaporated to dryness, the residue is heated strongly for some time, and allowed to cool.

Properties.—Clear, lustrous cubes; in presence of Na_2CO_3 crystallises in octahedra. Sl. sol. water; S. at 16° = 4·78 (Berzelius), at 15° = 4 (Fremy, *A. Ch.* [3] 47, 32). Scarcely more sol. hot than cold water. Insol. alcohol. Güntz (*A. Ch.* [6] 3, 5) gives [NaF,Aq] = −600. Decrepitates on heating, and melts at a high temperature without decomposition (Berzelius).

Reactions.—1. Partially decomposed by heating to redness in *water vapour*, with formation of NaOH and HF (Weldon).—2. Excess of *caustic potash* forms NaOHAq.—3. Boiling with *magnesia* partially decomposes NaF to NaOHAq and forms a double Na-Mg fluoride ($MgF_2.2NaF$) (Tissier, *C. R.* 56, 848).—4. Completely decomposed to NaCl by heating strongly in *hydrochloric acid gas* (Deville, *C. R.* 43, 970).—5. Partially decomposed to NaCl by heating with *ammonium chloride* (Rose, *P.* 74, 579). Fusion with *magnesium chloride* produces NaCl and MgF_2 (Geuther, *J. Z.* 2, 208).

Combinations.—1. With several *fluorides of less positive metals*; $3NaF.AlF_3$ occurs native as *cryolite* (*v.* Aluminium fluoride, vol. i. p. 145).—2. With *silicon fluoride* to form Na_2SiF_6 (*v.* Sodium silicofluoride, p. 483).—3. With *sodium borate* to form $6NaF.Na_2B_2O_4$ (*v.* *Fluoborates*, vol. i. p. 530).—4. With *sodium phosphate* to form $NaF.2Na_3PO_4.19aq$ and 22aq, and $NaF.Na_3PO_4.24aq$ (*v.* Baumgarten, *J.* 1865. 219; Brieglieb, *A.* 117, 95).—5. With *sodium sulphate* to form $NaF.Na_2SO_4$ (*v.* Marignac, *Ann. M.* [5] 12, 18).

Sodium-hydrogen fluoride $NaHF_2$ or NaF.HF. This compound is formed, according to Berzelius (*Lehrbuch* [5th ed.] 3, 217), by the spontaneous evaporation of a solution of NaF in HFAq. Forms small rhombohedral crystals, with a sharp, acid taste. Sl. sol. cold water, more sol. hot water. Decomposed by heat to NaF and HF (Marignac, *J.* 1857. 128). Güntz (*A. Ch.* [6] 3, 5) gives [NaF,HF] = 17,100 (to form NaF.HF).

Sodium, hydride of, Na_2H. Gay-Lussac and Thénard (*A. Ch.* 74, 203) observed that Na absorbed H when heated therein. The process was more accurately studied by Troost and Hautefeuille (*A. Ch.* [5] 2, 273). They found that absorption of H by Na began at c. 300° and ceased at c. 421°, when the gas was at the atmospheric pressure. The product gave, in a Sprengel pump, 237 vols. H. for 1 vol. Na; the formula Na_2H requires 238 vols. H. Na_2H is a soft, silver-white solid; it can be melted without decomposition in H; S.G. ·959. Traces of H are given off at 760 mm. pressure; heated *in vacuo* a regular dissociation takes place from 330° to 430° (for vapour-pressures of H given off *v.* Dissociation, vol. ii. p. 398). Moutier (*C. R.* 79, 1242) gives the thermal value $[Na^2,H]$ = 13,000 at c. 330°.

Sodium, hydrosulphide of, NaSH. (*Sodium sulphydrate.*) Sabatier (*A. Ch.* [5] 22, 5) obtained this compound by treating $Na_2S.9aq$ with H_2S in absence of air, and then evaporating the liquid so formed in an atmosphere of H_2S. A white, very hygroscopic solid. Passage of CO_2 into NaSHAq drives out H_2S and converts all the Na into Na_2CO_3. NaSHAq contains H_2S and NaOH, according to Gernez (*C. R.* 64, 86). NaSHAq dissolves S with evolution of H_2S; it ppts. PbS, or MnS, from a neutral solution of a Pb or Mn salt, giving off H_2S; Na_2SAq does not give off H_2S while dissolving S or ppg. PbS or MnS.

Sabatier (*l.c.*) obtained the *hydrate* $NaSH.2H_2O$ by passing H_2S over $Na_2S.9aq$, and then evaporating in H_2S till half the water was removed; very hygroscopic needles, becoming yellow in air.

Sodium, hydroxide of, NaOH. (*Caustic soda* *Sodium*, or *sodic*, *hydrate.*) Mol. w. not determined. Melts at 1098° (*v.* Meyer a. Riddle, *B* 26, 2443). S.G. 2·13 (Filhol, *A. Ch.* [3] 21, 415) 1·723 (Smith, *Am. J. Pharm.* 53, 145). S. (col water) c. 212 (Bineau, *C. R.* 41, 509). H.F [Na,O,H] = 101,870; [Na,O,H,Aq] = 111,810 $[Na^2O,H^2O]$ = 35,620 (*Th.* 3, 232).

Formation.—1. By the interaction of Na, o Na_2O, with H_2O.—2. By decomposing Na_2CO_3A with CaO_2H_2 (*v.* *Preparation*, No. 1).—3. B the action of CaO_2H_2 with NaFAq (Tissier *J. pr.* 90, 50).—4. By decomposing Na_2SO_4A by BaO or CaO under pressure.—5. Fro NaClAq by interaction with PbO (Knab, *B* 11, 1458).—6. By heating $NaNO_3$ with charcoal, or with Cu (Wöhler, *A.* 87, 373), or F (Polacci, *C. N.* 26, 288).—7. By decomposin Na_2SAq by CuO, Fe_2O_3, PbO, ZnO, &c. (Kopp *D. P. J.* 142, 341; Stromeyer, *A.* 107, 333).—8. By the interaction of NaF and stea (Weldon).—9. By heating soda felspar with lime

Preparation.—1. By causticising soda crystals by lime. A solution of pure Na_2CO_3 crystal in 4–5 parts water is boiled, in a dish of silve or polished iron, with milk of lime till a littl of the filtered liquid gives off no CO_2 whe acidified; the weight of CaO required is c. the wt. of soda crystals used, it should b suspended in about as much water as the wt. of soda crystals used; as the boiling proceeds a little water should be added from time to time, otherwise the NaOHAq will decompose some of the $CaCO_3$ formed to CaO and Na_2CO_3Aq. The $CaCO_3$ formed is allowed to settle, the vessel being closed, the NaOHAq is drawn off by a siphon and evaporated to dryness in a silver dish, and the residue is heated till volatilisation begins, and allowed to cool in an exsiccator. By dissolving in absolute alcohol, allowing to settle, drawing off the liquid, evaporating it to dryness on a water-bath in a silver dish, removing resinous matter from the warm semi-solid mass by a silver spatula, heating to bright redness, and pouring the molten mass on to a plate of polished iron—or, better, of silver—NaOH containing only traces of impurities, chiefly NaCl and Na_2CO_3, is obtained.—2. A large silver dish is surrounded by cold water; 2 or 3 drops of water are placed in the dish, and then a small piece of clean Na, 1 or 2 cms. long; the dish is constantly shaken, so that the Na flows over a large cold surface (explosions are thus avoided); when the reaction is finished 2 or 3 more drops of water are added, and then another piece of Na, while the dish is shaken, and so on. The semi-solid mass is heated till the water is all driven off and the NaOH melts, and the molten substance is poured on to a plate of polished iron or silver.

To obtain NaOH free from nitrites and nitrates Ilosva (*Bl.* [3] 2, 357) recommends to place Na in water with a layer of petroleum on the surface, the petroleum having been washed with water till free from nitrites and nitrates. He also says that if 2-4 p.c. ordinary NaOHAq is kept for some weeks in contact with granulated Zn all nitrites and nitrates are destroyed.

For preparation of ordinary caustic soda *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 480.

Properties.—NaOH is a white, hard, brittle solid. Melts below red heat; volatilises at very bright red heat, higher than temperature of volatilisation of KOH. Very deliquescent; dissolves in c. ·47 parts water. During solution in water much heat is produced, [NaOH,Aq] = 9,940 (*Th.* 3, 232); the maximum amount of heat is produced when H_2O is added to NaOH in the ratio NaOH : $20H_2O$, addition of water to this solution is attended with a slight disappearance of heat (*Th.* 3, 84). (For hydrates *v.* p. 480, *Combinations.*) Easily sol. alcohol. NaOHAq with 36·86 p.c. NaOH boils at 130°, with 70 p.c. boils 180°, with 77·5 p.c. boils 238°, with 78·7 p.c. boils 243°, and with 82·6 p.c. boils 260° (Lunge, *Soda-industrie*, 2, 543).

NaOHAq acts as a strong alkali; its affinity is c. equal to that of KOHAq and LiOHAq and c. 50 times greater than NH_3Aq (Ostwald). The properties of NaOHAq closely resemble those of *potassium hydroxide* solution (*q. v.* p. 302).

The table in the next column, given by Lunge, shows the composition of NaOHAq of different S.G. at 15°.

Regarding the freezing-points of NaOHAq of different concentrations *v.* Rüdorff (*P.* 116, 55); de Coppet (*A. Ch.* [4] 24, 551); and Pickering (who gives very complete data) *C. J.* 63, 890).

S.G. NaOHAq	Baumé	Twaddell	100 pts. by wt. contain		1 cub. metre contains kilos.	
			Na_2O	NaOH	Na_2O	NaOH
1·007	1	1·4	0·47	0·61	4	6
1·014	2	2·8	0·93	1·20	9	12
1·022	3	4·4	1·55	2·00	16	21
1·029	4	5·8	2·10	2·71	22	28
1·036	5	7·2	2·60	3·35	27	35
1·045	6	9·0	3·10	4·00	32	42
1·052	7	10·4	3·60	4·64	38	49
1·060	8	12·0	4·10	5·29	43	56
1·067	9	13·4	4·55	5·87	49	63
1·075	10	15·0	5·08	6·55	55	70
1·083	11	16·6	5·67	7·31	61	79
1·091	12	18·2	6·20	8·00	68	87
1·100	13	20·0	6·73	8·68	74	95
1·108	14	21·6	7·30	9·42	81	104
1·116	15	23·2	7·80	10·06	87	112
1·125	16	25·0	8·50	10·97	96	123
1·134	17	26·8	9·18	11·84	104	134
1·142	18	28·4	9·80	12·64	112	144
1·152	19	30·4	10·50	13·55	121	156
1·162	20	32·4	11·14	14·37	129	167
1·171	21	34·5	11·73	15·13	137	177
1·180	22	36·0	12·33	15·91	146	188
1·190	23	38·0	13·00	16·77	155	200
1·200	24	40·0	13·70	17·67	164	212
1·210	25	42·0	14·40	18·58	174	225
1·220	26	44·0	15·18	19·58	185	239
1·231	27	46·2	15·96	20·59	196	253
1·241	28	48·2	16·76	21·42	208	266
1·252	29	50·4	17·55	22·64	220	283
1·263	30	52·6	18·35	23·67	232	299
1·274	31	54·8	19·23	24·81	245	316
1·285	32	57·0	20·00	25·80	257	332
1·297	33	59·4	20·80	26·83	270	348
1·308	34	61·6	21·55	27·80	282	364
1·320	35	64·0	22·35	28·83	295	381
1·332	36	66·4	23·20	29·93	309	399
1·345	37	69·0	24·20	31·22	326	420
1·357	38	71·4	25·17	32·47	342	441
1·370	39	74·0	26·12	33·69	359	462
1·383	40	76·6	27·10	34·96	375	483
1·397	41	79·4	28·10	36·25	392	506
1·410	42	82·0	29·05	37·47	410	528
1·424	43	84·8	30·08	38·80	428	553
1·438	44	87·6	31·00	39·99	446	575
1·453	45	90·6	32·10	41·41	466	602
1·468	46	93·6	33·20	42·83	487	629
1·483	47	96·6	34·40	44·38	510	658
1·498	48	99·6	35·79	46·15	535	691
1·514	49	102·8	36·90	47·60	559	721
1·530	50	106·0	38·00	49·02	581	750

Reactions.—1. According to Deville (*C. R.* 45, 857), NaOH is decomposed to Na, O, and H by *heating to white heat* in an iron bottle.—2. Strongly heated with *non-volatile acidic anhydrides*, water and salts of Na are formed.—3. When molten NaOH is exposed for a considerable time to *air* or *oxygen*, some Na_2O_2 is formed (Gay-Lussac; Thénard).—4. Moist or molten NaOH is decomposed by *electrolysis*, with production of Na (Davy, *T.* 1802. 1).—5. Heating with *sulphur* produces polysulphides, sulphite, and sulphate; S heated with NaOHAq forms polysulphides and sulphite. Similar reactions occur by heating with *selenion* or *tellurium*.—6. Chlorine interacts with NaOHAq to form NaClOAq and NaClAq; on heating $NaClO_3Aq$ is formed. *Bromine* reacts similarly. If Cl is led into NaOHAq containing *iodine* in suspension, $NaIO_3$ is produced.—7. When NaOHAq is warmed with *phosphorus*, H and inflammable P hydride are given off.—8. Heated with *sodium*, Na_2O and H are formed.—9. Moist NaOH withdraws *carbon dioxide* from the air, forming $NaHCO_3$.—10. Reacts with *acids* to form Na salts.—11. NaOHAq ppts. metallic hydroxides, or oxides, from solutions of many *metallic salts*; in some cases the hydroxide dissolves in excess of NaOHAq—*e.g.* AlO_3H_3, ZnO_2H_2.—12. *Molten NaOH acts generally as an oxidiser*; *e.g.* As, Sb, Fe, Pt, &c. form arsenate, antimonate, ferrate, and platinate of Na. Salts are generally decomposed by molten NaOH, giving Na salts, and setting free the bases.—13. According to Schöne (*A.* 193, 241), addition of *hydrogen peroxide* to NaOHAq produces $Na_2O_2.8H_2O$ (*v.* Sodium dioxide, p. 482).

Pickering (*priv. comm.*) gives the following data:—

P.c. NaOH	S.G. NaClAq at 15° (water at 4° =1)	P.c. NaOH	S.G. NaClAq at 15° (water at 4° =1)	P.c. NaOH	S.G. NaClAq at 15° (water at 4° =1)
0	0·999180	17	1·88707	34	1·373453
1	1·010611	18	1·199783	35	1·383815
2	1·021920	19	1·210861	36	1·394092
3	1·033109	20	1·221933	37	1·404279
4	1·044317	21	1·233062	38	1·414363
5	1·055463	22	1·244119	39	1·424353
6	1·066602	23	1·255134	40	1·434299
7	1·077733	24	1·266092	41	1·444161
8	1·088856	25	1·277063	42	1·453929
9	1·099969	26	1·287990	43	1·463623
10	1·111069	27	1·298877	44	1·473249
11	1·122165	28	1·309708	45	1·482850
12	1·133250	29	1·320496	46	1·492406
13	1·144353	30	1·331213	47	1·501927
14	1·155450	31	1·341879	48	1·511412
15	1·666538	32	1·352472	49	1·520868
16	1·177619	33	1·362991	50	1·530282

Combinations.—1. With *water* to form *hydrates.* The *hydrate* $2NaOH.7H_2O$ was obtained by Hermes (*B.* 3, 122) by exposing NaOHAq S.G. 1·365 to the cold of a severe winter; monoclinic crystals, S.G. 1·405, melting at 6°; *in vacuo* gave off $3H_2O$. Göttig (*B.* 20, 543) obtained a *dihydrate*, $NaOH.2H_2O$, by heating NaOH in 96·8 p.c. alcohol very gradually to 100°. By cooling NaOHAq, Pickering (*C. J.* 63, 890) obtained the following hydrates, with the freezing-points noted:—

Hydrate	Freezing-point
$NaOH.H_2O$	64·3°
$NaOH.2H_2O$	12·5
$NaOH.3{\cdot}11H_2O$ (*sic*)	2·73
$NaOH.3{\cdot}5H_2O$	15·55
$\alpha NaOH.4H_2O$	7·57
$\beta NaOH.4H_2O$	− 1·7
$NaOH.5H_2O$	−12·22
$NaOH.7H_2O$	−23·51

2. With *carbon dioxide* to form $NaHCO_3$.

Sodium, iodide of, NaI. Mol. w. not known with certainty, but formula NaI is probably molecular. Melts at 628° (Carnelley, *C. J.* 33, 278); at 650° (V. Meyer a. Riddle, *B.* 26, 2443). S.G. 3·45 (Filhol, *A. Ch.* [3] 21, 415); 3·654 at 18·2 (Favre a. Valson, *C. R.* 77, 579). S.H. (26° to 50°) ·0881 (Schuler, *P.* 136, 70); (16° to 99°) ·08684 (Regnault, *A. Ch.* [3] 1, 129). Kremers (*P.* 108, 120) gives the following data for solubility in water:—

Temp.	S.	Temp.	S.
0°	158·7	80°	303
20	178·6	100	312·5
40	208·4	120	322·5
60	256·4	140	333·3

S. = 264·19 + ·3978*t*, when *t* varies from 64·7° to 138·1° (de Coppet, *A. Ch.* [5] 30, 411). Gerlach (*Fr.* 8, 285) gives following:—

S.G. NaIAq	P.C. NaI	S.G. NaIAq	P.C. NaI
1·04	5	1·36	35
1·082	10	1·432	40
1·128	12	1·51	45
1·179	20	1·6	50
1·234	25	1·7	55
1·294	30	1·81	60

Easily sol. alcohol. Saturated NaIAq boils at 141·1°. H.F. [Na,I] = 69,080; [Na,I,Aq] = 70,300 (*Th.* 3, 232).

Formation.—1. When Na and I are fused together only very small quantities combine (Merz a. Weith, *B.* 6, 1518).—2. By decomposing BaI_2Aq, or CaI_2Aq, by Na_2CO_3 or Na_2SO_4, filtering, and evaporating.—3. By neutralising HIAq by Na_2CO_3, and evaporating.—4. I is added to water and iron filings till the iron is almost all dissolved, the solution is filtered, and Na_2CO_3 is added so long as $FeCO_3$ ppts.; the liquid is filtered (if alkaline it is neutralised by HIAq) and evaporated, any Fe_2O_3 which separates being filtered off (Baup, *J. Ph.* 9, 37, 122).

Preparation.—1. Iodine is added to moderately conc. NaOHAq till a yellow colour is produced; finely-powdered charcoal, equal to c. $\frac{1}{10}$ of the weight of I used, is added; the liquid is evaporated to dryness and the residue is heated in a covered crucible to dull redness for some time; when cold, the residue is dissolved in water, the liquid is filtered (neutralised by HIAq if alkaline) and crystallised at 40°-50°. (For more details *v.* Potassium iodide, *Preparation*, p. 304.)—2. A quantity of NaOHAq is divided into two equal portions; I is added to one part till a yellow colour remains, an equal quantity of I is then added, and then the other portion of NaOHAq is saturated with SO_2 and added, and the whole is evaporated till NaI crystallises out; the salt is purified by recrystallisation from water at 40°-50° (Stephani, *J. Ph.* [3] 26, 450).

Properties.—Crystallises from aqueous solutions at 40° to 50° in cubes (Mitscherlich, *P.* 17, 385); the hydrate NaI.2aq separates at ordinary temperatures. Melts at 628°; volatilises less readily than KI, but at a lower temperature than NaCl (Mohr, *A.* 21, 66). Deliquesces in moist air, becoming rose-coloured with separation of some I and formation of some Na_2CO_3 (Girault, *J. Ph.* 27, 390).

Reactions and Combinations.—1. *Heated in air* some I is separated and O absorbed, and the reaction becomes alkaline (Berzelius, *Lehrbuch*

[5th ed.] 3, 215).—2. *Heated with charcoal in contact with air* much Na_2CO_3 is formed (Girault, *l.c.*). Most of the reactions of NaI are similar to those of KI (*v.* Potassium iodide, *Reactions*, p. 304).

Combines with most *iodides of less positive metals.* Forms a compound with *arsenious oxide* $NaI.As_4O_6$ (Rüdorff, *B.* 21, 3051). The *dihydrate* $NaI.2H_2O$ crystallises at the ordinary temperature from NaIAq in large monoclinic prisms; S.G. 2·448; melting at c. 65° and giving NaI; effloresces in dry air, and deliquesces in moist air.

Sodium, manganicyanide of, *v.* vol. ii. p. 342.

Sodium, manganocyanide of, *v.* vol. ii. p. 342.

Sodium, nitride of, Na_3N. A dark-grey solid; formed by heating $NaNH_2$ (*v.* Sodium amide, p. 475) to redness in absence of O. Resembles *potassium nitride* (*q. v.*, p. 304) (Gay-Lussac a. Thénard, *A. Ch.* 65, 325).

Sodium, nitroprusside of, *v.* vol. ii. p. 341.

Sodium, oxides of. Two oxides have been isolated, Na_2O and Na_2O_2.

Sodium oxide Na_2O. (*Sodium monoxide.*) It is doubtful whether this compound has been obtained pure. Davy (*T.* 1808. 24) said that when Na is fused with dry soda there is 'a division of the oxygen between the alkali and the sodium.' Na does not combine with O when exposed to quite dry air at the ordinary temperature (von Bonsdorff, *P.* 41, 296). According to Beketoff (*v. B.* 12, 856; 16, 1854), NaOH and Na do not react at a red heat. Beketoff (*J. R.* 1883. [i.] 277 [*v. B.* 16, 1854]) allowed Na to drop into a red-hot copper cylinder, then passed in a mixture of 1 vol. O and 4 vols. air, and heated by a blowpipe; in this way he obtained Na_2O, but always mixed with some Cu and traces of Na; considering the conditions under which Na_2O_2 is obtained (*v. infra, Sodium dioxide*) it is likely that B.'s Na_2O contained Na_2O_2.

Na_2O is described as a greyish solid; Beketoff's preparation was rose-coloured, but it contained Cu. Na_2O dissolves in water to form NaOHAq; B. gives $[Na^2O,Aq] = 55,500$; and from this and other data Thomsen (*Th.* 3, 232) calculates $[Na^2,O] = 99,760$. According to B. (*l.c.*), hot Na_2O reacts with H to form NaOH and Na; heated to c. 300° in CO it gives Na_2CO_3 and Na (B., *l.c.*). Combination with CO_2, to form Na_2CO_3, occurs at c. 400°. By heating Na amalgam with HgO, B. (*l.c.*) obtained the compound $Na_2HgO_2 = Na_2O.HgO$. Comey and Jackson (*B.* 21, 1589; *Am.* 11, 145) describe various compounds of Na_2O with ZnO and H_2O.

Sodium dioxide Na_2O_2. (*Sodium peroxide.*) The formation of an oxide with more O than Na_2O, by heating Na in air, was noticed by Gay-Lussac a. Thénard (*A. Ch.* 65, 325). Pure Na_2O_2 was obtained by Vernon Harcourt (*C. J.* 14, 267) by heating Na, in a flask of hard glass filled with N, till the Na melted, then sending in a slow stream of dry air, and heating till the metal was changed to a yellowish-white solid, and heating this for some time in dry O. Na_2O_2 is a white solid, becoming yellowish on heating. It deliquesces gradually in air, and then is gradually changed into solid Na_2CO_3. Soluble water, with production of much heat; on heating O is evolved; Na_2O_2Aq deposits crystals of the hydrate $Na_2O_2.8H_2O$ on standing over H_2SO_4 (*v. infra, Hydrates*). Na_2O_2 acts as an energetic oxidiser when heated; C, I, P, S, Sn are oxidised, more or less rapidly; heated with CO, Na_2CO_3 is formed; with N_2O the products are $NaNO_2$ and N (*v.* Harcourt, *l.c.*).

Hydrates of sodium dioxide. The *octohydrate*, $Na_2O_2.8H_2O$, was obtained by Harcourt (*l.c.*) by evaporating a solution of Na_2O_2 in water over H_2SO_4. Fairley (*C. J.* [2] 16, 125) obtained the same hydrate by adding H_2O_2Aq to NaOHAq and ppg. by alcohol. Schöne (*A.* 193, 241) also obtained the octohydrate by the action of H_2O_2Aq on NaOHAq, evaporating *in vacuo*, drying on a porous tile, washing with 90 p.c. alcohol, and drying between filter paper. By using a considerable excess of H_2O_2Aq, Schöne (*l.c.*) obtained crystals to which he gave the composition $Na_2H_4O_8.4H_2O = Na_2O_2.2H_2O_2.4H_2O$; on drying over H_2SO_4, $Na_2O_2.2H_2O_2$ remained. The *dihydrate* $Na_2O_2.2H_2O$ is obtained by drying the octohydrate for some time over H_2SO_4.

Sodium, phosphide of. A compound of Na and P was supposed by Gay-Lussac a. Thénard, and also by Davy, to be formed by heating the elements together in N. Vigier (*Bl.* [2] 3, 7) recommends to place a piece of Na in rock oil, boiling at c. 120°, in a retort, to add P little by little (much heat is produced and some oil distils) till there is an excess and some crystallises on the cold parts of the retort, to distil off the oil from the black phosphide formed, to wash with CS_2, and dry in a stream of CO_2.

The phosphide may be kept in dry air; in moist air, water, or acids it gives off inflammable P hydride (*v.* also Lüpke, *C. C.* 1890. [ii.] 642).

Bunsen (*A.* 138, 292) obtained a phosphide of Na by strongly heating a mixture of Na_2HPO_4 and Na in a narrow glass tube.

Sodium, platinocyanide of, *v.* vol. ii. p. 344.

Sodium, platinosulphocyanide of, *v.* vol. ii. p. 351.

Sodium, salts of. *Compounds formed by replacing H of acids by Na.* These compounds belong to the type NaX where X is a monovalent acidic radicle. The chief salts of Na derived from oxyacids are *antimonate*, *arsenate*, *bromate* and *hypobromite*, *carbonates*, *chlorate*, *perchlorate*, *chlorite* and *hypochlorite*, *chromate* and *dichromate*, *iodate* and *periodates*, *manganate* and *permanganate*, *molybdates*, *nitrate* and *nitrite*, *phosphates*, *phosphites* and *hypophosphite*, *selenates* and *selenites*, *silicates*, *sulphates*, *sulphites*, *thiosulphate* and *thionates*, *tellurates and tellurites* (*v.* Carbonates, Nitrates, Sulphates, &c.).

Sodium, selenides of. Two selenides have been isolated, Na_2Se and Na_2Se_2, corresponding with two of the sulphides and with the two oxides.

Sodium monoselenide Na_2Se. Obtained by mixing well-cleaned Na rubbed to powder with the proper proportion of Se (Rosenfeld, *B.* 24, 1658). Uelsmann (*A.* 116, 127) says Na_2Se is obtained, in large colourless crystals, by saturating NaOHAq with H_2Se, then heating in a stream of H and allowing to cool; it seems probable that these crystals were a hydrate of Na_2Se (*v.*

***infra*).** **Fabre (*C. R.* 102, 613) obtained Na_2Se** by heating $2Na_2Se.9H_2O$ (*v. infra, Hydrates*) in a current of N to not above 400°; F. describes Na_2Se as a hard, white, crystalline, deliquescent solid, becoming reddish-brown when fused; owing to its action on glass, F. did not get Na_2Se free from silica and alumina.

Hydrates of sodium monoselenide. By passing a rapid stream of H_2Se into NaOHAq (1 part NaOH in 4 water) Fabre (*l.c.*) obtained $Na_2Se.16H_2O$, melting at 40°, giving Na_2CO_3, a little Na_2SeO_3, and Se on exposure to air. By using more conc. NaOHAq (3:1), and keeping the temperature down, F. obtained $Na_2Se.9H_2O$; and when very conc. NaOHAq was used, he obtained $2Na_2Se.9H_2O$.

For data regarding heats of formation of Na_2Se and hydrates, *v.* Fabre, *C. R.* 102, 703.

Sodium diselenide Na_2Se_2. Wöhler and Dean (*A.* 97, 1) obtained a selenide of K by heating K_2SeO_3 with charcoal; Rathke (*A.* 152, 211) showed that the selenide was K_2Se_2, and Jackson (*B.* 7, 1277) using Na_2SeO_3 and charcoal obtained the corresponding selenide of sodium.

Sodium, seleno-antimonate of, *v.* vol. i. p. 286.

Sodium, selenocyanide of, *v.* vol. ii. p. 348.

Sodium, silicofluoride of, Na_2SiF_6. Prepared by adding H_2SiF_6Aq to conc. NaClAq, washing, and drying. Gelatinous when ppd., but becomes crystalline on drying. S.G. 2·7517 at 17·5° (Stolba, *Fr.* 11, 199). S. ·65 at 17·5°; 2·46 at 100° (S., *l.c.*). Insol. alcohol. Melts at red heat, giving off SiF_4 (Berzelius).

Sodium, sulphides of. Several compounds of Na and S exist, but there is considerable doubt as to the compositions of some of the substances that are described as definite sulphides of Na.

Sodium monosulphide Na_2S. Obtained by passing H_2S over dry NaOH, the heat produced suffices to remove H_2O formed (Kircher, *A.* 31, 339). Rosenfeld (*B.* 24, 1658) says that Na_2S is formed when 1 part thoroughly clean Na is rubbed to powder and mixed with 3 parts NaCl and ·7 part S; the combination is sudden, and light is produced; pressure must be avoided in mixing the substances. By heating 100 to 105 parts Na_2SO_4 with 20 parts charcoal, a flesh-coloured mass of Na_2S with some C is obtained; the reduction may also be effected in H. By dissolving the product of reduction in water and crystallising, the hydrate $Na_2S.9H_2O$ is obtained; by dissolving the crystals again, heating with Cu (to decompose polysulphides), and evaporating to dryness in a stream of H, Na_2S remains (Priwoznik, *A.* 164, 69).

Na_2S is also obtained, fairly pure, by gently heating $Na_2S.9H_2O$ in a stream of H (Weyl, *P.* 123, 362; *cf.* Sabatier, *A. Ch.* [5] 22, 5).

Na_2S is an amorphous, flesh-coloured, deliquescent solid, with a strongly alkaline reaction; easily sol. water, solution being colourless if polysulphides are quite absent. According to Weldon (*v.* Lunge's *Soda-industrie*, 2, 311), Na_2S is not fusible if it be quite free from polysulphides, thiosulphate, and NaOH.

Na_2SAq becomes yellow in moist air from formation of polysulphides (Kolb, *A. Ch.* [4] 10, 106); when air is blown into Na_2SAq, NaOH and $Na_2S_2O_3$ are formed, and then Na_2SO_4 (Lunge, *l.c.*, p. 531). Na_2S is decomposed by acids, even by CO_2, with evolution of H_2S (*v.* Stromeyer, *A.* 107, 372). Heating Na_2SAq with $NaHCO_3$ or $NH_4.H.CO_3$ produces complete decomposition to Na_2CO_3 (Lunge, *l.c.* p. 300). Boiling with AlO_3H_3, or heating Na_2S with Al_2O_3, forms Na aluminate (*v. W. J.* 1863. 713; 1865. 332). CaO is said not to decompose Na_2SAq (*v.* Kolb, *A. Ch.* [4] 10, 106). Several metallic oxides decompose Na_2SAq, forming NaOHAq, sometimes (*e.g.* with CuO) $Na_2S_2O_3Aq$ is also formed. Na_2S combines with various metallic sulphides (*v.* Schneider, *P.* 138, 302; 151, 446; Völcker, *A.* 59, 35; Berthier, *A. Ch.* [2] 22, 245).

Hydrates of sodium monosulphide. The hydrates $Na_2S.9H_2O$, $Na_2S.10H_2O$, and $Na_2S.5H_2O$ have been formed. The hydrate with $9H_2O$ is most easily obtained by saturating one half of a solution of NaOH with H_2S, adding the other half, and evaporating, when large colourless crystals separate (Rammelsberg, *P.* 128, 172); S.G. 2·471 (Filhol, *A. Ch.* [4] 28, 529). The pentahydrate is formed similarly to the hydrate with $9H_2O$, but using alcoholic in place of aqueous NaOH (Böttger, *A.* 223, 335; *v.* also Finger, *P.* 128, 635; Lemoine, *C. R.* 98, 45). For the preparation of $Na_2S.10H_2O$ *v.* Damoiseau (*C. C.* 1885. 36). Göttig (*J. pr.* [2] 34, 229) by partially saturating NaOH in alcohol with H_2S got hydrates with 5, 5½, and 6 H_2O.

Sodium disulphide Na_2S_2. This compound is supposed by Sabatier (*A. Ch.* [5] 22, 5) to exist in the solution obtained by heating Na_2SAq with solution of polysulphides formed by digesting Na_2SAq with S. Böttger (*A.* 223, 335) obtained the *hydrate* $Na_2S_2.5H_2O$ by dissolving S in an alcoholic solution of Na_2S.

Sodium trisulphide Na_2S_3 is formed, according to Schöne (*J.* 1867. 190), mixed with Na_2SO_4, by strongly heating Na_2CO_3 with excess of S (*cf.* Sabatier, *l.c.*). For the *hydrate* $Na_2S_3.3H_2O$ *v.* Böttger (*l.c.*).

Sodium tetrasulphide Na_2S_4 is said to be obtained by heating Na_2S_5 (Chapman Jones, *C. J.* 37, 461; *cf.* Sabatier, *l.c.*). For *hydrates v.* Schöne (*P.* 131, 380) and Böttger (*l.c.*).

The existence of a *pentasulphide* is doubtful (*v.* Schöne, *l.c.*; Sabatier, *l.c.*; Geuther, *A.* 226, 232; Chapman Jones, *l.c.*).

Soda liver of sulphur. This name is given to the brown solid obtained by heating S with Na_2CO_3 in a closed vessel; it contains various sulphides of Na, along with $Na_2S_2O_3$, Na_2SO_4, and generally some Na_2CO_3.

Sodium, sulphocyanide of, *v.* vol. ii. p. 352.

Sodium, sulphydrate of, *v.* Sodium hydrosulphide, p. 479.

Sodium, telluride of. According to Rosenfeld (*B.* 24, 1658), well-cleaned Na in powder readily combines with Te.

Sodium, thio-arsenates and thio-arsenites of, *v.* vol. i. pp. 316, 317.

Sodium, thio-carbonate of, *v.* vol. i. p. 703.

M. M. P. M.

SODIUM ETHIDE NaC_2H_5. This compound is not known in the free state. Sodium dissolves in cold $ZnEt_2$, separating zinc. The solution, cooled to 0°, deposits $ZnEt_2NaEt$ in trimetric tables [27°], sol. benzene, and decomposed by water. CO_2 acting on $ZnEt_2NaEt$

forms sodium propionate (Wanklyn, *A.* 107, 125; 108, 67). EtI attacks ZnEt$_2$NaEt, forming ethane and C_2H_4 (Frankland, *A.* 110, 107). Sodium methide may be obtained in like manner (Wanklyn, *A.* 111, 234).

SOJA OIL. The oil from *Soja hispida* contains tripalmitin and tristearin (Meisel a. Böcker, *M.* 4, 365).

SOLANINE $C_{52}H_{93}NO_{18}$ (?) (Firbas, *M.* 10, 541); $C_{42}H_{75}NO_{15}$; $C_{42}H_{87}NO_{15}$ (Hilger, *A.* 195, 317); $C_{21}H_{35}NO_7$ (Kletzinsky, *Z.* [2] 2, 127). [244°]. Occurs in the berries of the deadly nightshade (*Solanum nigrum*) (Desfosses, *J. Ph.* 6, 374), in berries of *S. verbascifolium* (Payen a. Chevallier, *J. Chim. Méd.* 1, 517), in small quantity in the tubers and green parts of the potato (*S. tuberosum*), in the shoots of sprouting potatoes (Baup, *A. Ch.* [2] 31, 109; Otto, *A.* 7, 150; 26, 232), to the extent of ·03 p.c. in diseased potatoes (Kassner, *Ar. Ph.* [3] 25, 402), in the flowers, stalks, and berries of the woody nightshade (*S. Dulcamara*), and in the root of *Scopolia japonica* (Martin, *Ar. Ph.* [3] 13, 336).

Preparation.—1. The berries are pressed, the juice ppd. by ammonia, and the pp. recrystallised from alcohol.—2. Fresh potato sprouts (200 kilos.) are digested with 2 p.c. acetic acid; the filtrate is ppd. by ammonia; and the pp. extracted with boiling 85 p.c. alcohol. To the hot alcoholic filtrate NH$_3$Aq is added until turbidity appears. On cooling, a mixture (125 g.) of solanine and solaneïn is deposited. These bases are separated by fractional crystallisation from hot spirit (Firbas; *cf.* Reuling, *A.* 80, 225; Zwenger a. Kind, *A.* 109, 244; 118, 129; Kromayer, *Ar. Ph.* [2] 116, 114; Missaghi, *B.* 9, 83; Gmelin, *A.* 110, 167).

Properties.—Colourless needles, v. sol. hot 85 p.c. alcohol, insol. CHCl$_3$ and ligroïn, sol. HClAq, almost insol. water and ether. The crystals are $C_{52}H_{93}NO_{18}4\frac{1}{2}aq$ (Firbas). Poisonous. Not affected by alcoholic potash. Sublimes at 190° (Blyth). Gives an orange colour with I and H_2SO_4. On heating with 2 p.c. HClAq it yields solanidine and a dextro-rotatory sugar that reduces Fehling's solution, $[\alpha]_D = 28{\cdot}6°$, yields with phenyl hydrazine an osazone [199°], and is oxidised by HNO$_3$ to mucic and saccharic acids; lævulose is not present. Solanine colours a mixture of alcohol and H_2SO_4 rose red. With ammonium selenite (1 g.) in conc. H_2SO_4 (20 c.c.) it gives a canary-yellow colour turning to brown, and, after three hours, to violet-red (Ferreira da Silva, *Bl.* [3] 6, 87; *C. R.* 112, 1267). A solution of ammonium vanadate in H_2SO_4 is coloured brown by dry solanine, the colour becoming red, and finally disappearing on dilution (Mandelin).

Salts.—$C_{43}H_{71}NO_{16}HCl$. Got by adding ether to an alcoholic solution of the base and HCl. Gelatinous pp. which dries up to a gummy mass.—$B'_2H_2PtCl_6$: yellow flocculent pp.—$B'H_2SO_4$: amorphous, v. sol. water.—$B'_2H_2C_2O_4 7aq$; crystalline crusts.

Acetyl derivative $C_{42}H_{69}Ac_6NO_{15}$. Needles (from ether), insol. water (Hilger).

Solaneïn $C_{52}H_{83}NO_{18}$ 4aq. [208°]. Obtained as above (Firbas). Amorphous. More sol. 85 p.c. alcohol than solanine. Decomposed by HClAq into the same products as solanine. Colours Mandelin's reagent red.

Solanidine $C_{40}H_{61}NO_2$. [191°]. Formed as above. Colourless needles (from ether). Affects Mandelin's reagent in the same way as solanin. Ac$_2$O at 140° gives a diacetyl derivative (Firbas). Converted by fuming HClAq in the cold into amorphous yellow solanicine $C_{26}H_{39}NO$ (?), which yields B'HCl and $B'_2H_2PtCl_6$ (Zwenger, *A.* 123, 341).

Salts.—$B'_3(HCl)_4aq$: crystalline powder.—$B'_3 4H_2SO_4 8aq$: colourless plates [247°].

SOLUTIONS. Inasmuch as many of the questions connected with the state of bodies in solution are not yet fully elucidated, and inasmuch as two very different conceptions are put forward regarding the compositions of bodies present in aqueous solutions of salts, the editor of that portion of the Dictionary to which the subject of solutions belongs thought it advisable to ask the originator of the electrolytic dissociation hypothesis of saline solutions to write a short article on solutions in general, and to invite one of the leading upholders of the hydrate hypothesis of saline solutions to summarise the arguments in support of that hypothesis.

SOLUTIONS I. A solution is a homogeneous mixture of two or more bodies in the liquid state. A distinction is made between the dissolved substance and the solvent; the substance present in greater quantity is generally spoken of as the solvent. In some cases the solvent is taken to be the substance with the lower temperature of solidification. In the cases of substances miscible in all proportions—a mixture, for instance, of equal parts of alcohol and water—there is no way of determining which should be regarded as the solvent and which as the dissolved substance. There are many instances of two bodies that cannot be mixed in all and any proportions; the solubility of such bodies is said to be *limited.* If the 'dissolved body' in such a case is present in excess, either as gas, liquid, or solid, a condition of equilibrium is finally attained wherein the solution can take up no more of the dissolved body as long as the external conditions (temperature and pressure) remain unchanged; such a solution is said to be *saturated.* The attainment of saturation is hastened by shaking.

Saturated solutions of gases. When a gas is placed over a liquid, such as water or alcohol, a portion of the gas dissolves in the liquid. There is a constant relation at constant temperature between the quantity of gas remaining per unit volume and the quantity dissolved by the liquid per unit volume (Henry's law). Inasmuch as the quantity of the gas, per unit volume, is proportional to the partial pressure of the gas, the law may be stated by saying that the quantity of the gas dissolved in the liquid is proportional to the partial pressure of the gas above the liquid. As all the gases that have been examined dissolve with production of considerable quantities of heat, the solubilities of these gases decrease as temperature increases, in accordance with the second law of thermodynamics. The measurements made by Bunsen (*Gasom. Methoden* [Braunschweig, 1877]) show that the solubilities of some gases are independent of temperature—for instance, the solubility of H in water and of O and CO in alcohol. Henry's law holds good, as indicated by theory, only so long as the quantity of the gas per unit volume, both undissolved and in solution, is small, and the molecules of the dissolved and the undissolved gas are of equal magnitude. Van't Hoff has made use of the law of Henry to prove the equality of the molecules of the same gas in the gaseous state and in dilute solution (*Z. P. C.* 1, 489 [1877]). When NH_3, HCl, and SO_2 are dissolved in water in large quantities these gases do not follow the law of Henry; neither does the law hold good for solutions of acetic acid in benzene or ether in water, because the molecular magnitudes of these compounds are not the same in the gaseous state and in solution, as is proved by determinations of the boiling-points of the compounds in question (Nernst, *Z. P. C.* 7, 97 [1891]).

Mutual solutions of liquids. When two liquids that are not miscible in all proportions, such as ether and water, are shaken together, two layers are formed, one floating on the other; one of these contains much water and little ether, while the other contains much ether and little water. The compositions of the two layers change with change of temperature. Generally speaking, the compositions become more alike as temperature rises, until a temperature is reached whereat they are identical; when this temperature, which corresponds to the critical temperature for the liquids, is passed, the two liquids dissolve in all proportions. This behaviour has been more fully examined by Alexejeff (*W.* 28, 305 [1886]) and has been represented by him in curves, some of which are reproduced here (fig. 1). The curve *a* represents the behaviour of water and phenol, *b* that of water and salicylic acid, *c* that of water and benzoic acid, *d* that of water and aniline phenolate, and *e* that of water and aniline. The abscissæ represent temperature, and the ordinates percentages of the dissolved substances in the solutions. To each temperature correspond two points in the curve showing the percentage composition of the solution of the substance in water, and that of the solution of water in the molten substance; thus, for phenol and water (curve *a*), at 20°, the solutions are composed of 92·5 p.c. water and 7·5 p.c. phenol, and 28 p.c. water and 72 p.c. phenol respectively. The two liquids are miscible in all proportions above 69°.

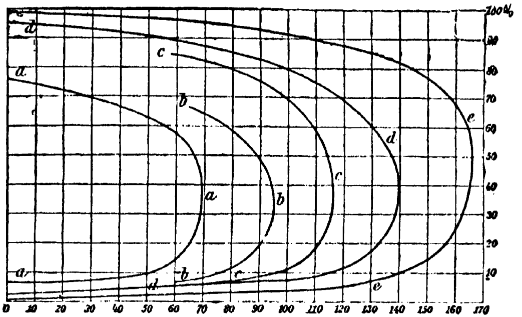


FIG. 1.

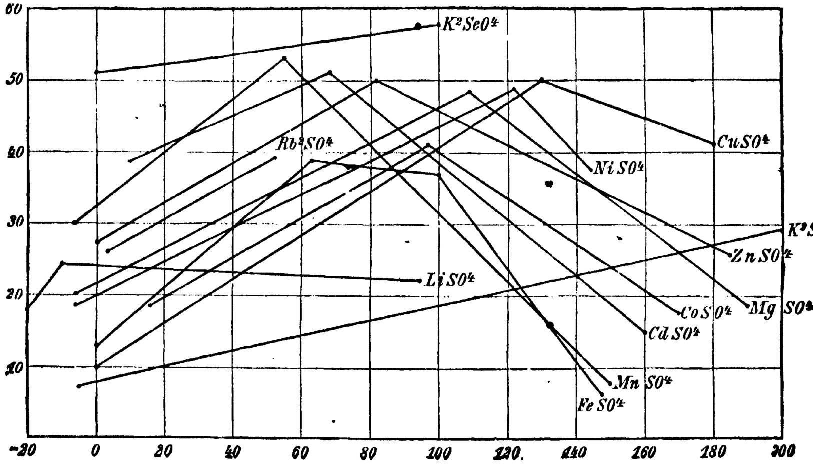


FIG. 2.

It happens sometimes that two liquids are miscible in all proportions below a certain temperature, but form two layers above this temperature; in such cases—for example, in the solution of di-ethylamine in water—the convexity of the curve is turned to the left.

Saturated solutions of solids. Most of the measurements that have been made deal with solutions of salts in water. The example of Gay-Lussac has generally been followed, and the solubility of the salt has been taken as the weight thereof dissolved by 100 parts by weight of the solvent. Étard and Engel have given solubility-curves for very large variations of temperature (*C. R.* 98, 993, 1276, 1432; 104, 1614; 106, 206, 740 [1884-88]). Some of these results are shown in fig. 2, p. 485; the abscissæ represent temperature and the ordinates parts by weight of the salts in 100 parts of the solution (not in 100 parts of the solvent). The change of solubility with change of temperature depends on whether the process of solution is accompanied by disappearance or production of heat; in the former case solubility increases, in the latter case it decreases, as temperature rises. Inasmuch as different hydrates of the same salt are dissolved with the production of different quantities of heat, these hydrates give different solubility-curves. Sodium sulphate is the salt that has been most carefully examined in this respect. The hydrate $Na_2SO_4.10H_2O$, that exists up to 33°, dissolves in water with disappearance of heat; hence the solubility of this hydrate increases as temperature increases. On the other hand, Na_2SO_4, stable above 33°, dissolves with production of heat, and its solubility decreases with increasing temperature. The so-called curve of the solubility of sodium sulphate consists, therefore, of two parts, one rising till the temperature reaches 33°, and one falling above that temperature. Looked at accurately, the first part of the solubility-curve holds good only for $Na_2SO_4.10H_2O$, and the second part only for Na_2SO_4. For the solubility of a chemical compound is determined only when the composition of the solid compound that is in contact with the solution is definitely stated. The compound $CaSO_4$ is considerably more soluble than the crystalline hydrate $CaSO_4.2H_2O$. The measurements made by Étard show that many other sulphates—$MnSO_4$ and $CdSO_4$, for instance—behave similarly to Na_2SO_4 (see fig. 2).

The solubilities of most salts increase as temperature rises; the solubility of NaCl varies very little with temperature. The solubilities of many compounds of calcium decrease with increasing temperature, *e.g.* hydroxide, acetate, isovalerate, isobutyrate, succinate, and isosuccinate of calcium. Barium succinate and $SrSO_4$ behave similarly, but not the other corresponding salts of Ba and Sr. Some calcium salts show maximum solubilities at certain temperatures—*e.g.* $CaSO_4.2H_2O$ at 35°; others show minimum solubilities—*e.g.* propionate at c. 55°, isobutyrate at 65°, also normal butyrate, valerate, iso-octoate, citrate, and benzoate (Allen, *C. N.* 57, 236 [1888]). Attempts have been made to express the connection between the solubilities of salts and temperature by a formula. The following expression holds good in many cases: $S=a+bt$ (t = temperature, and a and b are constants); *i.e.* solubility changes linearly with temperature—for instance, for KCl, $BaCl_2$, $NaNO_3$, and several sulphates, especially at high temperatures (Étard). In other cases it is necessary to add a th[illegible] or a fourth term, and to adopt the formula $S=a+bt+ct^2+dt^3$ (c and d are constants as well as a and b). The formula $\log. S=a+bt+..+...$ often gives a better representation with a smaller number of coefficients.

Supersaturated solutions. When a salt whose solubility increases with temperature is dissolved at a high temperature in water (or other solvent), and the solution is cooled, a temperature is reached whereat the solution is saturated with reference to a definite hydrate of the solid salt; but if the solution is further cooled salt does not separate, provided there is no crystal of the hydrate in question in contact with the solution. Such a solution is said to be supersaturated. A solution may be supersaturated with reference to one hydrate, but not supersaturated with reference to another hydrate. For example, $Na_2SO_4.7H_2O$ is more soluble in water than $Na_2SO_4.10H_2O$, and so a solution may be obtained, by dissolving Na_2SO_4, that is supersaturated as regards the decahydrate but not as regards the heptahydrate; that is to say, if a crystal of $Na_2SO_4.10H_2O$ is brought into the solution, at a certain temperature, the decahydrate crystallises out, but at the same time the solution is able to dissolve the hydrate with $7H_2O$. If temperature falls again the solution, of course, becomes supersaturated with reference to both the hydrates.

At one time the supposition was often held that the dissolved substances were present in supersaturated solutions in a state different from that in which they existed in ordinary solutions. More accurate investigations of the physical properties on both sides of the point of saturation have shown that there is no essential difference between the solution before and after saturation, but that the relation of a supersaturated to a saturated solution is exactly the same as that of a saturated solution to the solution before saturation.

Colloidal solutions. Certain substances, such as gelatin, absorb unlimited quantities of water and become swollen thereby; when much water has been taken up, liquids are formed which do not part with the dissolved body on cooling, as ordinary solutions do, but set to jelly-like substances. All compounds that form colloidal solutions have very large molecular weights; such compounds are acids of Mo, Si, Sn, Ti, and W; oxides of Sb, Fe, and Mn; sulphides of Sb, As, Bi, Cd, Co, Au, Fe, Pb, Hg, Ni, Pd, Pt, Ag, Tl, and W; many organic substances, such as caramel, dextrin, egg-albumen, tannin, &c.; and also some elements, such as Se and Ag. Some of these solutions are characterised by the fact that the addition of small quantities of foreign substances—as salts, acids, and bases—causes coagulation, whereupon the bodies in the colloidal solutions become insoluble. For that reason it is generally supposed that colloidal solutions are intermediate between emulsions and true solutions. Emulsions—*e.g.* a fine deposit of alumina—possess the special property that the emulsionised bodies are thrown down much more quickly in presence of electrolytes, and also of other foreign substances, than in absence of these (Barus a. Schneider, *Z. P. C.* 8, 291 [1891].) Colloidal substances having molecular weights under 30,000—gelatin or gum, for instance—are characterised by the fact that if their solutions are solidified by cooling they again become liquid and transparent when heated. Colloids having molecular weights greater than 30,000 do not share in this property, but behave, in this respect, like very supersaturated solutions (Sabanejeff, *J. R.* 1891. [1] 80; *Z. P. C.* 9, 89 [1892]). When colloids take up water, and swell but do not dissolve, heat is produced; when they dissolve heat disappears (Wiedemann a. Lüdeking, *W.* 25, 145 [1885]).

Reasons for assuming the existence of hydrates in solutions. When a dissolved substance is isolated, by various methods, from its solvent the solid generally separates in combination with water of crystallisation. It has, therefore, been generally supposed that a preponderating quantity of this hydrate must be present in the solution. This conclusion is not, however, tenable; for if only a minimum quantity of the compound that separates out were present in the solution this might suffice to cause the separation. The following consideration has been brought forward as an argument in favour of the existence of hydrates in solutions. A solution of 57 parts by weight HI and 43 parts water boils at 127°, and the distillate has the same composition as the residue; this lends some countenance to the view that this mixture behaves like a definite chemical compound. On adding water to this solution and distilling a more dilute acid at first passes over, and at last the acid with 57 p.c. HI distils off. If the solution contains more than 57 p.c. HI to begin with, the distillate at first contains a more conc. acid, and, later, acid of 57 p.c. This behaviour is simply explained in the following way. A solution of 57 p.c. HI possesses a minimum vapour-pressure, so that both less dilute and more dilute solutions at the same temperature have larger vapour-pressures. Speaking generally, the vapour from a solution does not contain both components in the same proportion as the solution itself. In the case under consideration the vapours from the more dilute solutions contain more water (in proportion to HI) than the solutions, and the vapours from the less dilute solutions contain, relatively, more HI. The dilute solutions increase in concentration as distillation proceeds, the boiling-point rises, and there is at last produced the 57 p.c. solution which possesses the lowest vapour-pressure at an equal temperature—*i.e.* the highest b.p. (127°) at an equal pressure. If, on the other hand, distillation is commenced with a more concentrated solution proportionally more HI passes over, and an approach is gradually made, from the other side, to the solution with highest b.p. There is, therefore, no binding reason for regarding this solution as a definite chemical compound. For, indeed, the composition of the solution changes according to the pressure under which the distillation is conducted; and this could not well be the case were the solution really a definite chemical compound.

In investigating the freezing-points and vapour-pressures of solutions it was found that in many cases the deviation from the freezing-point and vapour-pressure of the pure solvent was proportional to the quantity of substance (salt) in solution. But in other cases this proportionality seemed not to be maintained unless the supposition were made that a portion of the water had combined with the dissolved substance (Wüllner, *P.* 103, 529; 105, 85; 110, 564 [1858, 1860]; de Coppet, *A. Ch.* [4] 23, 366; 25, 502; 26, 98 [1871-2]; Rüdorff, *P.* 114, 63; 116, 59 [1861-2]; 145, 599 [1870]). It was, therefore, supposed that such compounds as HI, HCl, $BaCl_2$, $CaCl_2$, NaBr, &c., were combined in aqueous solutions with definite quantities of water of crystallisation. But the recently-discovered laws which express these phenomena lead to very different methods of explanation, so that the conclusion that these compounds exist as hydrates in solutions seems, in this respect, to be entirely without foundation.

Mendeléeff not long ago examined the changes in the S.G., accompanying changes in the composition, of aqueous solutions of alcohol and of sulphuric acid (*Z. P. C.* 1, 273 [1887]); he thought he had found abrupt irregularities in the changes of S.G. He supposed, without any theoretical foundation, that at the concentrations whereat these occurred the solutions corresponded to perfectly definite hydrates. Pickering (*Z. P. C.* 6, 10 [1890]) showed, as the result of more accurate investigations, that Mendeléeff's conclusions rested on inaccurate observations. Pickering, however, accepted Mendeléeff's idea, and supposed that the higher derivatives of the S.G. in reference to percentage composition showed similar irregularities. He treated the freezing-points and the electrical conductivities of solutions in the same way, and he supposed that in all these cases he had discovered such irregularities as indicated the existence of definite hydrates. It is absolutely impossible to reconcile the numbers for the electrical conductivities of dilute solutions of acids and bases (*e.g.* for acetic acid) with Pickering's views; nor do the most recent investigations on the freezing-points of very dilute saline solutions (Jones, *Z. P. C.* 11, 534; 12, 623 [1893]) in any way agree with these views. Moreover, the method used by Pickering is not free from objection under any conditions.

From an extended and systematic investigation recently made into the constitution of ammoniacal metallic compounds, and compounds analogous therewith, Werner (*Zeit. f. anorg. Chem.* 3, 267 [1893]) concluded that in electrolytically conducting salt solutions the metallic atoms of the salts might be expected to be generally accompanied by six molecules of water, and that those salts which readily combine with water of crystallisation would be the best conductors. This statement is not, however, in any way in keeping with the experimental results. The salts of ammonium, K, Rb, and Cs conduct better than any others that have been examined; after these come the salts of Na, Li, and the metals of the earths; and then, much behind these, come the salts of the heavy metals; but water of crystallisation combines most readily with the salts last mentioned, and least readily with those mentioned first.

Conclusions regarding the existence of hydrates of substances in solution have also been drawn from the results of investigations of other

properties, such as contraction or
, or production of heat, during solution,
osity, &c.

general, it has been supposed that where
roperties exhibited a maximum or mini-
r other purely mathematical character-
here existed a definite hydrate of corresponding composition. Attention may, however, be called to the fact that these points generally shift with changes of temperature, so that the hypothetical hydrate must have a different, and constantly changing, composition at different temperatures—a conclusion which is not in keeping with the representation of the hydrate as a definite chemical compound.

It is, indeed, in the highest degree likely that when definite hydrates separate from a solution the same hydrates were previously present in the solution, perhaps only in small quantity; but we have as yet no accurate knowledge as to the magnitude of the quantity. The methods that have been used in investigating this most interesting question have scarcely brought to light a single new result, although many and renowned investigators have carried out a very large amount of work in this direction.

The solubility of a salt, at constant temperature, is to a small extent dependent on pressure. Sorby was the first to carry out detailed investigations on this subject (*Pr.* 12, 538 [1863]). The following statement may be demonstrated by the use of the dynamical theory of heat. When the total volume of salt and solution is diminished (or increased) by the taking up of salt into the solution, then the solubility increases (or diminishes) with increased pressure. The researches of Braun (*W.* 30, 272 [1887]) have confirmed the theoretical conclusions.

Dilute solutions. *Osmotic pressure.*—If a quantity of the pure solvent is floated on a solution, a movement of the dissolved substance takes place and the substance strives to distribute itself throughout the whole of the solvent. This occurrence is completely analogous with another; if a cylinder is filled with CO_2 and the mouth is covered with a membrane, another cylinder is filled with H and placed mouth-downwards on the first, and the membrane is withdrawn, the two gases begin to diffuse into each other (notwithstanding the action of gravitation). The H is driven downwards by its partial pressure, and the CO_2 is driven upwards. The velocity of diffusion is proportional to this propelling force, otherwise it is dependent only on the freedom of motion of the molecules among each other. The inverse value of this freedom of motion is called *molecular friction.* The following statement expresses the results of experiment: the velocity of diffusion is proportional to the difference between the partial pressure of one of the two gases in the upper and lower parts, and is inversely proportional to the friction of the molecules. Solutions behave in a similar way. The substance in solution in the under layer strives to distribute itself into the upper layer; this striving corresponds to the pressure of a gas, and, as will be shown immediately, it is equal to the so-called osmotic pressure. The solvent is driven downwards by the same force. In this case also the velocity of diffusion is proportional to the osmotic pressure, and is inversely proportional to the friction of the molecules of the dissolved substance against the solvent. The only difference between this case and that of gases is that molecular friction is very much larger in liquids, a fact that is explained by the great number of molecules against which a molecule of the dissolved substance collides during its movements.

The amount of molecular friction is known in certain cases, viz. for electrolytes. Let a cubical trough (sides 1 cm.) be filled with the solution of an electrolyte (*e.g.* NaCl), and let an electric current be passed through the trough by the help of two electrodes A and B. The positive electricity is carried by the metallic parts (Na) of the electrolyte in the direction of the current (towards B); the negative electricity travels with the negative radicle (Cl) of the electrolyte towards A. If the Na and Cl atoms—or ions, as they are called in this case—are impelled by unit electrical force, the Na ions will move with a velocity v_1 and the Cl ions with the velocity v_2. These velocities can be determined, partly indirectly from the conductivity and the migration numbers of Hittorff, partly directly by chemical analysis. Putting the corresponding frictions as r_1 and r_2, then $v_1 = \frac{1}{r_1}$ and $v_2 = \frac{1}{r_2}$. The frictions of a large number of ions have been determined in this way. If we now have a layer of pure water floated on a solution of NaCl, in a vessel, then the velocity of diffusion, D, is equal to the quotient of osmotic pressure, O, and the frictions $r_1 + r_2$ of the salt. We have, therefore, $D = \frac{O}{r_1 + r_2}$. Nernst (*Z. P. C.* 2, 613 [1888]) has completely established the accuracy of this formula.

Osmotic pressure can be measured directly. Let us suppose that in the foregoing example we had a division separating the solution of NaCl from the water, and that the division allowed water, but not NaClAq, to pass through it (a so-called semipermeable membrane); *v.* fig. 3. Such a membrane is obtained by impregnating a plate of porous burnt clay with ppd $Cu_2Fe(CN)_6$. The water will then be driven downwards, and will be compressed in the lower part of the apparatus; the pressure in this division will increase; this may be confirmed by using a manometer (M, fig. 3). Equilibrium is attained after a time, and the manometer then indicates a certain pressure, which is called the

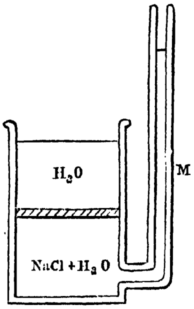


Fig. 3.

osmotic pressure of the solution. When no more water is driven downwards, then, in the case in point, the partial pressures of the water in the upper and lower parts of the apparatus are equal. The excess of pressure in the lower part—that is, the osmotic pressure—is then equal to the partial pressure of the NaCl molecules. Measurements of this kind have been made by Pfeffer, Tammann, and Adie (*Osmotische Untersuchungen*, Leipzig, 1877; *W.* 34, 229 [1888]; *C. J.* 59, 344 [1891]).

Semipermeable membranes are found in the lining of living cells which incloses the contents of the cell. De Vries made observations with cells of *Tradescantia discolor* and *Begonia manicata*; Donders and Hamburger used blood-cells. If a cell is immersed in water the cell swells because of the entrance of water; if a soluble substance is added to the water, in constantly increasing quantity, the water will at last be driven equally inwards and outwards; if this limit is overpassed, the water passes out of the cell and the protoplasmic contents of the cell shrink together. The whole process may be followed by the help of the microscope. The limit reached immediately before shrinkage begins is characterised by the attainment of equality between the osmotic pressure of the cell-contents and that of the surrounding solution. By bringing similar cells into solutions of different substances it is possible, in this way, to determine the concentration that must be attained by two solutions in order that they may possess equal osmotic pressures. Using the results of Pfeffer and de Vries, van't Hoff made an examination of the magnitude of osmotic pressures. He found that the osmotic pressures exerted in their solutions by non-conductors of electricity—such as cane sugar, urea, glycerin, &c.—were exactly the same as the pressures which these substances would exert, in accordance with Avogadro's law, were they present as gases in the same volume as the volume occupied by the solutions. The osmotic pressure is therefore proportional to the concentration and the absolute temperature (law of Boyle and Gay-Lussac); this was confirmed by Pfeffer's investigations (van't Hoff, *Handingar der Stockh. Ak.* 21 [1886]; *Ar. N.* 20 [1885]; *Z. P. C.* 1, 481 [1887]).

An explanation of gaseous pressure is found in representing it as the result of the bombardment of the walls of the vessel by the gaseous molecules. Similarly, osmotic pressure is thought of as resulting from the knocking of the molecules of the dissolved substance against the walls of the containing vessel. The gaseous laws hold good in all respects for osmotic pressure.

Vapour-pressures of solutions. Let there be a solution, say of cane sugar, in a trough, separated by a vertical semipermeable membrane from pure water, and let the membrane extend above the solution; the air above the liquid behaves exactly like the semipermeable membrane, inasmuch as it allows the water to pass through (as water-vapour), but it does not allow the cane sugar to pass through (because of the non-volatility of the sugar). The water has, therefore, a tendency to pass across through the air as well as through the semipermeable membrane from the water in the solution. This circumstance may be expressed by saying that the pressure of the water-vapour is greater over the water than over the solution. In like manner it follows that solutions which have equal osmotic pressures have also equal vapour-pressures. By making use of the second law of thermodynamics it can be shown (van't Hoff, *l.c.*) that a solution containing *n* molecules of dissolved substance to N molecules of solvent has a vapour-pressure, P, which is given by the formula

$$P=\left(1-\frac{n}{N}\right)p,$$

where p = the vapour-pressure of the pure solvent. (The molecular weight of the solvent must be taken as that of the substance in the gaseous state at the same temperature.) This formula was originally experimentally established by Raoult; it agrees well with experience (*C. R.* 103, 1125 [1886]).

Boiling-points of solutions. According as the vapour-pressure of a solution is less than that of the solvent (assuming that the dissolved substance possesses no marked vapour-pressure), so the solution begins to boil, under a definite external pressure, at a higher temperature than the pure solvent. The following formula may be deduced from the dynamical theory of heat:

$$E=\frac{0{\cdot}2\,\tau^2}{L}\cdot n,$$

where E is the increase in the boiling-point of the solvent brought about by dissolving *n* molecules of the substance in 100 grms. thereof, τ is the absolute boiling temperature, and L is the latent heat of vapourisation of 1 grm. of the solvent. Beckmann has contrived an apparatus for determining E, and therefore for finding *n*—that is, for determining the molecular weight of the dissolved substance when the quantity thereof in 100 grms. of solvent is known. He has shown that the formula gives results which agree closely with experience (*Z. P. C.* 5, 76 [1890]).

Freezing-points of solutions. When a solution is caused to freeze, in most cases only the pure solvent separates as a solid. The solid substance is in equilibrium with the solution at the freezing-point; hence, the vapour-pressures of the solvent over the solid and over the solution must be equal, as otherwise distillation would take place from the one to the other, and equilibrium would not be attained. For the sake of simplicity let us take water as the solvent. Ice and water have, therefore, the same vapour pressure at the freezing-point of the latter (0°); but an aqueous solution has a smaller vapour pressure at 0°; hence at 0° ice cannot have the same vapour pressure as an aqueous solution, but this equality occurs only at a lower temperature. In other words, the freezing-point of a solution is lower than that of the solvent. Van't Hoff (*l.c.*) has deduced the following expression from the dynamical theory of heat, $E=\frac{{\cdot}02\,\tau^2}{W}\cdot n$, where E is the difference between the freezing-points of the pure solvent and a solution therein, which solution contains *n* gram-molecules of the dissolved substance in 100 grms. of the solvent, τ is the absolute temperature, and W is the latent heat of fusion of 1 grm. of the solvent. This formula is of much importance, for the molecular weights of very many substances have been determined by its help. It is immaterial in this case whether the dissolved substance exerts a considerable vapour-pressure or not, for only the pure solvent freezes out. The following table gives some values calculated by the formula placed side by side with the values obtained by experiment, for the case where $n=1$:

	E observed	E calculated
Water. . .	18·9	18·9
Acetic acid . .	38·6	38·8
Formic acid .	27·7	28·4
Benzene . .	50·0	53·0
Nitrobenzene .	70·7	69·5

Electrolytic dissociation. When determinations of molecular weights are made, by the foregoing methods, based on osmotic pressures (de Vries), freezing-points (van't Hoff, Raoult), depressions of vapour-pressures (Raoult), or increments of boiling-points (Beckmann), the values obtained for all those substances whose solutions conduct electricity are much smaller than would be expected. For instance, the results obtained by working with a half-normal solution of NaCl lead to the value 31·6 for the molecular weight of the salt, a number which is 1·85 times smaller than the calculated value, 58·5 (NaCl). From this and many other considerations Arrhenius drew the conclusion that the molecules of electrolytes are largely dissociated in aqueous solutions; about 85 p.c. of the NaCl, for instance, in an aqueous solution of this salt is regarded as dissociated into Na and Cl. This conclusion is completely analogous with those which are drawn regarding the dissociation of the molecules of ammonium salts and other substances, in the gaseous state, from observations of the abnormal vapour densities of these substances. The development of the theory of electrolytic dissociation, based on these considerations, and confirmed in the fullest way by experience, has lent much support to the theory of solutions which has already been sketched. This part of the subject is treated by Ostwald in the article ELECTRICAL METHODS, to which reference should be made (this vol., pp. 187-221).

Some of the deductions regarding diffusion, solubility, and affinity must, however, be mentioned here.

Diffusion of mixtures. When a solution of HCl is placed in contact with pure water, the HCl gradually diffuses into the water. Inasmuch as most (almost all) of the HCl molecules are dissociated, one would expect the diffusion to result in a separation of the H and Cl from each other, just as the alums and the double salts of the sulphates of the alkalis and the magnesium metals, which are partially decomposed in aqueous solution, can be separated into their constituent salts in this way (Graham, *T.* 1850. 1, 805; Marignac, *A. Ch.* [5] 2, 546 [1874]). But this separation does not occur. The H moves into the water more quickly than the Cl, and, because of the positive electrical charge of the H ions, the water becomes positively and the solution negatively charged. If this charging is not carried off by metallically connected unpolarisable electrodes placed in the solution and in the water (*v.* this vol. p. 212), it prevents the separate diffusion of the H and the Cl. But there is another way whereby the restraining force of the electrical charge on the diffusion of the H may be diminished—namely, by addition of chlorides. For instance, the velocity of diffusion of HCl (properly speaking, of H) is increased in the ratio of 1:2·24 by adding 25 times the quantity of NH_4Cl (Arrhenius, *Z. P. C.* 10, 51 [1892]). Similar, although not so strongly marked, characteristic phenomena, which find an explanation in the dissociation theory, have been observed by Graham and Marignac.

Decrease of solubility by addition of foreign salts. Nernst (*Z. P. C.* 4, 372 [1889]) was the first to draw attention to the conclusion from the theory that a slightly soluble salt, *e.g.* silver acetate, must be more soluble in pure water than in a solution that contains other silver ions (*e.g.* $AgNO_3$) or acetate ions (*e.g.* $NaC_2H_3O_2$). Similar relations are shown by gases which partially decompose (*e.g.* NH_4SH); these exhibit smaller vapour-pressures when one of the two components (NH_3 or H_2S) is added. This lowering of solubility can be calculated from the laws of mass-action, with results which agree well with experience (Noyes, *Z. P. C.* 9, 603 [1892]).

Division of a dissolved substance between two solvents. Berthelot and Jungfleisch examined the distribution of succinic acid between ether and water, and found that the concentrations of the acid in the aqueous and in the ethereal solution were in a constant proportion, which appeared to be independent of the absolute concentration. Many other substances were found to behave in the same way (*A. Ch.* [4] 26, 396, 408 [1872]). This result corresponds completely with Henry's law for gases. It is readily deduced from the theory; but in doing this it is assumed that the dissolved substance has the same molecular weight in both solutions. If this is not the case—as, for example, in the distribution of benzoic acid between benzene and water—altogether different laws express the phenomena (these laws, also, are in keeping with experimental results; Nernst, *Z. P. C.* 8, 110 [1891]).

Reaction velocities. There are many so-called catalytic processes that are brought about by the H ions of acids—for instance, the inversion of cane-sugar, saponification of esters, &c. According to the theory, the velocity with which these reactions take place must depend only on the number of H ions that are present, and not on the nature of the reacting acid. This conclusion is confirmed by experience (Arrhenius, *Z. P. C.* 4, 226 [1889]; *cf.* AFFINITY, vol. i., especially pp. 77-81).

Division of a base between two acids present in equivalent quantities. Thomsen made investigations regarding the quantity of a base (NaOH) that reacts to form salts with two acids (*e.g.* HCl and HF) added in equivalent quantities. He found that, in the case quoted, 95 p.c. NaCl and only 5 p.c. NaF were formed in dilute aqueous solution. It may be deduced from the theory that the quantities of NaOH combining with the two acids (HCl and HF) are in the same ratio as the extents of dissociation of the acids at the same dilution. The observations of Thomsen and of Ostwald agree extremely well with this deduction from the theory (Arrhenius, *Z. P. C.* 5, 14 [1890]; *cf.* AFFINITY, vol. i. p. 81).

Influence of temperature on rate of solution. If a finely and equally powdered substance is shaken with a solvent at two different temperatures, for a very short time, the rapidity of solution is found to increase rapidly with the temperature. For instance, the rates of solubility in water of cream of tartar and benzoic acid increase between 0° and 17° in the ratios 1 : 3·8 and 1 : 3·1.

So-called solid solutions. Palladium is able to take up much H, but the mixture retains the solid form. There is, therefore, here no proper solution; nevertheless, van't Hoff has shown that the laws which hold good for solutions are valid for this phenomenon also (*Z. P. C.* 5, 322 [1890]). There is formed at first an alloy, Pd_2H, which possesses a definite dissociation pressure. If the pressure of the H is increased more H is absorbed, and the quantity absorbed is in direct proportion to the excess of pressure of the H. Henry's law, therefore, holds good. On this ground van't Hoff called mixtures similar to this 'solid solutions.' Solid solutions of thiophene and benzene have been examined by van Bijlert (*Z. P. C.* 8, 343 [1891]).

Heats of solution. A considerable quantity of heat is generally produced during the solution of a substance in a solvent. The heat of solution of a substance is defined to be the quantity of heat that appears during the solution of a gram-molecule of the body in much water. The following table gives the heats of solution of some of the commoner substances. Most of the numbers are taken from Thomsen (*Th.* 3, 195).

Gases.

Chlorine Cl_2	4870
Carbon dioxide CO_2	5882
Ammonia NH_3	8430
Hydrogen fluoride HF	11800
„ chloride HCl	17310
„ bromide HBr	19940
„ iodide HI	19210
„ sulphide H_2S	4560
Sulphur dioxide SO_2	7700

Liquids.

Methyl alcohol $CH_3.OH$	2000
Ethyl „ $C_2H_5.OH$	2540
Propyl „ $C_3H_7.OH$	3050
Ether $(C_2H_5)_2O$	5940
Acetic acid $C_2H_3O.OH$	420
Sulphuric acid H_2SO_4	17850

Solids.

Caustic potash KOH	12500
„ „ hydrate $KOH.2H_2O$	−30
Lithium chloride LiCl	8440
Sodium „ NaCl	−1180
Potassium „ KCl	−4440
Sodium bromide NaBr	−190
„ „ hydrate $NaBr.2H_2O$	−4710
Potassium sulphate K_2SO_4	−6380
Mercuric chloride $HgCl_2$	−3300
Sodium acetate $NaC_2H_3O_2$	4200
Sodium benzoate $NaC_7H_5O_2$	800
Benzoic acid $C_6H_5.CO_2H$	−6700
Silver chloride AgCl	−15800
„ bromide AgBr	−20200
„ iodide AgI	−26600
Cane sugar $C_{12}H_{22}O_{11}$	−800

Volume changes accompanying solution. In most cases the solution of a substance in water is accompanied by a considerable amount of contraction. For instance, a mixture of 100 c.c. alcohol with 100 c.c. water measures only 192·8 c.c. at 18°. The contraction may be so great that the volume of the solution is less than the volume of the water used as solvent: for instance, when Na_2CO_3, NaOH, or LiOH is dissolved in much water. The following table shows the volume change, in c.c., that takes place when one gram-equivalent of some of the most important compounds is dissolved in much water—*e.g.* in 10 litres:—

	H	Na	K	NH_4
OH	18	− 5·8	3·6	—
Cl	18·3	16·6	26·9	37·4
NO_3	29·0	28·0	38·5	48·2
$\frac{1}{2}SO_4$	16·2	6·4	15·7	24·2

A mixture of 40 grms. NaOH with 10 litres water occupies, therefore, a volume of 9994·2 c.c. only.

When the solvent is other than water an increase of volume sometimes takes place; for instance, a mixture of 100 c.c. alcohol with 100 c.c. CS_2 occupies about 202 c.c.

Specific heats of solutions. The water value of a solution of a salt in water is not equal to, but is generally less than, the sum of the water values of the water and the salt. In a few cases this decrease is so great that the water value of the solution becomes less than that of the water used as solvent. The following data show the water values of one gram-equivalent of the chief salts in extremely dilute solutions (according to the determinations of Thomsen):—

	H	Na	K	NH_4
OH	18	−27	−38	—
Cl	−28	−16·3	−30	−13
NO_3	−10·7	− 8·7	−16	7
$\frac{1}{2}SO_4$	9	−25	−36	−16

The water value of a solution of 40 grms. NaOH in 10 litres water, for instance, is not only not greater than that of the water alone (10,000), but is distinctly smaller (9,973).

Deviations shown by concentrated solutions. The laws that have been stated for the osmotic pressure, the lowering of freezing-point, the raising of boiling-point, and the lowering of vapour-pressure, brought about by substances in solution, are valid, strictly speaking, only for very dilute solutions. Deviations from these laws occur when the solutions are more concentrated. Sometimes the observed values are smaller than those theoretically deduced. In such cases it is supposed that molecular aggregates are formed. This occurs, for instance, with solutions in benzene of oxims, alcohols, phenols, and fatty acids, and also with fairly concentrated aqueous solutions of the sulphates of Mg, Cu, Zn, and Cd, and CdI_2 (Beckmann, *Z. P. C.* 2, 737 [1888]; Arrhenius, *Z. P. C.* 2, 496 [1888]). On the other hand, most concentrated aqueous solutions give values greater than the calculated values; this is made especially evident by Tammann's investigations into the vapour-pressures of salt solutions at 100° (*Mém. de l'Acad. de St. Pétersbourg* [7] 1, 85 [No. 9, 1887]). An explanation of this behaviour has been sought for in the attraction between the solvent and the dissolved substance (Arrhenius, *Z. P. C.* 10, 40 [1892]).

S. A.

SOLUTIONS II. The view that hydrates exist in aqueous solutions, and analogous compounds in non-aqueous solutions, is one which has long been held by many chemists; it is only in the last few years, however, that the hydrate or association theory has assumed a precise form, and that definite experimental evidence in support of it has been accumulated. In giving some account of the present position of this theory it will be convenient to collect the evidence on which it depends under the headings 'general' and 'special,' and to discuss separately the bearing which recent work on dilute solutions has upon it. Aqueous solutions have naturally been more studied than solutions in other solvents, but these other solutions have been investigated sufficiently to show that they are similar to aqueous solutions in every respect, except as regards electric conductivity. Although, therefore, to simplify matters in the present article, in most instances aqueous solutions alone are mentioned, it must not be understood that the arguments do not apply equally to other cases.

General. The changes accompanying dissolution seem to be in every respect similar to the recognised accompaniments of chemical combination: evolution of heat, a more or less profound alteration in the nature of the reagents, and an irregular variation in the properties of the resulting solution with regular variations in the proportions of dissolved substance and solvent. For reasons which will be mentioned below, these irregularities may often not be very pronounced, but it may safely be stated that every attempt which has been made to express the properties of any series of solutions by a simple expression agreeing, within the limits of experimental error, with the observed values throughout a wide range of concentration has been unsuccessful.

The affinity which a large number of substances possess for water, as evidenced by the many solid compounds which they form with it, and by the heat evolved in their formation, renders it *primâ facie* extremely improbable that these substances should exist in presence of excess of water without combining with it. It is, moreover, those very substances which exhibit the greatest tendency to form solid hydrates which are generally most soluble. A more careful study of the thermal phenomena of solutions places this argument beyond the range of mere speculation. From the known heat of fusion of water and of a few anhydrous salts we can obtain a very close estimate of what the heat of fusion of any hydrated salt would be, if no change beyond the mere passage from the solid to the liquid condition occurred; with hexahydrated calcium chloride, for instance, the heat of fusion under such circumstances would be 11,000 to 12,000 cal., and on the most exaggerated estimate could not exceed 14,000 cal., whereas if decomposition as well as mere liquefaction occurred the heat absorbed would be at least 25,000 cal., since the heat of fusion of the $6H_2O$ alone is 9,500 cal., and the heat of combination of $CaCl_2$ with $6H_2O$ (both solid) is 14,500 cal. The observed heat of fusion, however, is only 11,417 cal., a value which disproves that any considerable change beyond mere liquefaction has occurred during the fusion—*i.e.* the combination which existed in the solid must exist also in the liquid. The data in the case of sulphuric acid afford more striking evidence of a similar character. The heat of combination of solid water with the solid acid to form the solid monohydrate is 6,550 cal., and if, when the reagents are mixed in the liquid condition, they do not combine chemically, far less than this amount of heat would be evolved; whereas the heat actually evolved is found to be almost identical with the above, namely 6,667 cal.

The separation of a crystalline hydrate from a solution is an argument to which due weight has hardly yet been attributed in favour of the existence of that hydrate in the solution, although not necessarily in large quantity. If there are no molecules of the hydrate existing as such in the liquid, these must have been deposited in the solid form at the moment of their formation, whereas we know that whenever deposition occurs simultaneously with formation, as in the precipitation of an insoluble salt, the substance is deposited in the amorphous and not in the crystalline condition.

If, as would appear to be the case, it is necessary to admit the existence of hydrates in concentrated solutions, it is necessary to admit their existence in dilute solutions also. The mass action of an excess of one or other of the constituents of any composite fluid is well known, and is universally accepted: it must operate with hydrates as much as with other substances, and must do one of three things: either (1) it must increase the stability or amount of the particular hydrate present, or (2) it must combine with it to form a higher hydrate (if it is the water of which excess is added), or (3) it may decompose the hydrate by reacting with the non-aqueous constituent of it to form new compounds, as when free alkali and acid are produced (a decomposition, however, which can be proved in many cases to occur to but a negligible extent), but in no case could excess of water decompose the hydrate taken so as to liberate the dissolved substance in the anhydrous condition. The thermal phenomena of solution afford important evidence in this case also; to interpret them properly, however, it must be remembered that the dissolution of a substance in excess of solvent entails the separation of the particles of that substance from each other to the same extent as if it were vapourised, and that to effect this separation the same amount of heat must be absorbed in either case. The heat evolved due to the reaction of a liquid with excess of solvent is, therefore, the observed heat of dissolution *minus* the heat absorbed in vapourisation, and, in the case of a solid, the heat of fusion as well as that of vapourisation will have to be subtracted. Making allowance for these so-called physical changes, we find that the formation of every concentrated solution—that is, a solution which contains hydrates—is accompanied by the evolution of heat, and inasmuch as, with the same allowance, dilution is always accompanied by a further evolution of heat, the action of the diluent cannot be regarded as a reversal of the initial reaction, but rather as an extension and completion of it, the hydrates present in the concentrated solutions being increased in amount or in complexity thereby. When matters are simplified by dissolving a gas, instead of a liquid or solid, and adjusting the pressure of the gas or the quantity of solvent so that the former occupies the same volume after as before dissolution, we still find that a very considerable evolution of heat occurs; with the haloid acids this is as much as 17,000 cal., and though this may be glossed over by some of the advocates of the physical theory by stating that the decomposition of the acids into their ions, which they consider occurs, evolves a very large amount of heat, no such explanation can be offered in cases where no such decomposition is imagined, and it has been proved that the dissolution of gaseous non-electrolytes both in water and in other solvents is accompanied by the evolution of as much as 5,000 to 14,000 cal. In the face of such a considerable loss of potential energy, it is impossible to maintain that the substances losing it remain unchanged, and that the dissolved substance can, in any true sense, be still gaseous and uncombined with the solvent. It is important to note that van der Waals, through a different line of reasoning, has arrived at the same conclusion as to the necessity of recognising some action evolving heat between the substance and solvent, even when the former is in the so-called dissociated condition.

Amongst the general considerations favouring the view that dissolution consists in the formation of liquid compounds, not the least important is that this gives us some intelligible reason for dissolution occurring at all, whereas if the solvent is regarded as being inert and only playing the part of so much empty space (as some of the advocates of the physical theory have maintained), we have no explanation of why dissolutions occur; the presentation of empty space to a stable solid does not make the latter fill the empty space, and even attributing dissolution to the possession of a certain 'solution pressure' by the dissolving substance would appear to amount to no more than stating that a substance dissolves because it does do so.

Special. Berthelot determined the heats of dissolution of various series of solutions of different concentrations, and concluded that his results when plotted out showed the presence of changes of curvature or inflections at certain points, indicative of the existence of hydrates in the solutions. In many cases he adduced various special considerations in support of the existence of the hydrates thus indicated, but his determinations were not sufficiently numerous or accurate, nor were his methods of examining them sufficiently precise, to lead to more than vague conclusions. Thomsen's investigations on the same subject were equally unsatisfactory; he sought to disprove the existence of any such changes of curvature by finding empirical equations to represent each series of results, but in the four cases which he thus investigated the equations deduced express but a small portion of the whole series, leaving in the remainder errors ten and a hundred times greater than the experimental error. Mendeléeff next took up the question from a different point of view. Theoretical considerations led him to conclude that solutions consisted of different hydrates according to the amount of water present, and that, if not more than two hydrates were ever present together in the same solution, there would be definite changes of curvature in the figures representing the properties of the solutions at the concentrations corresponding to these hydrates; that is, that the rate of change in the property with change of concentration would be different when the solutions consisted of the hydrates A and B from what it would be when they consisted of B and C, so that there would be a change at a concentration corresponding to the composition of B, and further, he concluded that these rates of change (first differential co-efficients) in the case of the densities would be rectilinear functions of the percentage composition between the points A and B, B and C, &c. (It should be noticed in passing that the idea which lies at the root of Mendeléeff's conception—and, to a certain extent, of Berthelot's also—is that the water in any solution is nearly entirely combined with the dissolved substance, and not merely that the solution consists of a simple hydrate mixed with excess of free water.) That the concentration-rate of change of the densities is representable within experimental error by a series of straight lines is probably true in many cases, but in the two cases on which Mendeléeff chiefly relied for proof these first differences are conspicuously curvilinear throughout. The reason of this, doubtless, is that solutions of a given concentration generally contain more than the two hydrates which he postulated. Roozeboom's work on ferric chloride, and Pickering's on sodium hydroxide, render it probable that five or six hydrates may co-exist in the same solution; at any rate, as many as four have actually been obtained from certain solutions. Pickering next attacked the subject from a purely experimental point of view. The distinctive feature of his work is the search for changes of curvature (breaks) by the application of a flexible lath to his plotted results. A lath bent by the application of two couples near its extremities forms, for all practical purposes, a curve of a very simple nature; and it has been proved that the use of such a lath is tantamount to, and leads to precisely the same conclusions as, the application of ordinary parabolas with three or four constants deduced mathematically from the experimental values; and in several respects, besides expeditiousness of application, this method is superior to the mathematical method. The mere fact that a certain figure may be represented accurately by a series of parabolas is by itself no proof that it really consists of these independent curves, any more than the existence of breaks can be disproved by finding an artificial equation which will bridge them over; the correctness of any particular form of representation can be measured only by the results to which it leads, and in this respect the discontinuous expressions would appear to be highly satisfactory. The positions of the breaks are not dependent on the taste of the draughtsman: the figures examined seem to split up naturally into certain sections only, and when drawn in these sections it was found, in some dozens of series of experiments, that the apparent error of the points agreed within 5 or 10 per cent. with the known experimental error (though in a great number of the cases the true magnitude of the latter was not as [illegible] after the drawings were made), whereas drawings of a similar character, but placing the breaks at other points, or drawings obliterating the breaks altogether, represented the error of the points to be far larger, often 10 or 100 times larger, than the known experimental error. It must be remarked that, once the magnitude of the experimental error is known with certainty, no drawing can be accepted unless it agrees closely with it, and Pickering has devised a method by which the experimental error can be accurately determined independently of any considerations other than the examination of the final results themselves; he has also devised a means of obtaining a numerical estimate of the acceptability of any drawing, by combining together the various factors which are usually taken as affording a criterion of acceptability. Again, when sections of increasing lengths are taken, and these are represented by single parabolas, or bent-lath curves, there is little or no increase in the apparent error of the points till the sections extend beyond a point where one of the supposed breaks exists, but as soon as they do so there is a large and sudden increase, indicating that some real change at the point in question exists. Moreover, it has been shown that in a case where two parabolas will represent a series of results perfectly, a single parabola will not do so, even if it contain as many constants as the two parabolas together contain. The strongest argument, however, in favour of the reality of these breaks is that the various properties of any series of solutions, although they form figures differing from each other widely in general form, are yet all thoroughly concordant as to the positions at which the breaks occur. The properties of sulphuric acid which were investigated were the densities at four temperatures and the contraction on mixing deduced from them, the heat of dissolution, the thermal expansion, the electric conductivity (Kohlrausch's values), and the thermal capacity; subsequently also the freezing-points and van der Willigen's values for the refractive indices were investigated. Perkin also found indications of two of the breaks in his determinations of the magnetic rotations, and still more recently Féry has recognised some other of the breaks in his own measurements of refractive indices. Three different properties were also examined by Pickering in the case of calcium chloride and nitrate, and were found to show a similar concordance.

That the breaks are really due to, and indicate the presence of, compounds in solution is shown by the fact that, not only in the cases above mentioned, but also in many others where other solvents besides water were used, they always occur at points which correspond within small limits with definite molecular proportions —wherever, that is to say, the proportion of substance to solvent is sufficiently simple to permit of any conclusions at all being drawn in the matter. Further evidence on this point was also afforded from a study of the freezing-points of fourteen of the alkyl amines, where, with one exception, hydrates of the very compositions indicated by breaks in the case of some of the amines were isolated in the crystalline condition in the case of the others. Finally, as a more striking, though perhaps not more cogent, argument, we [illegible] the isolation in the crystalline condition of no less than six new hydrates, the existence of which had been foreshadowed in the properties (chiefly densities) of the solutions—namely, $H_2SO_4.4H_2O$, $HBr.3H_2O$, $HBr.4H_2O$, $HCl.3H_2O$, $HNO_4.H_2O$, and $HNO_3.3H_2O$—the last three being especially conspicuous examples, for the only marked breaks which the densities showed coincided with the only hydrates which were subsequently isolated.

Two important features of the conclusions drawn from the above-mentioned work on sulphuric acid should be mentioned: firstly, the large number (18–20) of hydrates of which indications were obtained; secondly, the complex nature of hydrates in very dilute solutions. Any improbability which might be considered to attach to the former conclusion (though, in reality, no data exist on which to found any estimate of the probabilities in such a case) is removed by the fact that a still larger number of hydrates (when equal ranges of concentration are compared) have been isolated in the crystalline condition from solutions of sodium hydroxide. The complexity of the hydrates indicated extends up to compounds with hundreds and even thousands of molecules of the solvent, but, with the explanation to be mentioned below as to their possible constitution, these hydrates can scarcely be branded as improbable; at any rate, the breaks which indicate their existence appear to be precisely similar in nature to those which indicate the presence of the simpler hydrates. Pickering has investigated the freezing-points of many dilute solutions besides those of sulphuric acid, and has found that nearly all of them show indications of similar changes, and those recognised in the cases of sodium chloride and sulphuric acid have received further confirmation from a series of results made by H. Jones; a confirmation of special importance, since Jones's determinations were made with the view of disproving the existence of breaks.[1] Complex hydrates, though of a comparatively small degree of complexity, would appear to exist in regions other than those of very dilute solutions; two such were indicated in the neighbourhood of the monohydrate of sulphuric acid, and a similar one, perhaps another also, has been isolated in the case of soda. These are probably compounds of two different hydrates.

It is important to note that the changes of curvature here described need not necessarily be absolutely abrupt. On the strength of experimental evidence only, where experimental error necessarily exists, it is obviously impossible to prove or disprove the abruptness of any change, and no satisfactory mathematical theory has yet been formulated to lead to any views on the subject. It is sufficient for the purpose that *comparatively* abrupt changes exist. Nor should it be expected that these changes would necessarily be of a very marked character, for a large proportion of the factors determining the properties of solutions must be of a purely physical or even mechanical character; the densities of sulphuric acid solutions, for instance, must rise more or less gradually from 1 to 1·85, and it is only in the variations from the 'more' to the 'less' that we can expect to find evidence of intermediate compounds.

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[1] It should be noted that Jones himself asserts that his results entirely disprove Pickering's 'breaks' (v. *B.* 26, 647, 1633).—M. M. P. M.

Application of the hydrate theory to explain the properties of dilute solutions. Diversity and irregularity are some of the most marked features of the properties of concentrated solutions, and though in dilute solutions these irregularities are much less conspicuous (as, indeed, we should expect them to be when the hydrates present become excessively complex and, consequently, excessively unstable), they are still recognisable, and it is only in the most extreme dilution, where the experimental error amounts to a large fraction of the total quantities measured, that the results can be expressed within the limits of this error as an apparently regular function of the concentration. It may safely be stated that any purely physical theory which confines itself to regions of extreme dilution, and which ignores some of the most marked features of dissolution, as well as the mass of direct evidence showing the existence of compounds in solution, cannot be accepted as a complete theory; nor, on the other hand, can the hydrate theory of solutions be accepted as satisfactory unless it can be shown to be consistent with the two main characteristics of weak solutions—the apparent quasi-gaseous independence of the dissolved substance in dilute solutions, and the approximately accurate results which are obtained when calculations are based on the assumption that electrolytes in dilute solutions are dissociated into their ions. However important the service rendered to science by the gaseous and dissociation theories of solution, there are many fundamental objections which militate against their universal acceptation. They offer no satisfactory explanation of why substances dissolve at all, and still less why water alone, of all ordinary solvents, should resolve salts, &c. into their ions. These ions are represented to be atoms charged with enormous electric charges, but no explanation is given of the origin of these charges, or of the peculiarities which they are supposed to exhibit; two atoms oppositely electrified are represented as being less combined than when not charged at all; the charged atoms are represented as swimming about in the water without decomposing it, and without giving up their charges to their oppositely electrified companions, although they can part readily with them to an electrode; and to explain the thermal phenomena of solution, it has to be boldly assumed that the decomposition of molecules (elementary or composite) into charged atoms often evolves a considerable amount of heat, and consequently that the charging of an ordinary atom must be a process which evolves heat also. The only crucial experiment which has so far not been susceptible of an opposite interpretation seems to disprove any real dissociation of electrolytes. The lowering of the freezing-point of a solvent is accepted as affording a measure of the number of acting units (molecules or ions) in any substance added to it, and when, for instance, to some acetic acid a weak solution of sulphuric acid is added, the depression produced proves that the latter contains fewer acting units than the water and sulphuric acid do separately, instead of more, as would be the case if the sulphuric acid molecules had to be split up into independent ions.

In a paper in the *Berichte*, Pickering has offered an explanation of the behaviour of dilute solutions based on the hydrate theory and on the views held by him as to residual affinity. The explanation may be rendered more intelligible by representing chemical attraction, as we represent electrical attraction, to be due to 'charges' on the surfaces of the attracting matter, but inalienable from the matter, owing to a repulsive force between the atoms similar to that which produces elasticity preventing the atoms ever coming close enough together to allow of the charges combining. The charges are represented as being always self-attracting. Each atom possesses one or more unit affinity-charge according as it is a monad or a polyad: with a free atom the charge would be uniformly distributed over its surface, whereas when two atoms are combined the greater part of the charges would be drawn to those sides of the atoms facing each other; but, as in the case of electric charges, a certain amount would still be left on the further sides capable of acting on, and being acted on by, other atoms or molecules in like condition, this residue, or unbound charge, forming what appears as residual affinity. As in the case of electrical charges, the nature of the matter composing different atoms will cause different degrees of mobility in the charges on their surfaces, and hence different pairs of atoms will be held together with different degrees of firmness, and different molecules will exhibit different amounts of residual affinity. When a molecule A B, possessing a certain amount of residual affinity, is surrounded by a number of other molecules CD possessing residual affinity also, the two residual charges will react on each other and increase the amount of the charges on the external portions of the molecules, leaving a smaller amount of charge on the portions of A and B which face each other; in the same way the charge on C will be partially withdrawn from the surface facing D, and will be able to retain a smaller amount of D's charge on the portion of D which is next to it, so that D will exhibit more residual affinity than formerly, and will be able to react in a similar manner on its neighbours, C′ D′. Thus, by a process precisely analogous to electric induction, the number of molecules of C D which are acted on by, and are more or less combined with, A B may be very large, and far greater than the number which are capable of coming into its immediate vicinity. The existence of the very complex hydrates which have been recognised in dilute solutions is thus easily explicable. It is evident that a molecule when thus surrounded by, and combined with, a large number of solvent molecules will be attracted equally in every direction, and as the magnitude of the force exerted on it by each individual solvent molecule must be very small, it will be able to move easily in any direction, especially as any of the solvent molecules from which it parts during the process will have their places supplied at once by other similar molecules, of which, owing to continuous dissociation and recombination, there is an abundant supply in the liquid. Thus, into whatever new position the central molecule moves, the *status quo ante* is immediately reproduced, and, consequently, the molecule will move almost unfettered by the presence of the solvent, and will act almost as if it were in the gaseous state. We thus obtain at once an explanation of why the application of the ordinary gaseous laws to dilute solutions yields very nearly true results; we should, indeed, expect that they would not be absolutely true, for certain definite numbers of solvent molecules would be capable of a more symmetrical arrangement about the central molecule than others, and such arrangements (definite hydrates) would be more stable than others, and the tendency to form them might have an appreciable effect on the regularity of the results: small irregularities of this sort are exactly what we find in the case of those dilute solutions which have been fully examined.

It is obvious that as the quasi-gaseous freedom of the molecule is dependent on its being combined with the solvent, this freedom obtains only so long as the molecule remains within the solvent, and would not admit of the possibility of its leaving the liquid, or of exerting an external gaseous pressure; for the same reason it would be impossible for it to pass through any crevice so small as not to allow it to retain as many solvent molecules as it was combined with in the solution. This gives us an explanation of the action of semipermeable diaphragms and all the phenomena of osmotic pressure; it, moreover, removes a difficulty which must be experienced in accepting the explanation given by the supporters of the physical theory of the action of these diaphragms—why it is that the water molecules (which are admittedly combined in great part into complex aggregates) can so easily pass through interstices which are impervious to what are held to be the single free molecules and ions of the dissolved substance. Direct experiment would seem to decide conclusively in favour of the explanation of osmotic pressure given above, for, when a suitable solution in a porous pot is immersed in *either* of the substances which compose the solution, osmosis through the pot towards the solution occurs in both cases, showing that osmotic pressure is not due to the impermeability of the pot to either of the constituents of the solution, but to its impermeability to the solution as a whole.

In a case where the atoms of the dissolved molecule possessed a considerable amount of residual affinity, the action and reaction between them and the solvent molecules would, in every respect, be proportionally great, and, consequently, those portions of the whole charges which are utilised in uniting the component atoms of the dissolved substance would be reduced, and, in extreme cases, might be reduced to the lowest possible limits—that is, till the amount of affinity utilised in holding them together was equal to that utilised in attaching them to the solvent molecules, in which case there would be an equal distribution of the affinity charges over the atoms. The atoms composing a molecule in such a condition would have a great amount of freedom of motion within the molecule; being attracted equally in all directions, they would be at liberty to start to move in any direction, and their movements might attain considerable amplitude under suitable conditions as to the rate at which the forces between them varied with the distance; for to explain the apparent independence of the atoms, and therefore the abnormal osmotic pressure of a salt molecule, 'it only requires,' according to Fitzgerald, 'the space within which [the atoms] are bombarding about to be small compared with the space rate of variation of the force between [them].' The atoms of the two molecules in such a condition would obviously change partners very readily during collision, and this gives us an explanation of why such an interchange does take place when two different salts, &c., are mixed. This ready exchange, moreover, would take place continuously, and in a definite direction, under the influence of any external force, such as a charged electrode, a Grothüss' chain being formed, and we should consequently expect to find that substances in this condition—*i.e.* those which give abnormally large osmotic pressures—were electrolytes; this is so: and since, moreover, the amount of electrolysis occurring in a given time under a given force would be proportional to the number of molecules in the condition postulated, it follows that this number—and, therefore, the osmotic pressure—could be calculated, at any rate approximately, from the conductivity. In short, whatever calculations hold good on the assumption that the atoms in the molecules are absolutely independent will also hold good if they are assumed to be in the peculiar condition of combination here described—a condition which is brought about by their great tendency to combine with the solvent, and not by a tendency to part company for no assignable reason. On the present view also it is possible to understand why it is that salts and acids are generally electrolytes, and why water is the solvent which makes them electrolytes, for both salts and water are composed of elements which have a strong attraction for elements of an opposite character, and in such a case the residual affinity of both the elements (basylous and chlorous) constituting the salt would be acted on by that of the two opposite elements constituting the water, and we would get an amount of mutual reaction which would be impossible in the case of other substances.

The memoirs referred to in this article are: Berthelot, *Méc. Chim.* 1, 394; 2, 142; Thomsen, *Thermochem. Untersuch.* 3, 1–216; Mendeléeff, *The Investigation of Aqueous Solutions according to their Specific Gravities* (1887); also *The Principles of Chemistry*; and *C. J.* 52, 779; Roozeboom, *Z. P. C.* 10, 477; Féry, *C. R.* 115, 1309; Van der Waals, *Z. P. C.* 8, 214; Perkin, *C. J.* 63, 70; Jones, *Z. P. C.* 11, 112, 536; 12, 623; Pickering, *C. J.* 53, 865; 55, 14; 57, 16, 331; 63, 99, 141, 436, 890, 998; *P. M.* [5] 29, 427; 30, 400; 32, 20, 90, 478; 33, 132, 436; 34, 35; 35, 127; 36, 111; *Z. P. C.* 6, 10; *B.* 24, 277, 1579, 3317, 3328, 3629; 25, 1099, 1314, 1589, 1854, 2011, 2518, 3434; 26, 277, 1221, 1977, 2307, 2766; 27, 30, 67; *C. N.* 57, 116; 63, 290, 305; 64, 1, 311. S. U. P.

SONNENSCHEIN'S REAGENT. Prepared by adding phosphoric acid to a warm solution of ammonium molybdate in nitric acid, boiling the pp. with aqua regia to destroy NH_3, evaporating to dryness, and dissolving in 10 p.c. nitric acid (*A.* 104, 45). This reagent gives yellow pps. with alkaloids.

SOPHORIN. S. ·009 in the cold; ·5 at 100°. S. (alcohol) ·8 in the cold; 7 at 78°. Obtained from Chinese yellow berries, the undeveloped flower buds of *Sophora japonica* (Stein, *J. pr.* 58, 899; 85, 351; 88, 280; Spiess a. Sostmann, *J.* 1865, 587; Förster, *B.* 15, 216). Decomposed by boiling dilute H_2SO_4 into isodulcite and yellow sophoretin, which resembles quercetin.

SOPHORINE. An alkaloid obtained from the pods of *Sophora speciosa* (Wood, *Ph.* [3] 8, 1047). Liquid, forming a crystalline hydrochloride, which gives a deep-red colour with $FeCl_3$. Poisonous. A poisonous alkaloid may also be obtained from the seeds of *Sophora tomentosa* (Greshoff, *B.* 23, 3539).

SORBIC ACID $C_6H_8O_2$ *i.e.* $CH_3.CH:CH.CH:CH.CO_2H$. Mol. w. 112. [134·5°]. (228°). H.C. 730,000 (Ossipoff, *J. R.* 20, 650). *Heat of neutralisation*: Gal a. Werner, *Bl.* [2] 46, 802). Occurs in the juice of unripe mountain-ash berries (Hofmann, *C. J.* 12, 43; *A.* 110, 129). The juice is partially neutralised with milk of lime, decanted from acid calcium malate, and distilled after addition of H_2SO_4. Needles (from dilute alcohol), v. sol. alcohol and ether, m. sol. hot water, volatile with steam. Partially decomposed on distillation (Barringer a. Fittig, *A.* 161, 307). Has no odour. Br in CS_2 forms tetra-bromo-hexoic acid [179°] and di-bromo-hexenoic acid [90°–95°]. Fuming HBr forms di-bromo-hexoic acid [68°] (Stahl, *B.* 9, 120). Very dilute alkaline $KMnO_4$ at 4° gives aldehyde, racemic acid, oxalic acid, and CO_2 (Doebner, *B.* 23, 2376). Sodium-amalgam forms hydrosorbic acid.

Salts.—BaA'_2. — CaA'_2: silvery scales. — AgA': white crystalline pp.

Ethyl ether EtA'. (195·5°). Liquid.

Chloride C_6H_7OCl. Converted by NH_3 and aniline into crystalline $C_6H_7O.NH_2$ and $C_6H_7O.NHPh$ respectively.

Hydrosorbic acid *v.* HEXENOIC ACID.

Isosorbic acid *v.* HEXINOIC ACID.

Reference.—OXY-SORBIC ACID.

SORBINOSE $C_6H_{12}O_6$ *i.e.* $CH_2(OH).(CH.OH)_3.CO.CH_2OH$ (?). S.G. $^{\underline{15}}$ 1·654. $[\alpha]_j = -47°$ at 7°. S. 200. An unfermentable sugar obtained from the fermented juice of mountain-ash berries (Pelouze, *A. Ch.* [3] 35, 292; Byschl, *J.* 1854, 664; Delffs, *C. N.* 24, 75). The juice is left to stand for a year, and then filtered and evaporated. Trimetric crystals, as sweet as cane sugar. Lævorotatory. V. e. sol. water, sl. sol. hot alcohol. Forms with NaCl a compound crystallising in cubes. Its aqueous solution dissolves CaO, PbO, and $Cu(OH)_2$. Not attacked by Br. Yields tri-oxy-glutaric acid on oxidation by HNO_3 (Kiliani a. Scheibler, *B.* 21, 3276), but no mucic or saccharic acid (Tollens, *A.* 249, 222). HIAq and P yield hexyl iodide. Reduced by sodium-amalgam to sorbite (Vincent a. Delachanal, *C. R.* 111, 52). Not turned brown by hot alkalis. Reduces Fehling's solution. Bromine water yields glycollic acid (Hlasiwetz a. Habermann, *A.* 155, 120). On heating sorbinose (1 pt.) on the water-bath with a solution of phenyl-hydrazine hydrochloride (2 pts.) and NaOAc (3 pts.) in water (10 pts.) it yields the osazone $C_{18}H_{22}N_4O_4$ [164°], which crystallises in yellow needles, sl. sol. hot water, v. sol. alcohol, v. sl. sol. ether (Fischer, *B.* 17, 582; 20, 827).

SORBITANNIC ACID. Obtained from the berries of *Sorbus aucuparia* (Vincent a. Delachanal, *Bl.* [2] 47, 492). Gives a yellow colour with alkalis; reduces silver salts in the cold; is not ppd. by alum or gelatin. Potash-fusion forms protocoatechuic acid and phloroglucin.

SORBITE $C_6H_{14}O_6$. Mol. w. 182. [111°]. $[\alpha]_D = -1·73°$. Occurs in mountain-ash berries (Boussingault, *A. Ch.* [4] 26, 376); in plums, cherries, and the fruits of nearly all the *Rosaceæ* (Vincent a. Delachanal, *C. R.* 108, 147; 109, 678; 111, 52). Formed on reduction of sorbin and of *l*-gulose (Fischer a. Stahel, *B.* 24, 2144). Formed also, as well as mannite, by reducing glucose (dextrose) with sodium-amalgam in the cold (E. Fischer, *B.* 23, 3684; Meunier, *C. R.* 111, 49). Pearly crystals (containing ½aq). Melts at 75° when hydrated. V. sol. water and hot alcohol. Neither ferments with yeast nor reduces Fehling's solution. Lævorotatory, becomes dextrorotatory on addition of sodium borate (Vincent a. Delachanal, *C. R.* 108, 354). HIAq yields (β)-hexyl iodide (Hitzemann a. Tollens, *B.* 22, 1048). Boiling with Ac_2O and some $ZnCl_2$ forms a hexa-acetyl derivative. Benzoic aldehyde and a little hydrogen chloride give $C_6H_{13}O_5(C_7H_5O)$, crystallising in rectangular prisms [c. 175°]; if more acid is present the insoluble compound $C_6H_{12}O_1(C_7H_5O)_2$ [162°] is formed (Meunier, *C. R.* 108, 148; 110, 577; *A. Ch.* [6] 22, 423). In like manner valeric aldehyde and HClAq form, on shaking, $C_6H_{12}O_4(C_5H_9O)_2$, crystallising in prisms, sol. alcohol and ether. Sorbite may be oxidised to glucose by heating in sealed tubes with bromine-water at 60° and treating the product with Pb and PbO (Vincent a. Delachanal, *C. R.* 111, 53).

SORDIDIN $C_{16}H_{18}O_7$. [180°]. A neutral crystallisable substance occurring in the lichen *Zeora sordida* (Paterno, *J.* 1875, 863). Insol. water, v. sol. alcohol and ether.

SPARTEÏNE $C_{15}H_{26}N_2$. Mol. w. 234. (311° at 723 mm.) (Bamberger, *A.* 235, 368). $[\alpha]_D = -14·6°$ at 26° (Bernheimer, *G.* 13, 451). Occurs in the common broom, *Spartium scoparium* (Stenhouse, *A.* 78, 1; Mills, *C. J.* 15, 1). Prepared by extracting the plant with water acidulated with H_2SO_4, evaporating, and distilling with NaOHAq. The distillate is acidified by HCl; evaporated to dryness; and the residue distilled with solid KOH. The base is finally rectified over sodium. Heavy oil, with peculiar odour and bitter taste, sol. alcohol and ether, insol. benzene and ligroïn (Houdé, *Fr.* 25, 568). Lævorotatory. Turns brown in air. Alkaline in reaction. Narcotic poison.

Reactions.—1. Yields (γ)-methyl-pyridine on *distillation with lime* (Ahrens, *B.* 21, 826).—2 HIAq at 200° yields MeI and $C_{14}H_{24}N_2$ (276°), which forms a platinochloride [230°], an aurochloride [157°], and a nitrosamine.—3. On passing the vapour through a red-hot tube it gives pyridine, (γ)-methyl-pyridine, C_2H_4, propylene, NH_3, HCy, and other bodies.—4. H_2O_2 forms a base $C_{15}H_{26}N_2O_2$.

Salts.—The hydrochloride is amorphous.—$B''H_2PtCl_6$ 2aq. Decomposed by boiling water (Oechsner De Coninck, *Bl.* [2] 45, 181).—$B''2HAuCl_4$. Decomposed by boiling water.—$B''HI$: tables, m. sol. cold water.—$B''H_2ZnI_4$.—$B''I_2$: green needles (from alcohol), insol. cold water.—$B''H_2SO_4$: prisms.—$B''2C_6H_3N_3O_7$.

Methylo-iodide $B''MeI$. Trimetric plates; *a*:*b*:*c* = ·899:1:1·601.

Ethylo-iodide $B''EtI$. Prisms (from water), v. e. sol. water and alcohol, insol. NaOHAq.—$B''EtIHI$. Got by heating sparteïne with EtI and alcohol at 100°. Prisms (from cold alcohol). Not coloured by alcoholic potash (De Coninck, *C. R.* 104, 513). Yields $B''EtClHClPtCl_4$.

Dihydride $C_{15}H_{28}N_2$. (283°). Got by reducing sparteïne with tin and HCl (Ahrens, *B.* 20, 2219). Colourless oil.—$B''HCl$: very deliquescent needles.—$B''H_2PtCl_6$. Blackens at 239°.—$B''HAuCl_4$. Blackens at 130°.—Picrate. [125°]. Needles, decomposing at 215°.—$B''HgCl_2$.

Oxysparteïne $C_{15}H_{24}N_2O$. [84°]. Formed by oxidising sparteïne, and extracting the solution with chloroform (Ahrens, *B.* 24, 1095; 25, 3607). White hygroscopic needles, v. sol. water, alcohol, and ether. Its solution is strongly alkaline. Reduces hot Fehling's solution.—$B''H_2Cl_2$ 4aq. Needles, v. sol. water.—$B'HCl$aq.—$B''_2H_2PtCl_6$4aq. Decomposed at 209°.—$B''H_2PtCl_6$ aq. Needles: decomposed at 223°.—$B''HAuCl_4$. — Mercury double chloride [58°]. — $B'HBr$ 2½aq. — $B'HBr$ 3½aq.—$B'HI$ aq.—$B'HNO_3$ aq.—Picrate [178°].

Methyl-iodide of oxysparteïne $B'MeI$. [193°].—$B'MeCl$.—$B'MeClHClPtCl_4$ aq. [229°]. $POCl_3$ at 150° converts oxysparteïne into an oily base $C_{15}H_{22}N_2$ which yields $C_{15}H_{22}N_22HAuCl_4$ [161°].

Di-oxy-sparteïne $C_{15}H_{26}N_2O_2$. [129°]. Formed by dissolving sparteïne in aqueous H_2O_2 (Ahrens, *B.* 20, 2220; 25, 3609). Prisms, v. e. sol. water and alcohol, sl. sol. benzene, insol. ether. Alkaline in reaction.—$B''H_2PtCl_6$. Blackens about 235°.—$B''HAuCl_4$. [c. 146°]. Needles.—$B''HI$. [137°].—$B'HBr$. [147°].—$B'H_2HgCl_4$. [193°].

Tri-oxy-sparteïne $C_{15}H_{24}N_2O_3$. Formed by action of H_2O_2 on oxy-sparteïne. Crystalline, v. sol. water and alcohol.—$B'_2H_2PtCl_6$ 3½aq.—$B'HAuCl_4$. [137°].

SPECIFIC GRAVITY *v.* DENSITIES, RELATIVE, vol. ii. p. 370.

SPECIFIC VOLUMES. The molecular weights of substances when divided by their respective specific gravities, taken under comparable conditions, furnish values which have been termed *atomic*, *molecular*, or *specific volumes*. The specific volume is, therefore, the space occupied by aggregates of atoms, including the interstitial spaces, whose weights are proportional to the molecular weights of the substances.

Objection has been raised against the term 'specific volume' on the ground that, as specific gravity is the weight of unit volume, specific volume should by analogy be the volume of unit-weight; hence of late years the term 'molecular volume' has been preferred. The term 'specific volume' has, however, acquired by definition and use a distinctive meaning. The adoption of the term 'molecular volume' is almost certain to be attended with confusion, owing to the different sense in which it is frequently employed by physicists and chemists. The specific gravity of solids and liquids, referred to water at 4°, is the weight in grams of the unit volume. If, then, the molecular weight be expressed in grams, we may define the specific volume of a solid or liquid substance as the number of cubic centimetres occupied by this mass.

The specific gravity of a gas is usually referred to hydrogen as unity. It follows, then, from the law of Avogadro that all gases should have the same specific volume. There are a few exceptions to the universal truth of this statement arising from so-called abnormal vapour densities, but the specific volumes of the exceptional substances stand in the same simple relation to the normal value that their molecular weights stand to what analogy would indicate as the normal molecular weight.

Inasmuch as the specific gravity of a substance is affected to a greater or less extent by heat, it is obviously necessary to determine this constant under comparable conditions of temperature—that is, at temperatures at which heat may be supposed to exercise the same effect on the substance. In the case of liquids Schröder suggested that temperatures at which the vapour pressures of the various liquids are the same—as, for example, their boiling-points under a standard atmosphere—should be regarded as comparable.

In the case of solids the effect of temperature is of course much less marked, and hence the specific gravity of these substances is usually taken at the ordinary temperature of the air.

Specific volumes of solids.

The first attempt to trace relationships between the chemical nature of substances and their equivalent volumes appears to have been made by Le Royer and Dumas in 1821 (*J. Ph.* 92, 408). They sought to determine the equivalent volumes of the elements by dividing their atomic weights by their respective specific gravities, the values so obtained being termed by them *atomic volumes*. They were led to infer that these volumes formed an arithmetical series—a supposition which was hardly warranted by the facts then known, and which has since been completely disproved by more accurate observations. This idea of combination among solids in definite volumetric proportion was further developed in 1824 by W. Herapath (*P. M.*, Nov. 1824), who sought to prove that the volume of the oxygen in a metallic oxide bears a simple ratio to that of the metal with which it is combined. Almost simultaneously the same problem was attacked by Karsten (*S.* 65, 394), and subsequently, in 1830, by Boullay, but with no definite general result.

Ammermüller, however, in 1840, concluded (*P.* 49, 341; 50, 406) that the specific volumes of compounds containing the same elements in different proportions are either identical or stand to one another in rational proportions. Persoz in his 'Introduction to the Study of Molecular Chemistry,' recognised that equivalent amounts of many bodies of analogous composition occupy the same volume, and he inferred that the specific volumes of all substances are multiples of one and the same number, a conclusion also drawn by Le Royer and Dumas, but which is not supported by facts.

Kopp (*P.* 47, 133), in 1839, first attempted to educe general formulæ from which he was able to calculate the specific gravities of certain oxides and haloid salts, with results which showed, in general, a fair agreement with the observed values. In the same manner he calculated formulæ for other anhydrous salts—such as sulphates, carbonates, and nitrates—on the supposition that such salts consist of combinations of oxides and acids, or that they are made up of a radicle, acid *plus* oxygen. By means of these formulæ he inferred that it is possible to draw conclusions concerning the specific gravity of metals for which this constant is unknown. Kopp, in this memoir, used the term *specific volume* for the first time, and he defined it as the molecular weight (*Mischungsgewicht*) of a substance divided by its specific gravity. He found that the specific volumes of similarly reactive elements—as, for example, chlorine, bromine, and iodine; tungsten, molybdenum, chromium, iron, manganese, nickel, cobalt, &c.—are equal or nearly equal. In other cases—as silver and gold, potassium and sodium—the specific volumes stand to each other in simple relations. Elements which, like barium and strontium, form isomorphous compounds have the same specific volume. Strictly speaking, this law can hold only for those substances which are perperfectly isomorphous. The more nearly the crystalline forms of isomorphous substances are identical, the more nearly will their specific volumes be the same. This is made evident by a comparison of the axial ratios of *witherite*, *strontianite*, *arragonite*, and *cerussite*; and also of the carbonates of zinc and magnesium (*mesitene*), the carbonates of iron and manganese, and dolomite and calc-spar. It is seen that there is a direct comparison in the case of the latter compounds between the length of the principal axis a and the specific volume V, such that $a^{4{\cdot}789} = 0{\cdot}0127671V$, from which it is possible, of course, to deduce the specific gravity of the substance from its crystalline form. It also follows that an increase of specific volume is occasioned by an increase in the length of the axis a. If we heat one of these crystals the density decreases; the axis a must therefore increase in length, while the angle R becomes less obtuse. This fact, indeed, was discovered by Mitscherlich, who found that the specific gravity of calc-spar decreased in the ratio of 1 to $\frac{1}{1{\cdot}001961}$ when calc-spar was heated through 100°. The specific gravity of calc-spar is 2·7220, when $a = 0{\cdot}8544$ and $R = 105° 5'$. By heating calc-spar through 100°, the specific gravity becomes 2·7167, or the specific volume changes from 36·73 to 36·80. If we determine the length of the axis a by means of the above formula, we find it to be 0·85672, corresponding to an angle R of 104° 57′, or a difference of 8′, which closely agrees with that actually observed by Mitscherlich (*P. M.* [3] 18, 255). Schröder (*P.* 1840. 553), starting from the observation of Ammermüller, that equal volumes of the two oxides of copper contain the same amounts of copper and multiple amounts of oxygen, assumed that the volume of the copper, as of the oxygen, is equal in the two substances, but that the amount of the oxygen in the cuprous oxide stands to that in the cupric oxide as 1 to 2. Hence Schröder drew the general conclusion that the same element can have different specific volumes in different compounds, but that the several values for the specific volumes stand in simple relations to each other. He saw in this hypothesis not only an explanation of the condensation which accompanies chemical union, but also a rational basis for the belief that the specific volume of a compound is equal to the sum of the specific volumes of its components.

Schröder found that if in a series of analogous bodies, AO, BO, CO, the specific volumes of which are known, we subtract from these values the primitive atomic volumes of A, B, and C respectively, we obtain a constant remainder. This he found to be the case with the oxides of lead, cadmium, and zinc, and hence he inferred that the metal in these oxides retains its primitive atomic volume. Kopp assumed that this is equally true of the salts of the heavy metals, but with the salts of the metals of the alkalis and alkaline earths this is impossible, as the specific volumes of the salts are, as a rule, smaller than the primitive atomic volumes of the component metals. He had consequently to assume for these metals a special atomic volume, which however, remains the same in all the salts. He determined these values as follows: Suppose $M + R$ to be a compound of a heavy metal, and $m + R$ the analogous compound of a light one; suppose A to be the known specific volume of $M + R$, and a that of $m + R$, B the primitive atomic volume of M, and b that of m.

$$\text{Then, } M + R = A,$$
$$\text{and } \quad M = B.$$

Therefore the atomic volume with which R is contained in the compound is $A - B$, say x.

It is assumed that R retains its value in $m + R$,

$$\text{and since } m + R = a,$$
$$\text{and } \quad R = x;$$

therefore b, *i.e.* the atomic volume of $m = a - x$.

Kopp also showed that the densities of the hydrated oxides, and of a number of hydrated salts, may be calculated with considerable accuracy by assuming certain definite values for water in a state of combination. It ought to be stated, however, in this connexion, that subsequent researches have indicated that Kopp's conclusions respecting the specific volume of water of crystallisation must be slightly modified. Schiff, many years ago, showed that the members of certain classes of hydrated salts have practically the same specific volume. Thus, all the alums have a specific volume of about 277; double sulphates of the form $M_2M''(SO_4)_2.6H_2O$ have a common volume of 207; and all the vitriols—that is, salts of the form $M''SO_4.7H_2O$—whether isomorphous or not, have the specific volume 146.

Thorpe a. Watts (*C. J.* 37, 102, [1880]) have shown that the volumes occupied by the several molecules of water vary with the degree of hydration of the salt. In the case of the so-called magnesian sulphates, the first molecule of water, the constitutional water, or 'water of halhydration' of Graham, occupies considerably less bulk than the remaining molecules; its mean relative value is 10·7. Each additional molecule appears to occupy a gradually increasing volume. The difference between the specific volumes of the monohydrate and dihydrate is 18·8; between the volumes of the dihydrate and trihydrate the difference is 14·5; between the trihydrate and the tetrahydrate it is 15·4; and between the hexhydrate and heptahydrate it is 16·2. These observations are so far in harmony with Kopp's general conclusions that in the compounds containing only a small number of water molecules (1 to 3) the specific volume of the water is 12·4; in others containing a larger number of molecules of water (2 to 7) it is 13·4; whereas, in a third class, containing the largest number of molecules of water (from 3 to 10), its mean value is 15·3.

Specific volumes of liquids.

Methods. The specific gravity of the liquid at its boiling-point may be determined either directly or indirectly. Ramsay (*C. J.* 35, 463 [1879]) devised a simple method by which the weight of a known volume of liquid at its boiling-point may be directly ascertained with approximate accuracy. The vessel containing the liquid consists of a thin glass lemon-shaped bulb of about 10 c.c. capacity. At the upper end of the bulb is a capillary tube, bent into the form of a hook; the lower end is provided with a similar hook of solid glass. The capacity of the bulb is ascertained by weighing it full of water at a known temperature. The bulb is filled with the liquid to be examined, in the usual way, by warming and dipping the capillary neck of the bulb beneath the surface of the liquid. It is not necessary to fill the bulb completely; two or three c.c. of the same liquid are then introduced into the wide tube, and the bulb is suspended within it by thin platinum wire attached to a piece of glass rod passing through a hole in the cork. The wide tube is then heated until the liquid within it boils violently, and it is kept in ebullition so long as liquid drops from the end of the capillary neck of the bulb. The lamp is now removed, and the whole allowed to cool. When cold the bulb is dried and weighed. The specific gravity of the liquid is given by the formula

$$\text{Sp. gr.} = \frac{W'}{1 + (0{\cdot}00015 \times TW)}$$

in which W′ is the weight of the liquid; W, that of the water filling the bulb at 0°; and T the temperature at which the liquid boils; 0·00015 is an empirically-determined co-efficient required in order to make the volume correspond with the real volume at T.

A somewhat similar method of determining the specific gravity of a liquid at its boiling-point is described by R. Schiff (*A.* 220, 78). The liquid is introduced into a flask of about 7 or 8 c.c. capacity, provided with a long narrow neck on which is a graduated scale. The capacity of the flask up to the zero point is accurately determined by weighing with mercury, and the value of the scale divisions in fractions of a c.c. is also carefully estimated. The flask is then suspended in the boiling tube; a few c.c. of the liquid under investigation are placed in this tube and heated to boiling. After a few minutes the position of the liquid in the graduated neck is noted, and the flask is withdrawn, wiped, and weighed. The specific gravity at the boiling-point compared with water at 4° is given by the equation

$$D_t = \frac{P}{V_t[1 + K(t-4)]}$$

in which P = corrected weight of the liquid in the flask,

and V_t = the apparent volume of the liquid at t°,

K = the co-efficient of expansion of the glass.

It will be noticed that Schiff assumes that the liquid in the flask actually acquires the temperature of the vapour by which the flask is surrounded. Lothar Meyer (*v.* Neubeck, *Z. P. C.* 1, 652) has slightly modified Ramsay's apparatus. The bulb is best made of Jena glass, and has the capacity of about 2·5 c.c., and its weight, capacity, and thermal expansion are accurately known. It is filled with the liquid, and is suspended by means of a bent platinised-nickel wire within the flask, the neck of which can be closed by a cork. The flask contains a few c.c. of the liquid under investigation, which, when heated, may if necessary be caused to boil at any desired temperature below the ordinary boiling-point by connecting a side tube with a condenser, pressure-regulator, and fall-pump. As soon as the liquid within the bulb has acquired the temperature of the boiling liquid, and no further expansion occurs, the source of heat is removed and the bulb is weighed when cold.

The specific gravity of a liquid at its boiling-point is, however, most accurately ascertained indirectly, although this method demands far more time and apparatus, and a greater number of experimental operations, than the direct method. The method consists in accurately determining (1) the boiling-point of the liquid; (2) the specific gravity of the liquid at some convenient temperature—best at 0°; and (3) the rate of thermal expansion of the liquid from 0° up to the neighbourhood of its boiling-point. From these data the specific gravity of the liquid at the boiling-point can be readily calculated.

1. *Determination of the boiling-point.* This is best made in an apparatus so arranged that the inner tube, containing the thermometer, is surrounded by a jacket of vapour from the boiling liquid. The boiling liquid should contain a few scraps of platinum foil or a spiral of platinum wire; or, what is even better, a few short lengths of fine capillary tubing. If the amount of the liquid is very small the bulb of the thermometer should be surrounded with a little fibrous asbestos, as suggested by Ramsay a. Young (*C. J.* 47, 42). The thermometer reading must, if necessary, be corrected for the emergent column, either by the tables of Rimbach (*B.* 22, 3072) or by that of Thorpe (*C. J.* 37, 159), and should be reduced to normal pressure by the method of Crafts (*B.* 20, 709). The correction to standard atmosphere may, however, be ascertained with approximate accuracy by the formula

$$\theta = (p - 760)\,\frac{273 + t}{8200},\ \text{or}\ \theta = (p - 760)\,\frac{273 + t}{10000},$$

in which θ is the correction, t the observed boiling-point, and p the barometric pressure reduced and corrected.

The first correction is applicable to the greater number of liquids, the second to water and the lower alcohols (Ramsay a. Young, *P. M.* 1885. 515).

2. *Determination of specific gravity.* This is most accurately effected, at least for substances which are liquid at ordinary temperatures, by Perkin's modification of the Sprengel apparatus. For liquids which are alterable on exposure to air a bottle with a graduated stem is most convenient. The bottle should be previously filled with dry nitrogen, and a special apparatus, analogous to that used by Thorpe (*l.c.*) must be employed to transfer the liquid to the bottle. A form of bottle for very viscid liquids has been described by Brühl.

3. *Determination of thermal expansion.* Of the various modes of ascertaining the thermal expansion of a liquid the so-called dilatometrical method is, on the whole, the most convenient. It consists in inclosing the liquid in a vessel of known capacity, shaped like a thermometer, and provided with a graduated and accurately calibrated stem. The instrument is placed in a bath of suitable liquid, the temperature of which can be raised to the desired point, as ascertained by a thermometer; and the height of the liquid in the stem of the dilatometer, and hence its apparent volume at the temperature of observation is noted. A series of such observations at various temperatures up to the neighbourhood of the boiling-point is thus made, from which an expression, say of the form $V_t = a + bt + ct^2 + dt^3 \ldots$, may be calculated. This expression must now be corrected for the expansion of the glass of the dilatometer (obtained by observations with mercury in the usual manner), and from the corrected expression the volume, and hence the specific gravity, at the boiling-point of the liquid may be deduced.

For details of the mode of carrying out these observations *v.* Kopp (*A.* 96, 1 *et seq.*); Thorpe (*C. J.* 37, 141).

Thorpe (*C. J.* 63, 262 [1893]) has devised a modification of the ordinary dilatometrical method, which permits the thermal expansion of a liquid to be determined with much greater ease and rapidity than has hitherto been possible. It obviates the use of large baths, and, by reducing the size of the dilatometers to the smallest limit consistent with the proper degree of accuracy, as determined by the error of a thermometer reading, it avoids the necessity for long stems and the consequent correction for the cooled 'emergent columns.'

Results.—The first accurate determinations of the various physical constants needed to ascertain the specific volumes of liquid substances were published by Kopp in 1855 (*A.* 96 [1855] 1-36, 153-185, 303-335; *A.* 100 [1856] 19-38; *v.* also *P.* 72 [1847] 1-62, 176, 223-293). Kopp concluded, from the results of a long series of observations, that:—

(1) The selection of the temperature of equal vapour-pressures as a basis of comparison seemed to be warranted by the fact that regularities are thereby made evident which otherwise are not apparent.

(2) Differences of specific volume are proportional to differences in chemical composition.

(3) Isomeric liquids of the same chemical type have equal specific volumes.

(4) The substitution of hydrogen for an equivalent amount of oxygen only slightly affects the specific volume.

(5) One atom of carbon can replace two atoms of hydrogen without altering the specific volume of the compounds.

Kopp further found that the specific volume of a liquid compound was conditioned, not only by the composition, but also by the constitution of the compound. Thus the relative position of an oxygen atom in a molecule affects its specific volume; carbonylic oxygen and hydroxylic oxygen have two very different values. Sulphur, in like manner, would appear to have two specific volumes, depending on its position or mode of combination in a molecule.

Definite values for the specific volumes of carbon, hydrogen, and oxygen were obtained from the following considerations. An increment of CH_2 corresponds to an increase of specific volume of 22. Since C and H_2 occupy the same volume, we have $C = 11$ and $H = 5{\cdot}5$. The replacement of H_2 by carbonylic O is attended by a slight increase in the specific volume. Kopp found that the most probable value for O in this form of combination was 12·2. For hydroxylic oxygen it is 7·8; obtained by subtracting the value for H_2 (11) from the specific volume of water, 18·8. Hence the specific volume of a compound $C_aH_bO_cO'_d$, where O is carbonylic oxygen and O′ is hydroxylic oxygen, may be expressed by the formula

$$V = 11{\cdot}0a + 5{\cdot}5b + 12{\cdot}2c + 7{\cdot}8d.$$

Determinate values for the specific volumes of the halogens—and, with less precision, for phosphorus, arsenic, and antimony, for silicon, titanium, and tin—were also obtained by Kopp. As regards nitrogen it was found that in the amines $N = 2{\cdot}3$. The group $CN = 28$; the group $NO_2 = 33$. If, then, carbon and oxygen preserved their ordinary values in these radicles N must possess at least three different values depending on the mode of combination. There is, however, no evidence to disprove the supposition that the values for the carbon and oxygen atoms are not equally affected in these groups. This, indeed, suggests the possibility that compound radicles like CO, HO, NO_2, CN, &c. may possess definite specific volumes which are not necessarily the sum of the specific volumes of the component atoms as ordinarily ascertained.

H. L. Buff (*A. Suppl.* 4, 129) sought to show that the specific volume of carbon, like that of oxygen and sulphur, is affected by its mode of combination—or, in other words, that carbon in unsaturated compounds has a greater specific volume than in saturated bodies—from which he surmised that the specific volume of an element is in general determined by its particular atomic value. Thorpe (*C. J.* 37, 392) found that isomeric liquids have not invariably the same specific volumes. There is a well-marked difference, for example, between ethylene and ethidene chlorides; indeed, ethylene compounds in general appear to have smaller volumes than those calculated by Kopp's values. Städel has shown that in the series of chlorinated and brominated ethanes and ethylenes, the isomeride of higher boiling-point, *i.e.* the ethylene derivative, has invariably the lower specific volume.

Since these compounds are all saturated, and the only variable constituent is a monovalent element (Cl or Br), it would appear probable that the specific volume of the halogen is also variable. Isomeric hydrocarbons manifest similar differences, whence it is obvious that either one or both of the elements must have a slightly variable volume, depending on grouping or mode of combination; it may be that the iso- group, like the groups carbonyl, hydroxyl, nitryl, &c., has a special volume, which is not necessarily the sum of the volumes of the component atoms as deduced from Kopp's values. Kopp himself found that the volumes of isomerides were in a number of cases only approximately equal, and in others quite unequal. The term 'chemical type,' used in the sense in which Gerhardt employed it, is not sufficiently distinctive to denote the differences, say, between the normal and iso- compounds, or between aniline and the picolines, and it is questionable whether Kopp would have considered such cases as coming within his rule.

The observed specific volumes of the aromatic compounds are frequently lower than the calculated values. Indeed, our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene, and the volumes of the derivatives which contain the benzene grouping, would probably be different from the values deduced from observations made for the most part on compounds of totally different constitution. Kopp (*A. Suppl.* 5, 303 [1867]) showed from Louguinine's observations that while benzene has an abnormally low specific volume, its homologues show the constant increase of 22 for an increment of CH_2, which is what might be anticipated, since these homologues are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group. Jungfleisch's observations on the specific volumes of the chlorine substitution products of benzene also seem to show that the positions of the chlorine atoms affect, in a very marked manner, the specific volume of the product (*C. R.* 64, 911).

Further observation has shown that Kopp's conclusion that liquid elements and radicles have the same volume in combination as in the free state is well founded. Thus the observed volume of $NO_2 = 32·0$, calculated $= 31·5$; observed volume of $Br = 53·6$, calculated $= 53·4$; observed volume of $CN = 28·9$, calculated $= 28·9$. The observed specific volume of Cl from Knietsch's determinations of the specific gravity of liquid chlorine is 22·8; the mean calculated value is 22·7. Kopp surmised that members of the same chemical family would be found to have the same specific volume; observation shows, however, that the specific volumes gradually increase with the increase of atomic mass (Thorpe, *l.c.*).

Schiff (*A.* 220, 71 [1883]) has concluded that while it is generally true that isomeric compounds have slightly different specific volumes, it is almost invariably the case that the substance possessing the higher boiling-point has also the higher specific volume (compare Städel). In the case of the metameric esters of the fatty acids, it is found that, as a rule, the specific volumes increase with the diminution of the number of carbon atoms in the acidic radicle and with the increase of the carbon atoms in the alcoholic radicle. At the same time, it would appear that the differences between the observed and calculated values are mainly due to the alcoholic radicle, the acidic radicle apparently having but slight influence. This is in conformity with Lossen's observations, that while the ethers and acids give experimental values which are almost in exact accordance with Kopp's values, the aldehydes and alcohols show wider variations, methyl alcohol giving too great an observed value, while the others give smaller and smaller values as the amount of carbon increases. It is, however, noteworthy that the differences between the aldehydes and derived alcohols remain almost constant, which is not the case with the aldehydes and acids, where the difference appears to increase with the molecular weight. Hence the differences between the homologous aldehydes are very nearly equal to those between the corresponding homologous alcohols (Lossen). The mode in which carbon is combined in an organic compound has, according to Schiff, a distinct influence on its specific volume; like Buff, he finds that a doubly linked carbon atom occupies a smaller volume than when singly linked. It is, however, very doubtful whether the facts at present known are sufficient to establish this conclusion.

There is, however, good reason to believe that what we call 'specific volume' is not a purely additive property. The specific volumes of substances are, in all probability, affected by many more conditions than those we have hitherto taken cognisance of. The value $CH_2 = 22$ has no other significance than as expressing the average increment in volume in successive members of a homologous series. Indeed, as the physical data increase it becomes doubtful whether even this mean value is correct. It would seem that the value augments as the series is ascended. The relation $C = 2H$ no longer applies to carbon compounds in general. What is true of carbon and hydrogen is equally true of oxygen, whether as carbonylic or as hydroxylic oxygen. No definite or uniform values can be assigned to oxygen such that the specific volume of a liquid compound containing this element can be accurately calculated. The values given by Kopp and others are simply mean values, but the actual volumes are affected by conditions of which, as yet, we have no very precise knowledge and which we have no certain means of measuring. The values for the other elements are, of course, affected by these considerations. Thus the specific volume of chlorine is obtained on the assumption that the values for carbon and hydrogen are constant.

Lossen (*A.* 254, 42) has devised formulæ which take note, or express the measure, of the influences which affect the uniformity in the values of specific volumes of organic compounds. These formulæ can only be considered as first approximations, but their value will be evident from the fact that they serve to reproduce the observed values with a greater approach to accuracy than has hitherto been possible. Out of the 407 compounds which furnished the experimental material on which these formulæ are based, the observed molecular volumes of 352 differ by less than 2 p.c. from the calculated volumes. Comparatively few of these differences are to be ascribed to experimental errors. In the main they are caused by influences of structure and composition which as yet we have no certain means of measuring, such as the effect of substituted chlorine, or the special effect of iso- grouping, or of the ortho-, meta-, or para- position, &c.

According to Lossen, the specific volumes of the greater number of compounds containing carbon, hydrogen, and oxygen which have hitherto been determined, may be calculated by the formula

$$\begin{aligned}\text{Sp. vol. } C_nH_mO_p(\mu) = & \,(10{\cdot}24 \pm x0{\cdot}5)(n+p)\\ + & \,(5{\cdot}12 \pm x0{\cdot}25m)\\ \pm & \,\tfrac{1}{4}(n-2)^2 \pm 1{\cdot}4\mu\end{aligned}$$

In this equation x denotes a number between 0 and 1, which varies with different homologous series but which is constant for the members of the same series. The sign μ represents the number of hydrogen atoms required to convert the formula into that of a saturated compound. The term $\frac{1}{4}(n-2)^2$ is introduced to compensate for the increase in the value corresponding to CH_2 as the molecular weight increases. Gartenmeister (*A.* 233, 304) having shown that in the case of the fatty esters the mean increase corresponding to CH_2 is 0·5, Lossen adds the term $\left(\frac{1}{2}+\frac{2}{2}+\frac{3}{2}+ \ldots \frac{n-3}{2}\right)$, which he erroneously states is equal to $\frac{1}{4}(n-2)^2$, a number always subsequently employed, but which, as comparison shows, serves to give good agreement with observed values.

For the majority of fatty compounds the formula

$$C_nH_mO_p = 10{\cdot}45(n+p) + 5{\cdot}225m + \tfrac{1}{4}(n-2)^2 + 1{\cdot}5\mu$$

gives results agreeing with the observed values. For the alcohols, however, the expression becomes

$$C_nH_mO_p = 10{\cdot}1(n+p) + 5{\cdot}05m + \tfrac{1}{4}(n-2)^2 + 1{\cdot}35\mu.$$

If it be supposed, as seems highly probable, that for all the members of a series of similarly constituted compounds the same influences are existent, whereby the specific volumes exhibit variations from the additive quantities assumed by Kopp, then we may regard the variable x as a term which takes account, and may be regarded as the measure, of these disturbing influences, and which, though constant for the members of the same series, should, as before stated, vary for other homologous series of compounds (Thorpe a. Jones, *C. J.* 63, 289).

Schröder regards the specific volume of an element in combination as variable within limits determined by the nature of the chemical compound. In any one compound, however, all the elementary atoms are regarded as occupying either equal or multiple volumes. Hence every specific volume is a multiple of a certain *space-unit* or *stere*, the value of which may vary between 6·7 and 7·4, depending on the number, nature, and mode of union of the atoms. Schröder thus obtains his determinate values. The specific volumes of formic, acetic, and propionic acids increase about 22 units for each increment of CH_2; in the case of alcohols the increase is about 20 units. The volume of formic acid is 41·8, *i.e.* 2 × 20·9; that of methyl alcohol is 42·8 or 2 × 21·4. Hence in formic acid, CH_2O_2, the O_2 occupies the same volume as CH_2; and in methyl alcohol, CH_2O, the H_2O has the same volume as CH_2. In like manner ethyl alcohol, C_2H_6O, has the volume 62·1, *i.e.* 3 × 20·7. Since 2 × CH_2 = 2 × 20·7, then $H_2O = 20{\cdot}7$. Acetic acid has the volume 63·6, *i.e.* 3 × 21·2; $2CH_2$ is 2 × 21·2 and $O_2 = 21{\cdot}2$. The volume of acetaldehyde is 56·9, *i.e.* about 6·6 smaller than that of acetic acid; this would indicate that the substitution of OH by H lowers the volume by 6·6. Since $H_2O = 21{\cdot}4$, it follows that the hydrogen and oxygen in hydroxyl each occupy one space-unit or stere. As $CH_2 = 21$, we find that carbon also occupies one stere or space-unit. Now, from the volume of formic acid which contains 6 steres, it is found on subtracting 3 steres for CH_2 and 1 stere for hydroxylic oxygen, that the carbonylic oxygen must occupy 2 steres.

We obtain, then, the following rule: *The number of space-units or steres of the saturated compounds of carbon, hydrogen, and oxygen corresponds to the number of the atoms increased by as many units as there are atoms of carbonylic oxygen present.*

If we calculate by means of this rule the steres of the saturated compounds, we find that they vary within narrow limits, and for the most part increase with increasing molecular weight. In the greater number of cases the values range between 6·9 and 7·2. Ostwald has determined the value of the stere for a large number of saturated fatty compounds, with the following results:—

Hydrocarbons	6·89, 6·99, 6·82, 7·11, 7·23.
Alcohols .	7·12, 6·91, 6·77, 6·88, 6·78, 6·78, 6·81, 6·74, 7·09
Acids . .	6·97, 7·06, 7·11, 7·19, 7·24, 7·24; 6·85.
Esters . .	7·04, 7·08, 7·05, 7·14, 7·26, 7·43, 7·45, 7·47.
Aldehydes .	7·11, 7·05, 7·18, 7·01, 7·18, 6·93, 7·27.

In the series of the hydrocarbons, the acids, and the esters, the steres in the cases of the normal compounds increase regularly with increasing molecular weight; in the series of the alcohols the steres decrease up to the third member and then increase. The secondary and tertiary compounds have, as a rule, smaller steres than the normal compounds. Kopp concluded from the approximately equal volumes of the alcohols and corresponding acids that H_2 and O are volumetrically equivalent; and from the equivalence of the volumes of benzyl and amyl compounds he inferred that C_2 and H_4 are mutually replaceable without alteration of volume. Hence he assumed that the hydrogen atom occupies only half the volume of the oxygen or carbon atom. Schröder established the volume equivalence of CH_2, HOH, and O′O, and he inferred from the difference in volume between alcohol and aldehyde that hydroxylic oxygen has the same volume as hydrogen and carbon, while carbonylic oxygen has twice the volume. While, then, Kopp assumes approximately $H_2 = C = O$, Schröder makes $H = C = O$ (Ostwald, *Lehrbuch*, [2nd ed.] vol. i. p. 388).

In the case of unsaturated and aromatic compounds, Schröder assumes that each double linkage is attended with an increase of volume amounting to one stere; hence the above rule has to be modified in this sense when applied to compounds of this class. The value of the stere in a number of unsaturated compounds is found to be:—

Hydrocarbons	6·87, 7·09, 6·93, 6·99.
Alcohols	6·72.
Esters and ethers	7·14, 7·13.

These values vary, practically, within the same limits as in the saturated compounds.

As regards aromatic compounds, it would seem to follow from the identity in the volumes of benzoyl and amyl compounds, as indicated by Kopp, as well as from the corresponding relation between the isobutyl and phenyl compounds, that C_6H_5 comprises the same number of steres as C_4H_9—that is, 13. Of these, 5 are occupied by hydrogen; so that the carbon group C_6 occupies 8 steres.

The values of the stere in a number of aromatic compounds are as follows:

Hydrocarbons	6·85, 6·94, 6·98, 7·00, 6·95, 7·04, 7·04, 7·04, 7·06, 6·84
Other compounds	6·91, 6·87, 7·05, 6·97, 7·16, 7·26, 7·50, 7·28, 7·14, 6·96, 7·07.

The value of the stere here also varies within the usual limits; it is comparatively small for the hydrocarbons (6·8–7·0), larger in the case of the alcohols, and still larger in that of the esters (7·2–7·5) (Ostwald, *l.c.*).

There is one consideration which is vital to the whole question, and to which, therefore, a brief reference must be made. It relates to the choice of conditions under which the values we term specific volumes are really comparable. Although Horstmann and Lossen have advanced reasons against the practice, contending that at any other temperature, say 0°, relations similar to those now established are made manifest, it has been the custom, in accordance with Kopp's direction, to compare the specific volumes of liquids at the temperatures of their respective boiling-points under a standard atmosphere. Whether, however, the temperature of the boiling-point, under these circumstances, is a truly comparable condition is open to question. It has been urged by Horstmann that, since what we call atomic volume is the space not merely filled by an atom but also that in which it moves, it is not *a priori* probable that at temperatures which differ, say by 300°—as, for example, in the case of C_4H_{10} (boiling-point 1°) and $C_{18}H_{38}$ (boiling-point 317°)—these volumes will be the same. Moreover, as pointed out by Bartoli, the boiling-point cannot in the nature of things be a strictly comparable condition, since it is affected by pressure to a different extent in the case of different liquids. Objections of even greater weight may be urged against the suggestions of Tschermak and Krafft to take the melting-point as a comparable state.

No doubt, theoretically speaking, a valid condition should be when pressure, volume, and temperature are expressed in terms of their critical values. But that certain regularities in the molecular volumes at the boiling-points have, in spite of this, been discovered may be explained, as Guldberg has shown, when we compare the values of T_1, the absolute boiling-point, with those of T, the absolute critical temperature; in those cases in which these two constants are known, the ratio $\frac{T}{T_1}$ approximates to $\frac{2}{3}$. Hence it follows that qualities like molecular volumes, which alter only slowly with temperature, are comparable at the ordinary boiling-points (*Z. P. C.* **5**, 374).

It ought, perhaps, to be stated that subsequent observations show that the so-called 'corresponding temperatures' deduced from Van der Waal's generalisations have not that degree of validity as temperatures of comparison which they were originally assumed to possess. Indeed, the present condition of knowledge warrants the statement that Kopp's original method of comparison is as valuable as any yet indicated (Thorpe, *C. J.* 63, 775 [1893]). T. E. T.

SPECTROSCOPIC ANALYSIS *v.* PHYSICAL METHODS, section *Optical methods*, subsection *Spectroscopic methods*, this vol. p. 239.

SPELTER. A commercial name for *zinc.*

SPERGULIN $(C_5H_7O_2)_n$. Occurs in the seed-coverings of *Spergula vulgaris* and *S. maxima* (Harz, *C. C.* 1879, 24). Amorphous. Its alcoholic solution exhibits dark-blue fluorescence, which is destroyed by sunshine. A small quantity of potash or Na_2CO_3 added to the alcoholic solution causes it to fluoresce green. Conc. H_2SO_4 forms a dark-blue liquid.

SPERMINE $C_{10}H_{26}N_4$ (Poehl, *B.* 24, 359); $C_4H_{10}N_2$ (S.). Occurs as phosphate in the spermatic fluid, in calves' liver and heart, and in some pathologic preparations that have been kept under alcohol (Schreiner, *A.* 194, 68). It is not identical with pyrazine hexahydride (Majert a. Schmidt, *B.* 24, 241; *cf.* Ladenburg, *B.* 20, 442; 21, 758; Poehl, *C. R.* 115, 515; Duclaux, *C. R.* 115, 155, 549). Crystals (from alcohol), v. sol. water, v. sl. sol. alcohol. Alkaline in reaction. Absorbs CO_2 from the air. Its aqueous solution is ppd. by phosphomolybdic acid and by potassium bismuth iodide. — $C_{10}H_{26}H_4 4HCl$: prisms, v. e. sol. water.—$C_{10}H_{26}N_4 2H_2PtCl_6$.—$C_{10}H_{26}N_4 4HAuCl_4$.—$C_{10}H_{26}N_4(H_3PO_4)_2$ 6aq: [170°]; rosettes of pyramids, sl. sol. hot water.

SPIKE OIL. S.G. above ·900. Slightly dextrorotatory (Schimmel, *Ph.* [3] 22, 329). $[\alpha]_D = 1° 24'$ (Voiry a. Bouchardat, *C. R.* 106, 551) or lævorotatory (Bruylants, *J. Ph.* [4] 30, 139). An essential oil obtained from the blossoms of *Lavandula aspica latifolia* (Lallemand, *A.* 114, 197; Sauer a. Grünling, *A.* 208, 75). Smells like lavender. Contains a terpene (175°) or (158°), which yields crystalline $C_{10}H_{16}HCl$, camphor, borneol, and a resin. According to Voiry and Bouchardat, oil of spike contains inactive spikol $C_{10}H_{18}O$ [0°] and $C_{10}H_{16}$ (155°–160°) $[\alpha]_D = 24°$, which yields a hydrochloride [129°] $[\alpha]_D = -2°$.

SPIROGRAPHIN *v.* PROTEÏDS, *Appendix C.*

SPONGIN *v.* PROTEÏDS, *Appendix C.*

STACHYDRIN $C_7H_{13}NO_2$. [210°]. Occurs with glutamine, tyrosine, and stachyose in the tubers of *Stachys tuberifera* (Von Planta a. Schulze, *B.* 26, 939). Colourless, deliquescent crystals (from water). Behaves like betaïne with regard to alkaloidal reagents.—B'HCl. Prisms, v. sol. water, sol. cold water (difference from betaïne).—$B'_2H_2PtCl_6$ 2aq. Trimetric crystals; $a:b:c = ·608:1:·828$.—$B'HAuCl_4$. Small yellow prisms (from water).

STACHYOSE $C_{18}H_{32}O_{16}$ 3aq. $[\alpha]_D = 148°$. Occurs in the roots of *Stachys tuberifera* (Planta a. Schulze, *B.* 23, 1692; 24, 2705). Tablets, with sweetish taste, v. sol. water. Dextrorotatory. Has no action on Fehling's solution until after boiling with mineral acids, by which it is converted into galactose and an isomeride (? glucose). HNO_3 forms mucic acid, galactose, glucose, and cane-sugar. Gives a red colour on heating with resorcin and HClAq. Gives no pp. with lead acetate until NH_3Aq is added.

STANNATES, and salts related thereto; *v.* under Tin.

STAPHISAGRINE *v.* Delphinine.

STARCH. *Amylum.* $nC_{12}H_{20}O_{10}$. The value of n has not been definitely settled; it is undoubtedly high. Brown and Morris (*C. J.* 55, 462), employing Raoult's method for determining molecular weights, show n for soluble starch (see below) $= 100$, *i.e.* molecular weight $= 32,400$. The molecular weight of starch cannot be less than this. From O'Sullivan's work (*C. J.* 35, 783) it would seem that n is not less than 36. Pfeifer a. Tollens (*B. C.* 1882, 775; *A.* 210, 295), from the composition of some sodium and potassium compounds prepared from starch, arrive at the value $n = 2$; the substances are probably compounds, not of starch, but of some decomposition products thereof. Sachsse (*C. C.* [3] 8, 732) and Nägeli (*A.* 173, 218) proposed $6C_6H_{10}O_5 + H_2O$ as the formula. Other observers (Mylius, *B.* 20, 694; Salomon, *J. pr.* [2] 28, 82) have suggested different formulæ, but the evidence is not satisfactory; we may take it, however, that the molecule of starch is not less than $n = 100$.

Occurrence.—Starch is present at some time or the other in all green plants. It is said to be found in almost all parts of the plant, but it is specially stored up in seeds, the pith of stems, in bulbs, tubers, rhizomes, and roots—generally those parts of the plant which serve as a store for reserve material. It is, however, a question whether the granules recognised as starch in leaves, sap, &c., outside the reserve organs, are chemically identical with the starch of these organs. The evidence, one way or the other, is unsatisfactory. Starch is not known to be an animal product. It is present in some fungi (Bourquelot, *J. Ph.* [5] 24, 197).

Formation.—Starch has not been prepared artificially. It is produced in the chlorophyll cells of plants, light, carbon dioxide, and water being necessary; oxygen is eliminated at the same time. No doubt, intermediate products—amylan-like bodies, sugars, &c.—are at first produced, but the granules are the first visible products of the assimilation found in the leaves. The starch thus formed is transferred to the reserve organs as such, or, more probably, as some sugar or other transformation product or products, as leaves are known to contain transforming agents (Baranetzky, *Die stärkeumbildenden Fermente in den Pflanzen*, Leipzig, 1878; Brasse, *C. R.* 99, 878).

Preparation.—Starch of commerce is prepared from various sources—viz., amongst others, wheat, rice, maize, potatoes, *Maranta indica* (American starch), *Maranta arundinacea* (arrowroot), the roots of *Jatropha Manihot* or *Manihot utilissima* (tapioca), the stems of several species of *Sagus* or *Cycas* (sago). For manufacturing methods see Thorpe's Dictionary, art. 'Starch.' In the laboratory, starch can be prepared from any starch-containing material as follows:—

From materials that can be ground, such as the cereals, &c., wheat, barley, maize, rice, &c. The material is ground in a coffee-mill, and the meal steeped in a 0·6 to 1 p.c. sol. KHO or NaHO. After standing 24–36 hours the coarser portions are separated by straining, with rubbing, and a slight flow of water through a wire sieve of about 20 wires to the inch. The strained milky liquid is allowed to stand for a short time, when a layer of crude starch settles at the bottom of the vessel. The liquid, with the matter in suspension, is transferred to another vessel, and again allowed to stand, when a second deposit of crude starch takes place. The process may be repeated a third and a fourth time. The whole of the suspended matter is thus allowed to settle, when the fairly clear supernatant liquid is decanted off and rejected. The deposit is then rubbed through a fine hair sieve, with a slight flow of water, and allowed to deposit a layer of starch as before. This is repeated as long as a starch layer separates. The whole of the starch layers are then collected, again suspended in water, and allowed to settle. At times a layer contaminated with much brown matter falls out first; from this the supernatant liquid with the starch in suspension is decanted off and allowed to stand, when a fairly pure deposit of starch is obtained. Further crops can be got from the residue, but it is difficult to free them from fibre, &c.

From materials that cannot be ground, such as potatoes, bulbs, rhizomes, other roots, and pith. The well-washed material is rubbed down with a grater into water, to which afterwards the alkali is added. The first deposit in these cases contains, as a rule, earthy matter, but it is easily separated by allowing it to settle, which it does in a short time, and then decanting off the starchy liquid. Two or three depositions and strainings through a fine hair sieve give a clean starch.

In dealing with the cereals the starch can be also separated by what is known as the acid process. The meal is steeped in water and kept at a temperature of from 25° to 27° until acid is developed. On then stirring up with water the light flocculent cell walls and undissolved albuminoids separate and allow the starch to deposit on standing. By repeated suspensions, stirrings, and depositions, clean crops of starch are obtained.

These products, like the starches of commerce, are not pure, but, as a rule, contain ash, oil or fat, albuminoids, &c. Some of them are slightly alkaline, some acid, from the condition of the water used in the last washing. Purification is effected by treatment with dilute KHO solution (0·5 p.c.), then dilute HCl (up to 1 p.c.), then with strong alcohol, and finally with water. They then can be dried by exposure to the air on layers of filter-paper.

Structure.—The starch thus obtained varies much in appearance, from the glistening silky white of potato starch to the dead chalky white of rice or maize starch. It consists of microscopic granules, varying in size from about 0·2 mm. to 0·002 mm. The same plant always yields granules of specifically the same size and shape, with as little variation as the size and shape of the leaf, hence, from the microscopic appearance of the granules, it is always possible to tell the source of a sample of starch. If it is wished to determine the source of any sample of starch, the following classification of the starches will be of some use. If, under the microscope, the granules are

(*a*) large, rounded, and more or less marked with rings: the starch may be potato, tapioca, sago, &c.

(*b*) rounded, very slightly ring-marked: barley, rye, wheat, &c.

(*c*) reniform: beans, peas, &c.

(*d*) intermediate in size, rounded, and irregular: crocus, tulip, and other bulbs.

(*e*) irregular in figure, bounded by surfaces more or less plain: maize, oats, rice, &c.

(*f*) small granules, rounded or irregular: fern, chestnut, parsnip, &c.

It will be observed that some of these are round, oval, or reniform, while others are irregular figures bounded by surfaces more or less plain. The microscopic appearance does not always give the true form of the granule, but a form which is the result of the pressure of the cover glass; for example, the well-marked star with central spot in rye starch and the split and striated appearance of maize starch are produced by the pressure of the cover glass on the granules. The granules of some starches are marked with well-defined more or less concentric rings, well shown in potato starch; in others there are no markings, the granules appearing as a clear, transparent cell. It is not absolutely agreed upon whether the starch granule consist of a single body or is made up of two or more. Some hold that the properly purified granule is a single substance, the coating or layers of which differ from the contents simply in containing less water and being thus more dense. According to Nägeli (*Die Stärkekörner*) and others, the dense portions consist of *starch cellulose*, while the less dense, transparent plasma is *granulose*. The stratified structure is the result of the mode of growth of the starch granule, the additions being made by intussusception, *i.e.* from within outwards. It is said that when the granule is ruptured the granulose dissolves in cold water, leaving the starch cellulose; the former gives the well-known blue reaction of starch with iodine, while the latter is only coloured yellowish (Jessen, *P.* 106, 497; *J. pr.* 105, 65; Brown a. Heron, *C. J.* 35, 610; Brukner, *M.* 4, 889). On heating the insoluble portion with water it also gives the characteristic blue reaction with iodine. Granulose may be separated from starch cellulose (*a*) by digesting the granules for several days with a saturated solution of NaCl containing 1 p.c. HCl—the cellulose remains undissolved (F. Schulze, *Henneberg's Jour. Landwirth.*, new ser., 7, 214); (*b*) by digesting starch with saliva at 45°-55°, this dissolves the granulose (Nägeli, *Die Stärkekörner*, 110; (*c*) by the action of certain schizomycetes, which decompose the granulose of starch-paste and leave the cellulose untouched (Fitz, *B.* 10, 282); and (*d*) by the action of malt-extract on starch paste in the cold, the cellulose is left undissolved. A. Mayer (*C. C.* 1887, 6; *Bot. Zeit.* 1886, 698) considers that the starch granule is a homogeneous substance, and that the terms 'granulose' and 'starch cellulose' must be abandoned, for he points out that the delicate transparent skeletons left when the gelatinised granules are acted on by saliva, dilute acids, &c., are produced by the action of the reagent on the starch, and are identical with amylodextrin. I am inclined to the view that starch granulose differs from starch cellulose in being less dense in consequence of containing less water of hydration. Starch granules act on polarised light, and when examined with the microscope between two Nicols, produce very pretty effects; *v.* Bailey (*P. M.* [5] 2, 123).

Properties.—Air-dried starch sometimes contains over 20 p.c. H_2O; this it loses, slowly towards the end, in a vacuum over sulphuric acid; by gradually raising the temperature to 100°, under these conditions, it soon becomes absolutely free from H_2O. The specific gravity of air-dried starch varies very considerably, the variation being due in the main to the quantity of moisture. Dry starches, however, would appear not to be absolutely alike in specific gravity; that of anhydrous potato starch is 1·650, whilst anhydrous arrowroot starch is 1·5648 (Flückiger, *Fr.* 5, 305; Saare, *J.* 1884, 1654). Dry starch takes up water, with the evolution of much heat. It does not dissolve in H_2O, and has neither taste nor smell.

(*a*) *Action of heat.* Dry starch is not coloured at 100°, and, indeed, the temperature can be increased considerably beyond that point without being changed. Starch containing water is, however, coloured by a moderately low temperature, and if the heat be increased to 160° a soluble product is obtained which is known as dextrin or British gum. It is a mixture of undescribed composition. The action of heat on *dry* starch has not yet been accurately recorded. When the heat is increased beyond 160°, and destructive distillation begins, carbon dioxide, gaseous hydrocarbons, water, acetic acid, and an empyreumatic oil are evolved, and finally a carbonaceous porous cinder is left.

(*b*) *Action of water.* As long as the granules are uninjured, starch is insoluble in cold water; when, however, the water is heated, the granules swell up, and a gelatinous, more or less transparent mass, known as *starch-paste*, is produced. This varies in transparency with the starch employed, as does the temperature at which the gelatinisation takes place. E. Lippmann (*C. C.* 1861, 859; *J. pr.* 83, 51) gives the following table on this point:

Source	Swelling-up temp.	Commencement of gelatinisation	Perfect gelatinisation
Rye	45°	50°	55°
Maize	50°	55°	62·5°
Barley	37·5°	57·5°	62·5°
Potato	46°	59°	62·5°
Rice	54°	59°	68°
Wheat	60°	65°	67·5°

If the paste is sufficiently dilute it can be filtered, but it is doubtful if the filtrate is a true solution (Picton a. Linder, *C. J.* 61, 156). The consistency or stiffness of starch-pastes, containing the same amount of dry starch, seems to vary with the variety of starch employed, and, indeed, with the method of preparation, even with the same starch; but I feel inclined to think that if closer attention were given to the amount of dry starch and its purity much of this apparent difference would disappear. On the relative stiffness of flour or starch pastes, and the mode of estimating it, see Thomson (*S. C. I.* 1886, 143). If the paste be heated under pressure to temperatures above the boiling-point, maltose and dextrin are said to be produced, but the change has not been accurately studied.

(*c*) *Action of glycerol.* Starch heated with glycerol to 190° is dissolved; alcohol ppts. soluble starch from the solution. If the heating be continued at 200°, dextrins are formed (Zulkowski, *B.* 13, 1895; 23, 3295; *C. C.* 1888, 1060).

(*d*) *Action of acids.* Moderately strong HCl in the cold converts starch, in a few days, without changing materially its microscopic appearance, into a modification perfectly soluble in water. This body is identical with soluble starch prepared by the limited action of malt extract on starch paste (C. Lintner, *J. pr.* 34, 378; Brown a. Morris, *C. J.* 55, 450). Prolonged action of 12 p.c. HCl in the cold produces amylo-dextrin (Nägeli, *Beiträge z. Kenntniss d. Stärkegruppe*; Brown a. Morris, *C. J.* 55, 450). Boiling dilute acids convert starch, first into soluble starch, then into dextrin and maltose, intermediate products, *amyloïns*, are said to be formed (Brown, Morris a. Moritz, *E. P.* No. 1809 of 1889), and finally dextrose. The complete conversion takes place the more quickly and perfectly the higher the temperature and the longer the period of the reaction (Allihn, *J. pr.* 22, 46; *D. P. J.* 250, 534). This is only accomplished by employing diluted acid. Carbonic acid, oxalic acid, &c., act like HCl and H_2SO_4, but less energetically. For the manufacture of dextrose (glucose) from starch, *vide* THORPE'S DICTIONARY. The action of acids has been studied chiefly by Kirchhoff, Guérin-Varry, Payen (see *Gm. K.*), Musculus (*A. Ch.* [3] 60, 203; *J. pr.* [2] 28, 496; *Bl.* 30, 4; O'Sullivan (*C. J.* 25, 581); Musculus a. Gruber (*C. R.* 86, 1459; *Bl.* [2] 30, 54); Bondonneau (*C. R.* 81, 972); Salomon (*J. pr.* [2] 25, 348; 26, 342; 28, 82 a. 122); Sachsse (*C. C.* [3] 8, 732); Schulze (*J. pr.* [2] 28, 311); Sostegne (*G.* 15, 376); Seyberlich a. Trampedach (*C. C.* 1887, 376); Nägeli (*Stärkegruppe*, Leipzig, 1874, 83, 99). As a summary of this work it may be stated that dextrose is the final product, but that acids act on this, to some extent yielding products still imperfectly investigated; that intermediate substances, dextrin and maltose and compounds thereof, are first produced; that the rapidity of the change varies with the strength of the acid, with the temperature, and with the pressure at which the change is effected, the most complete and perfect production of dextrose resulting when the conversion is hastened under pressure in presence of a small percentage of acid, 1½ to 2 p.c. or less, and the proportion of dry starch to dilute acid does not exceed 1 to 3. *Gallasin* (C. Schmitt a. Cobenzl, *B.* 17, 1000; Rosenbek, *B.* 17, 2456), a gummy body, is found in commercial glucose. This is identical with isomaltose obtained by Fischer (*B.* 23, 3687) by the action of strong HCl on dextrose (Scheibler a. Mittelmeier, *B.* 24, 301).

Action of diastase (malt extract). Diastase does not act on ungelatinised starch in the cold (O'Sullivan, *C. J.* 30, 133; Brown a. Heron, *C. J.* 35, 596), but Kjeldahl has shown that this is not true of all starches. This is probably due to some condition of the starch connected with the state of ripeness of the material whence it was obtained. The action, and the products thereof, of diastase on starch paste has been the subject of much study, but as yet only the broad facts are agreed upon. When starch paste is heated to 60° or thereabouts, and a little prepared diastase solution or cold water extract of malt added, the pastiness begins immediately to disappear, the solution rapidly loses the power of giving a blue colour with iodine, and acquires, for a short time, the property of giving with that reagent a deep reddish-brown colour. This, too, it rapidly loses if the diastase is in sufficient quantity. The solution is then perfectly clear when some starches are employed, with others there is more or less flocculent suspended matter in a clear solution. In the cold this dissolution takes place slowly. So far the reaction can be followed with little trouble, but when it comes to a question of the products of the action, the subject becomes more difficult. Musculus (*A. Ch.* [3] 55, 203) states that when diastase dissolves starch paste at 70°–75°, the products consist of 1 mol. sugar and 2 mols. dextrin, and that no further action takes place. Payen (*A. Ch.* [4] 4, 286) asserts that more than 50 p.c. of the solid matter dissolved by the reaction is sugar, and says (*A. Ch.* [4] 7, 382) that four samples taken from an operation in the space of 1½ hours contained 17·9, 20·9, 25·8, and 26·03 p.c. sugar on the total solids dissolved. Schwarzer (*J. pr.* [2] 1, 212) agrees with Musculus in finding equivalent quantities of dextrin and sugar in solution, but differs from him in supposing that dextrin is formed first, then sugar, and that the action ceases when definite equivalent proportions are produced. He says less sugar is produced at 65° than at lower temperatures; above 65°–70° the proportion of sugar to dextrin is as 1 eq.: 3 eqs.; below 60°, when the principal phase of the reaction is finished, the dextrin and sugar are in the proportion of 1 to 1. The change was considered complete when the solution no longer gave a colour with iodine. These investigators took the sugar as dextrose and estimated the dextrin by difference. O'Sullivan (*C. J.* 25, 581; 30, 137) showed that the sugar produced was not dextrose but *maltose*, and that the method of estimating the *dextrin* was wrong. He also demonstrated that dextrin and maltose were the invariable products of the transformation, and that by continuing the action the whole of the dextrin could be converted into maltose. It was, however, indicated in this work that another body—from which it was impossible to eliminate the cupric reducing power, and which seemed to be a mixture of maltose and dextrin—was amongst the products. Although this work laid the foundation of all that has since been done in the transformation products of starch, it received for a time no attention from the Continental chemists. Musculus (*Bl.* 22, 32) states that the saccharification of starch paste with diastase ceases when half the matter in solution is sugar. He attributes his original impression that only one-third was converted into sugar to the varying structure of the starch granules, the coating of one variety offering a greater resistance to the action of the diastase than that of another. He still holds that the action is a molecular splitting-up of the starch molecule, attended with hydration, into dextrin and sugar. Bondonneau (*C. R.* 81, 1212) concludes that the action is not a splitting-up, but that the starch molecule must pass through four isomeric modifications, viz., amylogen $[\alpha]_D = +216°$, α-dextrin = + 186°, β-dextrin = + 176°, and γ-dextrin = + 164°, before it arrives at the end-product, *glucose*. These bodies increase in cupric-reducing power as they descend to the final product. Petit (*Bl.* 24, 519) mentions, as a constituent of the transformation products, a sugar soluble in alcohol, fermentable, and without action on alkaline copper solution. This is, undoubtedly, to be traced to the fact that maltose does not reduce as much copper oxide as dextrose. O'Sullivan (*C. J.* 30, 125; 35, 770) showed conclusively when working under clearly-defined conditions that maltose and dextrin were the only products of the action, although, as stated, he pointed out the presence of a body which gave a reduction with copper oxide equal to 9–10 p.c. dextrose. The opticity of this body ($[\alpha]_j = +204°$–$206°$) was such as to indicate a mixture of 12·3-15·3 p.c. maltose from the reduction, and the remainder dextrin. He concluded that if the amount of reduction of the products be calculated as maltose, and the opticity due to this be subtracted from the total opticity observed for them, the remainder will agree with the activity of an amount of dextrin obtained by subtracting the determined maltose from the total products. He further showed that: (*a*) malt extract begins to dissolve starch at the temperature of gelatinisation, or a few degrees lower; (*b*) perfectly gelatinised starch is almost completely dissolved in the cold (10°-20°); (*c*) at 63° the action takes place according to the equation

$$\text{A. } \underset{\text{Starch}}{C_{18}H_{30}O_{15}} + OH_2 = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{C_6H_{10}O_5};$$

(*d*) at 64°-70° to

$$\text{B. } \underset{\text{Starch}}{\left.\begin{matrix} C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \end{matrix}\right\}} + OH_2 = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{4C_6H_{10}O_5};$$

(*e*) at 70°-71° (*C. J.* 1879) to

$$\text{B}'.\ C_{72}H_{120}O_{60} + 3OH_2 = 3C_{12}H_{22}O_{11} + 6C_6H_{10}O_5;$$

(*f*) and 71°-75° to

$$\text{C. } C_{72}H_{120}O_{60} + OH_2 = C_{12}H_{22}O_{11} + 10C_6H_{10}O_5;$$

(*g*) and he stated that although the proportions of maltose and dextrin indicated by these equations are easily obtainable when the strict conditions are adhered to, it was only necessary to vary the proportions of malt extract and starch, and time and temperature, to obtain with ease products containing from 16 to 92 p.c. maltose. It is further pointed out that the final product, maltose, was very slowly converted into dextrose by some samples, at least, of *malt extract*. O'Sullivan (*C. J.* 35, 770) showed that soluble starch was the first product of the action, and that the changes afterwards brought about may be expressed:

$$\text{C. } \underset{\text{Starch}}{C_{72}H_{120}O_{60}} + OH_2 = \underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + \underset{\alpha\text{-Dextrin}}{C_{60}H_{100}O_{50}}$$

$$\text{B. } C_{72}H_{120}O_{60} + 2OH_2 = 2C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-I}}{C_{48}H_{80}O_{40}}$$

$$\text{B}'.\ C_{72}H_{120}O_{60} + 3OH_2 = 3C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-II}}{C_{36}H_{60}O_{30}}$$

$$\text{A. } C_{72}H_{120}O_{60} + 4OH_2 = 4C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-III}}{C_{24}H_{40}O_{20}}$$

and finally:

$$C_{24}H_{40}O_{20} + 2OH_2 = 2C_{12}H_{22}O_{11}.$$

From the action of malt extract on these products he concluded that it is possible that only one β-dextrin exists. The theory of splitting up and breaking down of the starch molecules, as represented by the equations, does not account for all the facts eliminated. A theory which arranges all the molecules in solution in groups, dependent one on the other—and capable, therefore, of undergoing a simultaneous change, or of being moved at the same time—and the re-arrangement of these groups attendant upon the hydration of a definite proportion of the molecules in each of them, is more in accord with the eliminated facts. Märker (*L. V.* 22, 69) states that at 60° four molecules starch yield three of maltose and one of dextrin, at 65° there is less maltose, and at a higher temperature two molecules starch yield one of maltose and one of dextrin. Musculus and Gruber (*Bl.* 30, 54) look upon starch as a polysaccharide containing at least five times the group $C_{12}H_{20}O_{10}$. When this is acted upon by diastase, or dilute acids, it is broken down with hydration into maltose and a dextrin containing a $C_{12}H_{20}O_{10}$ group less than starch; that this dextrin is broken down in the same way, maltose and a dextrin containing a $C_{12}H_{20}O_{10}$ group less than the first one, and so on through the series by successive stages, until finally the solution contains only maltose. They point to the existence of three dextrins giving no reaction with iodine, and call them α, β, and γ achroo-dextrins. From the optical activity and K they attribute to these bodies, they do not agree with O'Sullivan; these factors do not agree with those of a mixture of maltose and dextrin. Brown and Heron (*C. J.* 35, 596) have eliminated out of the possible varying proportions of maltose and dextrin indicated by O'Sullivan eleven distinct transformations: viz. soluble starch, erythro-dextrin α and β, achroo-dextrins α to η, and maltose. They agree with O'Sullivan that the dextrins are without action on alkaline copper solution, and that the dextrins and maltose are the only products of the reaction. They do not mention the body from which O'Sullivan could not eliminate the reducing power, and they did not observe dextrose amongst the final products with malt extract. They agree with him that the higher the temperature at which the transformation takes place the less maltose is found amongst the products. They represent the normal reaction taking place between 10° and 60° by the equation

$$\underset{\text{Starch}}{10C_{12}H_{20}O_{10}} + 8H_2O = \underset{\text{Maltose}}{8C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{4C_6H_{10}O_5}.$$

They consider the starch molecule to be at least $10C_{12}H_{20}O_{10}$, and that the hydrolysis of it begins by the formation of maltose and erythro-dextrin α, containing $9C_{12}H_{20}O_{10}$; that this, in its turn, yields maltose and erythro-dextrin β, $8C_{12}H_{20}O_{10}$, and so on to the end—product, maltose. They thus agree with Musculus and Gruber as to the

character of the action, but disagree with them as to its quantitative nature.

Herzfeld (*B.* 12, 2120; 13, 3469) agrees with O'Sullivan and others that erythro- and achroo- dextrins are without reducing power on copper solution, but he points to the presence of a substance amongst the transformation products which seems to hold a position between dextrin and maltose; he names it *malto-dextrin.* K = about $\frac{1}{3}$ maltose, $[\alpha]_j = +171{\cdot}6°$; thus K corresponds to 33·3 p.c. maltose. A mixture consisting of one-third maltose and two-thirds dextrin would have an opticity $[\alpha]_j = +199°$; hence this contradicts the statement of O'Sullivan, confirmed by Brown and Heron, that, taking the reducing power as maltose, the opticity of the remainder of the transformation products corresponds to dextrin. Herzfeld considers that Bondonneau's γ-dextrin is malto-dextrin.

Brown a. Morris (*C. J.* 47, 527) confirm the presence of malto-dextrin, but they show that Herzfeld was dealing with an impure body, and that when its true K and $[\alpha]_j$, viz. K = 21·1 and $[\alpha]_j = +193{\cdot}1°$, are examined it is found that they correspond with a mixture of maltose and dextrin. It is completely converted into maltose by malt extract at 50° to 60°. They do not agree with Herzfeld that it is a hydration product of dextrin, but hold that it is produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, thus $\left\{\begin{array}{l}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_2\end{array}\right.$. They have discarded the series of equations, and consider that equilibrium is attained when a condition of things represented by the equation

$$\underset{\text{Starch}}{10C_{12}H_{20}O_{10}} + 8H_2O = \underset{\text{Maltose}}{8C_{12}H_{22}O_{11}} + \underset{\text{Dextrin}}{2C_{12}H_{20}O_{10}}$$

is arrived at. This is always the result when the change takes place at 50° to 60°, or when a higher transformation-product is degraded at that temperature. This degradation is due to the hydrolysis of the more complex polymeric dextrins and malto-dextrin. Bourquelot (*C. R.* 104, 576) looks upon the action of diastase on starch as a successive fixation of a water molecule with the production of maltose and a lower dextrin until the reduction of the degraded products is K = 51·52 (about 82·5 p.c. maltose), but he does not describe his dextrin or dextrins, and he concludes, as has already been clearly proved, that heat alters, not alone the quantity of diastase, but the quality.

Brown and Morris (*C. J.* 55, 462), from determination of the molecular weights of some of the transformation products, conclude, as suggested by O'Sullivan in 1879, that the dextrins are metameric, and not polymeric, as they hitherto considered them. They therefore abandon their former theory of the hydrolysis of starch by diastase, and, as far as I can see, come to a broad agreement with the theory enunciated by O'Sullivan. They mention another product, amylo-dextrin, $[\alpha]_j = +206°$, K = 9·0. Like malto-dextrin, it appears to be a compound of maltose and dextrin, $\left\{\begin{array}{l}C_{12}H_{22}O_{11}\\(C_{12}H_{20}O_{10})_8\end{array}\right.$. Its opticity and K agree with the body described by O'Sullivan in 1872, and mentioned above.

A new phase has been given to the transformation by C. J. Lintner (*Zeit. ang. Ch.* 1892, 263). He says he has isolated a body, which he calls *isomaltose*, from amongst the products. It is less fermentable and less soluble in alcohol than maltose, with $[\alpha]_D = +139$ and K = 52, the opticity being nearly that of maltose and the reducing power about 84 p.c. thereof. Diastase converts it into maltose completely.

Since the publication of the above Morris a. Wells (*Transactions of the Institute of Brewing*, 5, 133), and Moritz (*ibid.* 4, 141) point to the presence of a whole series of amyloïns or malto-dextrins amongst what they call restricted starch-conversions, and they assert that isomaltose is a low amyloïn—*i.e.* one in which the maltose constituent largely predominates. These amyloïns begin with a high proportion of the dextrin residue, and end with a high proportion of maltose. Their optical activity and reducing power are such as would be yielded by mixtures of maltose and dextrin.

Schifferer (*In. Dissertation*, Basel) denies *in toto* the existence of the amyloïns, and asserts that nothing is to be found amongst the products of the action of diastase on starch but achroo-dextrin, isomaltose, and maltose. His dextrin, however, is a reducing dextrin; even otherwise, the work will not bear criticism.

Action of other enzymes. Ptyalin (ptyalase). This enzyme of saliva liquefies starch paste (Nägeli, *Die Stärkekörner*, p. 113; Lefberg a. Georgieski, *Bl.* [2] 25, 393; Dobroslavine, *Bl.* [2] 26, 452; Maercker, *L. V.* 22, 69; Watson, *C. J.* 1879, 539; Musculus a. De Mering, *Bl.* [2] 31, 105; Lea, *J. Physiol.* 11, 226). The products are maltose, a reducing, unfermentable dextrin, and a little dextrose. Ungelatinised starch is not acted upon by ptyalase; at a temperature slightly below the gelatinising point the starch is dissolved, and the action is most rapid when the ferment acts at 60° on previously-boiled starch paste (Bourquelot, *C. R.* 104, 71 a. 177).

Enzymes capable of dissolving starch have been observed in the pancreatic juice (Brown a. Heron, *Pr.* 1880, 394), in the small intestine (Hoppe-Seyler, *Phys. Ch.* 275; Brown a. Heron, *l.c.*), in the liver (Wittich, *Pf.* 7, 28; Bernard, *C. R.* 85, 519; Abele, *Th. J.* 6, 271), and in many other animal tissues (Ellenberger a. Hofmeister, *Th. J.* 12, 501; Paschutin, *Th. J.* 1, 304). The stomach, pancreas, and peritoneal lymph of fishes contain an enzyme capable of dissolving starch (Richet, *Th. J.* 14, 359; Kruckenberg, *Unter. Phys. Inst.* Heidelberg, 1, 2). Blood contains a diastatic enzyme, for starch injected into the blood yielded maltose and dextrin (Bimmerman, *Pf.* 20, 201; Ploz a. Tiegel, *Pf.* 6, 249).

Starch-dissolving enzymes exist in the leaves and other parts of most plants (Baranetzky, *Die stärkeumbildenden Fermente in den Pflanzen*, Leipzig, 1878; Vines, *Ann. Bot.* 1891, 409).

Certain organisms, bacteria, moulds, &c., are capable of secreting an enzyme or enzymes having the power of dissolving starch. The nature of the dissolution products has, as yet, been very imperfectly studied; we have simply the general statement that they are sugar or sugars and dextrin (Wortman, *Z. P. C.* 6, 287; Fitz, *B.* 10, 282; Marcona, *C. R.* 95, 345 a. 856; Gayon a. Dubourg, *C. R.* 103, 885;

Atkinson, *Pr.* 32, 299; Takamine, *E. P.* 5700 a. 17874, 1891). *Bacillus amylobacter* yields dextrin and a small quantity of a crystalline body (Villiers, *C. R.* 112, 435 a. 113, 144 a. 536). Under the influence of *Bacillus suaveolens*, dextrin, glucose, alcohol, aldehyde, formic, acetic, and butyric acids are produced. Amylic alcohol is the result of the action of *Bacillus amylozymicus*, no doubt intermediate bodies; dextrin and sugar are at first produced. Atkinson states that the moulds grown on steamed rice in the manufacture of saké, in Japan, secrete an enzyme, which first converts starch into dextrin and maltose, and further acts on the maltose and dextrin, with the production of dextrose.

Some gums of the arabin group contain a starch-dissolving enzyme (O'Sullivan, *C. J.* 1891, 1061).

Maize, malted and raw, and other grains contain an enzyme capable of dissolving starch and yielding as a final product dextrose (Cuisinier, *C. C.* 1886, 614). Its action on starch is not very vigorous, but it acts more rapidly on dextrin and converts maltose very rapidly into dextrose (Geduld, *Wochenschrift f. Brauerei*, 8, 620; Lintner, *Zeit. f. ges. Brau.* 1892, 123). It would be interesting to determine in what respect this enzyme differs from that of the moulds, and to establish their separate existence.

Action of the halogens. Chlorine does not stain starch. Bromine colours it yellow. Iodine gives with it an intense blue. This reaction is a distinctive test for starch. The colour is destroyed by heating, but returns on cooling; but if the solution be boiled for some time, the colour does not reappear. The blue colour is also discharged by arsenious and sulphurous acids, by alkalis and carbonates thereof, and, indeed, alcohol can remove the iodine. A solution of iodine in strong alcohol does not colour dry starch. Some observers consider that the production of this blue colour is not due to a definite chemical combination of iodine with starch (Vogel, *N. Rep. Pharm.* 22, 349; 25, 565; Pellet, *M.* [3] 7, 988; Tomlinson, *P. M.* [5] 20, 168; Duclaux, *A. Ch.* [4] 25, 264), while others attribute a definite formula to the combination. According to Bondonneau (*C. R.* 85, 671), it is $(C_6H_{10}O_5)_5I$; Mylius (*B.* 20, 688) considers it to contain HI, and gives the formula $(C_{24}H_{40}O_{20}I)_4IH$ as probable. He finds that the HI can be displaced by metallic iodides. Stocks (*C. N.* 56, 212; 57, 183) and Seyfert (*Zeit. ang. Ch.* 1, 15) contradict this. Rouvier (*C. R.* 114, 128 a. 1366) attributes the formula $(C_6H_{10}O_5)_8I$ to the compound. Starch is oxidised by chlorine and by bromine to gluconic acid (Habermann, *A.* 172, 11; Herzfeld, *A.* 220, 364).

Action of alkalis. Weak solutions of the alkalis do not act on starch in the cold, but solutions containing over 3 p.c. real alkali cause the granules to swell up with the formation of a thick transparent paste, and, finally, a clear solution, a compound of starch with the alkali being formed (Schmidt, *A.* 51, 31; Ventzke, *J. pr.* 25, 65) which, according to the latter, is optically inactive, but this, no doubt, is incorrect, for Béchamp (*C. R.* 39, 653) gives the opticity $[\alpha]_j = +211°$ for the starch dissolved, and Thomsen (*B.* 13, 2168) shows that the activity of dilute soda solutions is $[\alpha]_D = +168$. On neutralisation this becomes much higher, corresponding, in fact, with Béchamp's number. The product does not reduce alkaline copper solution (Brown a. Heron, *C. J.* 35, 617). The potassium compound is obtained by ppg. the solution in dilute KHO with alcohol, pressing the pp., dissolving in H_2O, and re-ppg. with alcohol. This process repeated three or four times is said to yield a pure compound of the composition $C_{24}H_{39}O_{20}K$ (Pfeiffer a. Tollens, *A.* 210, 288). A sodium compound $C_{24}H_{39}O_{20}Na$ has been obtained in the same way (Reichardt, *Z.* 1870, 404). These formulæ are, however, very improbable. Alcoholic soda does not act on starch (Dragendorf, *J. f. Landwirthschaft*, 7, 206).

Starch heated with ammonia yields brown, amorphous, nitrogenous bodies (Thénard, *C. R.* 52, 444).

Fused with KHO, starch, like other carbohydrates, yields oxalic acid, acetic acid, and other products.

Action of alkaline earths. Barium, strontium, and calcium compounds similar to the sodium and potassium bodies have also been prepared. When solutions of soluble starch are ppd. with solutions of lime in sugar syrup, pps. are produced which are not very definite in composition, the percentage of lime showing a variation between $C_6H_{10}O_5CaO$ and $(C_6H_{10}O_5)_4CaO$. Similar baryta compounds have been examined. When a solution of soluble starch is saturated with strontia and alcohol added, a strontium compound is ppd. (Lintner, *Zeit. f. ang. Ch.* 1888, 232). On distilling starch with lime acetone, mesityl oxide, isophorone, and ketones are produced (Harvat, *C. C.* 1887, 38).

On digesting starch with acetic anhydride, a triacetate is said to be formed $C_6H_7O_2(C_2H_3O_2)_3$ (Schützenberger a. Naudin, *Bl.* [2] 12, 110; *A. Ch.* [4] 21, 235; Michael, *Am.* 5, 359). This substance is amorphous; it is stained blue by iodine, and is decomposed by alkalis, with the reproduction of starch.

Qualitative determination. The presence of starch is indicated by the granular appearance under the microscope, and starch granules are distinguished from all others by being stained blue by iodine solution and yellow by bromine. If the plasma in which the granules are contained is alkaline, it must be rendered slightly acid, or sufficient iodine solution must be employed to destroy the alkalinity. A solution of iodine in potassium iodide is usually employed, but an alcoholic solution answers the purpose. When the test is applied for starch in solution, the solutions must be cold and slightly acid and the reagent must be added in small quantities at a time. It is sometimes necessary to test a solution for soluble starch in presence of α-dextrin—*i.e.* the dextrin giving a reddish-brown colour with iodine. If this is in excess the reddish-brown colour covers the blue; ammonia added cautiously, drop by drop, discharges the reddish-brown, and if soluble starch be present the blue becomes definite and distinct. Care must be taken to avoid excess of ammonia (O'Sullivan). Small quantities of starch, which would otherwise not be observable, may be detected in the 'last runnings' of malt wort by adding a little

tannin and then alcohol to the solution. The starch is ppd. in this way, and on washing the pp. with water will yield the characteristic reaction with iodine (Burckhardt, *Chem. Zeit.* 1877, 1158). Starch, when moistened with an alcoholic solution of α-naphthol and a few drops of warm concentrated sulphuric acid added, acquires a deep violet-red colour (Ihl, *Chem. Zeit.* 11, 19).

Quantitative determination. There are very few materials containing starch of which a sufficiently accurate average sample can be obtained to render a definite estimation of the starch therein of much value.

In some cases separation of the starch, by one of the methods given for its preparation, gives results of sufficient accuracy to satisfy the requirements.

In the case of potatoes, the percentage of starch is deduced from the specific gravity, a set of specially-constructed tables being used; but this method, on the face of it, cannot yield more than an approximation. The specific gravity of the washed potatoes is taken in the usual way, a balance constructed to meet the requirements of the case being employed. About 5 kilos. of the potatoes are weighed in a strong wire basket in air, and then in water; thence,

$$\text{specific gravity} = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in water}}.$$

According to the tables of Behrend, Märker, and Morgan, we have from

Sp. gr.	Per cent. of starch	Sp. gr.	Per cent. of starch
1·080	13·9	1·120	22·5
1·090	16·0	1·130	24·6
1·100	18·2	1·140	26·7
1·110	20·3		

In cases in which fair average samples of the material can be obtained, several methods have been proposed, all depending on the conversion of the starch, or the starch transformation products, into dextrose by digestion with dilute HCl or H_2SO_4, the dextrose being estimated with Fehling's solution, volumetrically or gravimetrically, and the starch calculated therefrom according to the equation $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$ (*v.* Sachsse, *C. C.* [3] 8, 732; Märker, *Handb. der Spiritusfabrication*, 4 Auf., Berlin, 1886, 93; Soxhlet, *Zeit. f. ges. Brau.* 1881, 177; Faulenbach, *Zeit. f. phys. Chem.* 7, 510; Zipperer, *Rep. An. Chem.* 6, 699). Dubrunfaut dissolved the starch by rubbing the material with concentrated HCl, diluting the solution with water to a certain volume, and determining the opticity. The starch was calculated from $[\alpha]_j = 192{\cdot}4^\circ$.

Effront (*Bl.* [2] 47, 5) dissolves the starch with malt extract, determines the optical activity of the solution, then heats it with ammonia, after which he treats it with sodium hypochlorite and with HCl, and again determines the opticity; but this method is open to many objections.

These methods are unsatisfactory, inasmuch as it is difficult, if not impossible, to completely convert starch or starch products into dextrose, there being a probable error at one time from over-conversion, at another from under-conversion; and, indeed, both may occur at the same time, the amount of reduction of Fehling's solution taken as dextrose never being a correct measure of the starch transformed. Another objection to the method is due to the fact that dilute acids convert other substances besides starch into bodies capable of reducing copper oxide.

Girard (*C. R.* 104, 1629) titrates starch with iodine solution, 1 grm. of starch taking up 0·157 grms. iodine.

Asboth (*Chem. Zeit.* 11, 785) proposes to add an excess of baryta water to the gelatinised starch and then alcohol. The dried pp. contains 19·8 p.c. BaO, the remainder is starch. This method, too, cannot be of any use.

O'Sullivan (*C. J.* 45, 2) described a method by which starch in most materials can be estimated with accuracy. If a fair average sample of the material cannot be obtained by grinding and powdering alone, it is first dried in warm, dry air and then powdered. The following is the method as applied to the cereals, but it is also applicable to all materials when treated as just described.

Five grams, or thereabouts, accurately weighed —more if the material contains less than 40 p.c. starch—of the finely-ground material are introduced into a wide-necked flask of 100 to 120 c.c. capacity. To this sufficient alcohol of sp. gr. 0·82 is added to saturate it, and after a time 20 to 25 c.c. ether are introduced. The clear, ethereal solution is decanted off after standing for a few hours, and the residue again treated two or three times with ether. It is then extracted with alcohol, sp. gr. ·90, at 35° to 38°, and treated with a large bulk of water, with which it is left in contact for at least 24 hours. If any sign of fermentation shows itself, a little salicylic acid solution may be used with the water. The residue, after being completely extracted with water, together with the filter, through which all the extracts should have been passed, is transferred to a beaker of about 100 c.c. capacity, and made up with water to about 40 to 45 c.c. This is heated to boiling for a few minutes in a water bath, care being taken, by continual stirring, to insure a homogeneous paste; then cooled to 62° to 63°, and 0·025 to 0·035 gram prepared diastase or its equivalent of malt extract added, the digestion being then continued at the temperature stated for a few hours. At the end of that time the contents of the beaker are boiled for a few minutes, thrown on to a filter, and the filtrate received in a 100 c.c. measuring flask. The residue is carefully washed with small quantities of boiling water at a time, and the filtrate made up at 15·5° to 100 c.c. A determination of the reducing power calculated as maltose, and of the remainder of the optical activity as dextrin, gives the data for calculating the quantity of starch. This holds good even though the amyloïn theory of the breaking down of starch be proved to be accurate.

Example.—5 grms. barley-flour treated as described, 0·03 grm. prepared diastase being employed,[1] gave 100 c.c. solution of sp. gr. 1·01003 = 2·539 grms. solid matter. 9·178 grms. this sol. reduced 0·241 grm. CuO. Opt. act. in

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[1] If cold-water malt extract be used, a portion of it must be heated for the same time and at the same temperature as the assay; then boiled, and the opticity and reducing power determined; these factors calculated on the quantity employed must be allowed for.

200 mm. tube = +21·1 divs. (Soleil-Ventzke-Scheibler saccharimeter). Hence

0·241 + 0·7256 (K of maltose = 62·5)
= 0·1748 grm. maltose;
9·178 grms. : 101·003 (the wt. of 100 c.c. sol.)
:: 0·1748 : x;
x = maltose in the 100 c.c. sol. = 1·923;
Opt. act. maltose $[\alpha]_j$ = +154° and of dextrin $[\alpha]_j$
= +222°.

Hence 1 grm. maltose in 100 c.c. sol. in 200 mm. tube = 8·52 divs. of instrument mentioned, and 1 grm. dextrin under like circumstances = 11·56 divs. Then 1·923 × 8·02 = 15·422 divs. opt. activity of the maltose, 21·1 − 15·422 = 5·678 divs. opt. activity of the dextrin, and 5·678 ÷ 11·56 = 0·491 grm. dextrin in the 100 c.c. sol. Dextrin is derived from starch without any increase of weight: 100 grms. starch yield 105·5 maltose; hence

1·055 : 1·923 :: 1 : x starch − maltose;
x = 1·822 grms. starch.

1·822 + 0·491 (as dextrin) = 2·313 starch; in the 5 grms. taken = 46·26 p.c.

It is clearly shown in the paper quoted that if starch is not estimated in the way indicated no reliance can be placed on the results. It happens when dealing with some varieties of material that the aqueous extract contains *soluble starch* (blue colour with iodine). This cannot be looked upon as starch; it must be estimated in the solution as the soluble modification.

Soluble starch may be prepared (*a*) by triturating starch with sharp sand or powdered glass so as to disintegrate the granules and extracting with cold water; (*b*) by the limited action of malt-extract or of acid.

Delffs (*P.* 109, 648) prepared soluble starch by triturating starch with sand and water; the solution gave a dark-blue colouration with iodine. Flückiger (*Z.* 1861, 104) prepared a similar solution by acting on starch with a concentrated solution of calcium chloride and treating the resulting gummy mass with water, when, on filtration, a solution is obtained which exhibits all the characteristics of soluble starch. Musculus (*Bl.* [2] 22, 26; *A. Ch.* [5] 2, 385) does not consider this a true solution; he prepares the body by boiling starch with very dilute sulphuric acid, saturating the solution with chalk, and evaporating to a syrup. This deposits small granules which gradually increase in size, are soluble in hot water, and may be purified by precipitation with alcohol. It possesses no reducing power; its rotatory power is four times that of glucose. Bondonneau (*C. R.* 80, 671) has prepared soluble starch by this method, but does not find it altogether soluble under all conditions. Soluble starch is undialysable. Fuming nitric acid converts it into a mononitro-derivative, $C_6H_9(NO_2)O_5$; dilute nitric acid oxidises it to carbonic and oxalic acids; bromine and silver oxide to gluconic acid (Reichardt, *B.* 8, 1020; 7, 424).

Nägeli (*Beiträge z. näheren Kenntniss der Stärkegruppe*, Leipzig, 1874, p. 33, 99; *A. Ch.* 173, 218) gives the following method: 1 kilo. potato starch is allowed to stand 6-8 weeks with 6 litres hydrochloric acid, S.G. 1·06; this is then purified by solution in hot water; it crystallises in sphæro-crystals (Jaquelain, *A. Ch.* [2] [illegible], 178). According to Brown a. Morris, this is not soluble starch (*v.* above). Zulkowski (*B.* 13, 1395) prepares soluble starch by heating dry potato starch with glycerol at 180°-190° for half an hour. The solution is cooled, precipitated by alcohol, and the precipitate purified by solution in water and reprecipitation by alcohol.

Salomon (*J. pr.* [2] 28, 82) finds that soluble starch is the first product of the action of dilute acids on starch; it does not reduce Fehling's solution, and has an optical activity $[\alpha]_D$ −211·5°. O'Sullivan (*C. J.* 1879, 772) prepares soluble starch by dissolving starch paste at 73°–74° with the least possible quantity of cold water extract of malt, boiling the solution as soon as it becomes clear, filtering, and concentrating. The soluble starch falls out on cooling as a white precipitate, which is purified by dissolving in hot water and allowing to cool when it separates out again. It has a reducing power, 3·5–0·78, and an optical activity $[\alpha]_j$ = 219·5–222·0, the reducing power being probably due to a small quantity of maltose; *v.* also *Action of acids on starch*, above. C. O'S.

STEARIC ACID $C_{18}H_{36}O_2$. Mol. w. 284. [69°]. (232° cor. at 15 mm.) (Krafft, *B.* 17, 1629); (359°–383°) (Carnelley a. Williams, *B.* 12, 1360). H.F. 126,000 (Von Rechenberg). S.G. (liquid) $\frac{69}{}$ ·845; (solid) $\frac{0}{}$ 1·01; $\frac{10}{}$ 1·00. S.V.S. 332·6 (R. Schiff, *A.* 223, 264). S. (alcohol) 2·5 in the cold. S. (benzene) 22 at 23°. S. (CS_2) 30 (Vogel, *J.* 1866, 892). Occurs as glyceryl stearate in very many fixed animal and vegetable fats and oils (Chevreul, *A. Ch.* 88, 225; [2] 2, 354; 23, 19; Braconnot, *A. Ch.* 93, 250; Redtenbacher, *A.* 35, 46; Bromeis, *A.* 35, 86; 37, 303; Stenhouse, *A.* 36, 57; Erdmann, *J. pr.* 25, 497; Francis, *A.* 42, 256; Gottlieb, *A.* 57, 35; Laurent a. Gerhardt, *A.* 72, 272; Hardwick, *C. J.* 2, 232; Crowder, *P. M.* [4] 4, 21; Berthelot, *A. Ch.* [3] 41, 216, 432; 47, 297; Pebal, *A.* 91, 138; Heintz, *A.* 92, 295; Johnston, *C. J.* 29, 8).

Formation.—**1.** By saponification of cetyl-acetoacetic ether, obtained from cetyl iodide and sodium acetoacetic ether (Guthzeit, *A.* 206, 351). 2. By heating cetyl-malonic acid at 150°.—3. From ricinoleïc acid by treatment with water, P, and I, followed by zinc and HClAq (Claus, *B.* 9, 1916).—4. By heating oleïc acid with iodine (1 p.c.) for several hours at 275° and distilling the product in a current of superheated steam (De Wilde a. Reychler, *Bl.* [3] 1, 295).

Preparation.—Suet or cacao fat is saponified by NaOHAq, the acids ppd. by H_2SO_4 and crystallised from alcohol. An alcoholic solution of the impure stearic acid (4 pts.) saturated at 0° is heated to 60° and mixed with a boiling alcoholic solution of $Mg(OAc)_2$ (1 pt.). The ppd. magnesium stearate is boiled with HClAq and the stearic acid recrystallised from alcohol (Heintz). Stearic acid can also be readily obtained from shea-butter which contains no other solid fatty acid (Buff a. Oudemans, *J. pr.* 89, 215).

Properties.—Pearly plates, insol. water, sol. alcohol and ether. Tasteless and inodorous. May be distilled *in vacuo* and, in small quantity, under atmospheric pressure, but in this case it is partly decomposed with formation of hydrocarbons, stearone, water, CO_2, acetic acid, and butyric acid. Fusion with P_2O_5 forms $C_{18}H_{34}O$ [54°–60°]. Nitric acid forms sebacic, glutaric, succinic, and other acids. Br and water at 140° form bromo- and dibromo-stearic acids (Oudemans, *J. pr.* 89, 193). Distillation *in vacuo* with NaOMe yields $C_{17}H_{34}$ (Mai, *B.* 22, 2133).

Salts.—KA′. Hygroscopic crystals. S. 4 in hot water. Partially decomposed by a large quantity of water into an insoluble acid salt and free potash.—KHA′₂. Silvery scales (from alcohol). S. (alcohol) ·36 in the cold; 27 at 78°. Boiling water converts it into a more acid salt. NaA′.—NaHA′₂: insol. water.—BaA′₂: minute laminæ, insol. water.—CaA′₂.—SrA′₂.—MgA′₂: minute laminæ (from alcohol).—CuA′₂: light-blue amorphous powder.—PbA′₂: amorphous powder, insol. ether.—$Pb_2OA'_2$.—AgA′: white pp.

Methyl ether MeA′. [38°]. Crystalline, insol. water (Hanhart, *C. R.* 47, 230).

Ethyl ether EtA′. [33°]. (224°). Formed by heating the acid with alcohol at 200° (Lassaigne, *A.* 13, 168; Berthelot, *A.* 88, 312) by passing HCl into an alcoholic solution of stearic acid (Redtenbacher, *A.* 35, 51) and by heating stearin with a little NaOEt (Duffy, *C. J.* 5, 197; Bouis, *C. R.* 45, 35). Crystalline mass, partially decomposed by distillation. V. sol. alcohol.

Ethylene ether $C_2H_4A'_2$. [76°]. From AgA′ and $C_2H_4Br_2$ (Wurtz, *A. Ch.* [3] 55, 436).

Isoamyl ether $C_5H_{11}A'$. [25°].

Octyl ether $C_8H_{17}A'$. [45°].

Cetyl ether $C_{16}H_{33}A'$. [55°-60°]. Laminæ (from ether) (Berthelot, *A. Ch.* [3] 56, 70).

Glyceryl ethers v. vol. ii. p. 622. A mixture of stearic acid and glycerin saturated with HCl at 100° forms $C_3H_5Cl(OH)(OC_{18}H_{35}O)$ [28°].

Phenyl ether PhA′. [52°]. (267° at 15 mm.) (Krafft a. Bürger, *B.* 17, 1380).

p-Tolyl ether C_7H_7A'. [54°]. (276° at 15 mm.).

Chloride $C_{18}H_{35}OCl$. [23°]. (215° at 15 mm.). Crystalline mass.

Amide $C_{18}H_{35}O.NH_2$. [109°]. Formed by distilling ammonium stearate at 230° under pressure; the yield being 50 p.c. (Hofmann, *B.* 15, 984; *cf.* Carlet, *Bl.* 1859, i. 76). Formed also by the action of NH_3 on the ether or on the chloride. Converted by the action of Br and NaOHAq into stearyl-heptadecyl-urea (Turpin, *B.* 21, 2486).

Anilide $C_{18}H_{35}ONHPh$. [94°]. Formed by distilling aniline over stearic acid at 230° (Pebal, *A.* 91, 152). White needles.

Phenyl hydrazide $C_{17}H_{35}.CO.N_2H_2Ph$. [107°]. Formed by heating stearic acid with phenyl-hydrazine. White unctuous plates (from alcohol), sl. sol. cold alcohol, benzene, and ether (Strache a. Iritzer, *M.* 14, 37).

Nitrile $C_{17}H_{35}CN$. [42°]. (275° at 100 mm.). S.G. $\frac{15}{4}$ ·815; $\frac{100}{4}$ ·779. Formed by distilling stearamide with P_2O_5 (Krafft a. Stauffer, *B.* 15, 516, 1730) or by heating cyanostearic acid at 250° (Hell a. Sadomsky, *B.* 24, 2779).

References. — Bromo-, Di-bromo-iodo-, Chloro-, Iodo-, Nitro-, and Oxy-stearic acid.

Isostearic acid $(C_8H_{17})_2CH.CO_2H$. [38·5°]. (278° at 101 mm.). Formed from di-octyl-acetoacetic ether or di-octyl-malonic acid (Conrad a. Guthzeit, *A.* 204, 11, 165). Colourless leaflets (from alcohol).—NaA′: needles (from alcohol).—AgA′: thick white pp.

Ethyl ether EtA′. (275°-280° at 100 mm.).

STEARIC ALDEHYDE $C_{18}H_{36}O_2$. [64°]. (213° uncor. at 22 mm.). Formed by distilling calcium stearate with calcium formate (Krafft, *B.* 13, 1417). Plates with bluish glitter, sl. sol. ether.

STEARIN *v. Stearyl derivative* of Glycerin.

STEAROLIC ACID $C_{18}H_{32}O_2$. Mol. w. 280. [48°]. (260°). Formed by heating bromo-oleïc acid or the dibromide of oleïc acid with alcoholic potash at 100° (Overbeck, *J. pr.* 97, 159; *A.* 140, 49). Needles (from alcohol), insol. water. Br forms $C_{18}H_{32}Br_2O_2$ and $C_{18}H_{32}Br_4O_2$ [70°]. I and FeI_2 in CS_2 form $C_{18}H_{32}I_2O_2$ [51°] (Liebermann a. Sachsse, *B.* 24, 4116). Potash-fusion yields myristic acid $C_{14}H_{28}O_2$ and an acid $C_{16}H_{30}O_2$ [21°] (Marasse, *Z.* [2] 5, 571; *B.* 2, 359). Alkaline $KMnO_4$ oxidises it to suberic and stearoxylic acids (Hazura a. Grüssner, *M.* 9, 952). HNO_3 yields azelaïc, stearoxylic, pelargonic, and nitroso-pelargonic acids (Limpach, *A.* 190, 294). Phenyl-hydrazine at 140° gives $C_{17}H_{31}CO.N_2H_2Ph$ [82°] (Holt, *B.* 25, 2670).—BaA′₂.—CaA′₂aq.—AgA′.

STEARONE $(C_{17}H_{35})_2CO$. *Di-heptadecyl ketone.* [88°]. S.G. (liquid) $\frac{89}{4}$ ·7979 (Krafft, *B.* 15, 1715). Formed by heating stearic acid (9·5 g.) with P_2O_5 (5 g.) at 210° (Kipping, *C. J.* 57, 537; *cf.* Bussy, *A.* 9, 269; Redtenbacher, *A.* 35, 57; Varrentrapp, *A.* 35, 80; Rowney, *C. J.* 6, 97; Heintz, *P.* 94, 272; 96, 65). Got also by distilling the stearyl derivative of heptadecyl-urea with lime (Turpin, *B.* 21, 2486). Plates, sl. sol. hot alcohol. Br forms $C_{35}H_{68}Br_2O$ [72°].

Oxim $(C_{17}H_{35})_2C:NOH$. [63°]. White powder, m. sol. hot benzene and alcohol, insol. water and alkalis (Spiegler, *B.* 17, 1575; Kipping, *C. J.* 57, 540).

STEAROXYLIC ACID $C_{18}H_{32}O_4$. Mol. w. 312. [86°]. Formed by the oxidation of stearolic acid (Overbeck, *A.* 140, 63; Hazura a. Grüssner, *M.* 9, 952). Plates or needles, sl. sol. cold alcohol. BaA′₂.—AgA′: crystalline powder.

STEARYL-GLYCERIN *v.* Glycerin.

STEEL *v.* Iron, vol. iii. p. 53, and Dictionary of Applied Chemistry, vol. ii. p. 360.

STIBINE. Synonym of *antimony hydride*, *v.* vol. i. p. 288.

STILBENE *v.* Di-phenyl-ethylene.

STILBENE ALCOHOL *v.* Hydrobenzoïn.

STILBENE DIBROMIDE *v.* Di-bromo-phenyl-ethane.

STILBENE DICARBOXYLIC ACID *v.* Di-phenyl-maleïc acid.

STILBENE DICHLORIDE *v.* Di-chloro-phenyl-ethane.

STOÏCHIOMETRY. The laws of chemical combination, and their application to chemical calculations; *v.* Combination, chemical, Laws of, vol. ii. p. 235.

STORAX. A balsam produced by *Styrax officinalis*, a shrub growing in the Levant. It occurs in two varieties, liquid storax and reed storax, the latter containing a large quantity of bark. Liquid storax is a brownish-yellow sticky mass containing styrene, styracin, cinnamic acid, phenylpropyl cinnamate, a little ethyl cinnamate, a substance [65°] smelling like vanilla (possibly ethyl-vanillin), and (α) and (β)-storesinol (W. von Miller, *N. R. P.* 24, 1; *B.* 9, 274; *A.* 188, 184; 189, 338).

(α)-Storesinol $C_{36}H_{58}O_3$ *i.e.* $C_{36}H_{55}(OH)_3$. [160°-168°]. Amorphous, v. sol. dilute KOHAq.

but conc. KOHAq ppts. $C_{36}H_{50}O_4K$. Yields a mono- and tri-acetyl derivative.

(β)-**Storesinol.** [140°–145°]. Amorphous. Forms amorphous $C_{36}H_{50}O_4K$, which is more sol. water than its (α)- isomeride.

STRONTIA. Oxide of strontium (*q.v.* p. 516).

STRONTIUM. Sr. At. w. 87·3. Mol. w. not known. Very little known about properties. Doubtful if approximately pure Sr has yet been isolated. S.G. c. 2·4 to 2·58 (Franz, *J. pr.* 107, 253; Matthiessen, *J.* 8, 324). For emission-spectrum *v. B. A.* 1884. 444. H.C. [Sr,O] = 128, 440 (*Th.* 3, 258).

Occurrence.—Compounds of Sr are widely distributed, but not in very large quantities. $SrCO_3$ occurs in small quantities in all specimens of *arragonite*; very small quantities are found in many *calc-spars*, *marbles*, and *dolomites*. $SrSO_4$ is an ingredient of many *heavy spars*. $SrCO_3$ is found as *strontianite*, and $SrSO_4$ as *celestine* in a few localities; *brewsterite* contains Sr silicate, with silicates of Ba or Ca. Traces of $SrSO_4$ and $SrCl_2$ are found in many mineral springs, in some hard river-waters, in sea-water, and in the ashes of certain plants, especially *Fucus vesiculosus*.

Historical.—A mineral found at Strontian, a village in Argyleshire, in 1787, and supposed to be barium carbonate, was observed to colour flame reddish by Crawford and Cruikshank in 1790 (*Mem. Manchester Soc.*). The supposition made by C. a. C. that the mineral contained a new element was confirmed by Hope (*T. E.* 4, 3), Klaproth (*Crell's Ann.* 1793 [ii.] 189; 1794 (i.) 99), and Kirwan-Higgins (*Crell's Ann.* 1795 (ii.) 119, 205). The metal was isolated by Davy in 1808 (*T.* 1808. 345).

Formation.—1. By electrolysing moist SrO_2H_2 or $SrCl_2$ in contact with Hg and a little naphtha, and heating the amalgam so formed (Davy, *T.* 1808. 345).—2. By heating saturated $SrCl_2Aq$ with Na amalgam to 90°, quickly washing the Sr amalgam so formed, drying it by filter paper, and distilling off the Hg in a stream of H (Franz, *J. pr.* 107, 253).—3. By heating SrO or SrO_2H_2 intimately mixed with Mg powder, a mixture of Sr with MgO is obtained (Winkler, *B.* 23, 125, 2647).

Preparation.—A porous clay cylinder is placed in a crucible, and $SrCl_2$, mixed with a little NH_4Cl, is placed in the crucible and in the cell, so that when the mixture is fused the surface of it is at a higher level in the cell than in the crucible. A cylinder of sheet iron surrounding the cell serves as the positive electrode, and an iron wire passing through a tobacco pipe, the bowl of which dips under the molten mixture in the cell, serves as the negative electrode. The crucible is heated till the mixture of $SrCl_2$ and NH_4Cl melts, temperature being kept so that there is always a solid crust on the surface of the mixture in the porous cell. A current from 5 or 6 Bunsen cells is passed through the molten mass; Sr is separated and runs into small pieces, which are protected from the air by the solid crust of $SrCl_2$ and NH_4Cl; the pieces of Sr are removed by an iron spoon and kept under petroleum.

For the preparation of pure Sr salts from *strontianite v.* Barthe a. Falières (*Bl.* [3] 7, 104).

Properties.—A yellowish-white metal, somewhat harder than Ca or Pb; can be beaten into thin leaves; melts at full red heat. According to Mallet (*A.* 190, 62), Sr is slightly volatilised at a very high temperature. Easily oxidised by exposure to air; decomposes cold water rapidly; dissolves in dilute acids, not in HNO_3Aq, giving salts and H. Combines directly with S and the halogens. Sr is a strongly positive metal, less positive than the alkali metals and Ca, but more positive than Mg; it is closely related to Ca and Ba, less closely to Mg; it also shows resemblances to Zn, Cd, and Hg (*v.* ALKALINE EARTHS, METALS OF THE, vol. i. p. 112; and MAGNESIUM GROUP OF ELEMENTS, vol. iii. p. 163). The atomic weight of Sr has been determined (1) by determining CO_2 in $SrCO_3$ (Stromeyer, *S.* 19, 228 [1816]; Salvétat, *C. R.* 17, 318 [1843]); (2) by ppg. Cl from $SrCl_2$ by Ag (Rose, *S.* 19, 228 [1816]; Pelouze, *C. R.* 20, 1047 [1845]; Marignac, *A.* 106, 168 [1858]; Dumas, *A. Ch.* [3] 55, 191 [1859]); (3) by determining water in $SrCl_2.6H_2O$ (Marignac, *A.* 106, 168 [1858]); (4) by transforming $SrCl_2.6H_2O$ into $SrSO_4$ (Marignac, *l.c.*). The S.H. of Sr has not been determined directly. The V.D. of no compound of Sr has been determined.

Reactions and Combinations (*v.* Bunsen, *A.* 94, 111).—1. Exposed to *air* or *oxygen* rapidly forms SrO, or SrO_2H_2 if moisture is present.—2. Burns brilliantly when heated in *oxygen*, *sulphur* vapour, *chlorine*, *bromine*, or *iodine* vapour; also in dry *carbon dioxide*.—3. Decomposes cold *water* rapidly, giving off H and forming SrO_2H_2.—4. Dissolves rapidly in *dilute hydrochloric* or *sulphuric acid*; reacts slowly with *conc. sulphuric acid*; scarcely acted on by *nitric acid*, even when hot and conc.—5. Reduces *silica* and *silicates* when heated therewith to full redness.

Strontium, antimonate of; *v.* vol. i. p. 286.

Strontium, arsenates of; *v.* vol. i. p. 309.

Strontium, arsenite of; *v.* vol. i. p. 307.

Strontium, borates of; *v.* vol. i. p. 530.

Strontium, bromide of, $SrBr_2$. Mol. w. not determined. By heating Sr in Br. By dissolving $SrCO_3$ in HBrAq and evaporating, long white needles of the *hydrate* $SrBr_2.6aq$ are obtained (Löwig, *Mag. Pharm.* 33, 7); S.G. 2·358 (Favre a. Valson, *C. R.* 77, 579); these crystals do not effloresce over H_2SO_4 (Rammelsberg, *P.* 55, 238), but on heating give off their water, leaving $SrBr_2$ as a white solid, S.G. 3·985 (F. a. V., *l.c.*), that melts at red heat without decomposition (R., *l.c.*). $[Sr,Br^2] = 157,700$ (*Th.* 3, 258). Carnelley (*C. J.* 33, 279) gives melting-point as c. 630°. Combines with *ammonia* to form $2SrBr_2.NH_3$ (Rammelsberg, *P.* 55, 238).

Strontium, chloride of, $SrCl_2$. Mol. w. not determined.

Formation.—1. By burning Sr in Cl.—2. By passing Cl over hot SrO (Weber, *P.* 112, 619).—3. By heating SrO in a stream of HCl (Chevreul, *A. Ch.* 84, 285).—4. By decomposing $SrCO_3$ by conc. $CaCl_2Aq$ or $MgCl_2$ by heating together, then dissolving out $SrCl_2$ and crystallising ($SrCO_3 + MgCl_2Aq = SrCl_2Aq + MgO + CO_2$; *Wackenroder's Patent*; *v. B.* 19, *Ref.* 633).—5. By heating a mixture of $SrSO_4$, $CaCl_2$, and charcoal with a little chalk, lixiviating, and crystallising ($SrSO_4 + CaCl_2 + 4C = SrCl_2 + CaS + 4CO$; Mactear, *D. P. J.* 262, 288).

Preparation.—*Strontianite* ($SrCO_3$) is dissolved in HClAq, the solution is digested in absence of air with more $SrCO_3$ (to remove iron, &c.), poured off and evaporated to the crystallising point; the crystals of $SrCl_2.6aq$ that separate are purified by re-crystallisation, then dried and heated to 100° until they cease to lose weight.

Properties.—A white, crystalline powder, with a sharp, bitter taste. Melts at 825° (Carnelley, *C. J.* 33, 280) to a glass-like mass with an alkaline reaction. S.G. 2·96 at 0°; 2·77 at m.p. (Quincke, *P.* 138, 141). S. 44·2 at 0°, 48·3 at 10°, 53·9 at 20°, 60 at 30°, 66·7 at 40°, 74·4 at 50°, 83·1 at 60°, 87·5 at 65°, 88·8 at 66·5°, 89·6 at 70°, 92·4 at 80°, 96·2 at 90°, 101·9 at 100°, 109·1 at 110°, 116·4 at 118·8°; saturated $SrCl_2Aq$ boils at 118·8° (Mulder). Gerlach (*Fr.* 8, 245) gives the following data:—

S.G. $SrCl_2Aq$	P.c. $SrCl_2$	S.G. $SrCl_2Aq$	P.c. $SrCl_2$
1·0453	5	1·2580	25
1·0929	10	1·3220	30
1·1439	15	1·3633	33
1·1989	20		

$SrCl_2$ is insol. absolute alcohol; it dissolves in aqueous alcohol in proportion to the amount of water present (Gerardin, *A. Ch.* [4] 5, 156). $[Sr,Cl^2] = 184,550$; $[Sr,Cl^2,Aq] = 195,690$ (*Th.* 3, 258). For connection between solubility in water of $SrCl_2$ and temperature *v.* Étard (*C. R.* 113, 854).

Reactions and Combinations.—1. Heated to redness in *water vapour*, HCl is given off and SrO remains (Kraus, *P.* 43, 138; Kahnheim, *J.* 1861. 149).—2. Heated with *bromine* to 200° is partially decomposed to $SrBr_2$ (Potilitzin, *B.* 7, 733; 8, 766); the amount of decomposition varies with temperature and the relative masses of $SrCl_2$ and Br.—3. Combines with *water*. Solution of $SrCO_3$ in HClAq evaporated yields long, six-sided, hexagonal needles of the *hexahydrate* $SrCl_2.6H_2O$; S.G. 1·933 at ·17°. By keeping these crystals over H_2SO_4 *in vacuo* for some months the *dihydrate* $SrCl_2.2H_2O$ is formed.—4. Combines with *ammonia* to form $SrCl_2.8NH_3$ (H. Rose, *P.* 20, 155).

Strontium, cyanide of; *v.* vol. ii. p. 347.

Strontium, ferrocyanide of; *v.* vol. ii. p. 337.

Strontium, fluoride of, SrF_2. A white, crystalline powder; scarcely sol. water or HFAq. Prepared by the action of HFAq on SrO or $SrCO_3$ (Berzelius, *P.* 1, 20); also by fusing 2 parts $SrCl_2$ with 1 part NaF and 1 part NaCl, and lixiviating the product (Röder, *Dissertation* [Göttingen, 1863] 14; Feldmann, *B.* 21, *Ref.* 866 [*Patent*]). Poulenc (*C. R.* 116, 987) obtained SrF_2, as an amorphous powder, by the reaction of HFAq and $SrCl_2Aq$; S.G. 2·44; partly decomposed to SrO by heating in air to c. 1000°. By fusing with alkali chlorides, or with KHF_2, P. obtained SrF_2 in regular octahedral crystals.

Strontium, hydride of. By heating to redness a mixture of 103 parts SrO (made from $SrCO_3$) with 24 parts Mg powder, in an iron tube, in an atmosphere of H, Winkler (*B.* 24, 1975) obtained a greyish-brown powder that quickly oxidised in air to SrO_2H_2 with evolution of H, and was decomposed very rapidly by water or HClAq with violent evolution of H. Analyses indicated that the substance might be a mixture of c. 66 p.c. SrH with c. 29 p.c. MgO, c. 4 p.c. SrO, and a very little Mg.

Strontium, hydrosulphide of, $SrS_2H_2.xH_2O$. By saturating SrOAq with H_2S and evaporating *in vacuo* over H_2SO_4; or by dissolving SrS in water, evaporating, filtering from SrO_2H_2, and evaporating over H_2SO_4 *in vacuo*. Large, white crystals; melts when heated in water of crystallisation, and then gives SrS. Aqueous solution boiled gives off all H_2S and forms SrO_2H_2 (*v.* Rose, *P.* 55, 430; Berzelius, *P.* 6, 442).

Strontium, hydroxide of, SrO_2H_2. Mol. w. not determined. Prepared by the action of water on SrO. Also by heating *celestine* ($SrSO_4$) with charcoal, dissolving SrS so formed in water, heating with CuO or ZnO, filtering from CuS or ZnS, evaporating to dryness, and heating to redness (*cf.* BARIUM HYDROXIDE, vol. i. p. 442).

A white solid; S.G. 3·625 (Filhol, *A. Ch.* [3] 21, 415). Sol. water, forming a markedly alkaline solution reacting similarly to BaO_2H_2Aq and CaO_2H_2Aq. Scheibler (*C. C.* [3] 13, 33) gives the following data, showing solubility in water, expressed in terms of SrO, and the hydrate $SrO_2H_2.8H_2O$, dissolved:—

Temp.	S.		Temp.	S.	
	SrO	$SrO_2H_2.8H_2O$		SrO	$SrO_2H_2.8H_2O$
0°	·35	·90	55°	2·54	6·52
5	·41	1·05	60	3·03	7·77
10	·48	1·23	65	3·62	9·29
15	·57	1·46	70	4·35	11·16
20	·68	1·74	75	5·30	13·60
25	·82	2·10	80	6·56	16·83
30	1·00	2·57	85	9·00	23·09
35	1·22	3·13	90	12·00	30·78
40	1·48	3·80	95	15·15	38·86
45	1·78	4·57	100	18·60	47·71
50	2·13	5·46	101·2	19·40	49·75

Dry SrO_2H_2 takes up only traces of CO_2 from the air (Heyer, *B.* 19, 2684); but the hydrate $SrO_2H_2.H_2O$ absorbs CO_2 till it is changed to $SrCO_3$ (H., *l.c.*); according to Finkener (*B.* 19, 2958) a basic carbonate is formed.

The *octohydrate*, $SrO_2H_2.8H_2O$, crystallises in tetragonal crystals ($a : c = 1 : \cdot6407$) from SrOAq; S.G. 1·396 at 16°; in air falls to powder, giving the *monohydrate* $SrO_2H_2.H_2O$, which loses H_2O at 100° (*v.* Finkener, *l.c.*; Müller-Erzbach, *B.* 19, 2874; 20, 1628). Weisberg (*B.* 11, 511) says that Cl reacts with the hydrates of SrO_2H_2 to give $SrCl_2$ and $Sr(ClO_3)_2$.

Strontium, iodide of, SrI_2. A white solid; by dissolving $SrCO_3$ in HIAq, evaporating, and heating the *hexahydrate*, $SrI_2.6H_2O$, which crystallises out. S.G. 4·415; melts at red heat; strongly heated in air gives SrO and I (Croft, *J. pr.* 68, 420). Thomsen gives $[Sr,I^2,Aq] = 143,460$ (*Th.* 3, 258).

Strontium, manganocyanide of; *v.* vol. ii. p. 342.

Strontium, nitride of. By heating Sr amalgam containing from 20 to 25 p.c. Sr (prepared by electrolysis and heating the product *in vacuo*) in a stream of N, Maquenne (*Bl.* [3] 7, 366) obtained a dark-coloured compound of Sr and N to which he gave the formula Sr_3N_2.

Strontium, oxides of. Two oxides have been isolated, SrO and SrO_2.

Strontium oxide SrO. (*Strontium monoxide. Strontia.*) Mol. w. not known. Prepared by strongly heating SrO_2H_2, $Sr(NO_3)_2$, $SrCO_3$ (Brügelmann, *Fr.* 29, 127; Heyer, *B.* 19, 2684); also by strongly heating SrI_2 in air (Croft, *J. pr.* 68, 420). Best prepared similarly to BaO (*v.* Barium monoxide, vol. i. p. 443). A grey-white, porous, infusible solid; prepared by heating $SrCO_3$ or SrO_2H_2 forms a mass of regular cubes with S.G. 4·75 referred to water at 4° (Brügelmann, *l.c.*). According to Moissan (*C. R.* 115, 1034), SrO melts to a transparent liquid at c. 3000°, and this solidifies to a crystalline mass. Thomsen gives $[Sr,O] = 128,440$ (*Th.* 3, 258). Dissolves in water (for data *v. Strontium hydroxide*); from this solution the octohydrated hydroxide $SrO_2H_2.8H_2O$ separates on evaporation. By passing moist air over SrO the monohydrated hydroxide, $SrO_2H_2.H_2O$, is formed (Heyer, *B.* 19, 2684). SrO is a strongly basic oxide, reacting with acids to form salts SrX, where $X = SO_4$, $2NO_3$, $\frac{2}{3}PO_4$, &c.

Strontium dioxide SrO_2. (*Strontium peroxide.*) Mol. w. not known. Addition of H_2O_2Aq to SrOAq ppts. the *octohydrate* $SrO_2.8H_2O$ (Thénard, *A. Ch.* [2] 8, 312; Schöne, *B.* 6, 1172; *cf.* Conroy, *C. J.* [2] 11, 812). By drying this pp. at 100° SrO_2 is obtained as a white powder, having similar properties to those of *barium dioxide* (*q.v.* vol. i. p. 443). SrO_2 is not obtained by methods similar to those generally used for making BaO_2.

Strontium, oxychloride of. According to André (*A. Ch.* [6] 3, 66) crystals of the compound $SrCl_2.SrO.9H_2O (= Sr_2OCl_2.9H_2O)$ are deposited from a mixture of saturated $SrCl_2Aq$ and saturated SrOAq; the crystals are very unstable in air.

Strontium, oxysulphide of. Schöne (*P.* 117, 59) obtained $SrS_4.SrO.12aq (Sr_2OS_4.12aq)$ by slow oxidation of SrS_4Aq.

Strontium, platinocyanide of; *v.* vol. ii. p. 344.

Strontium, salts of. *Compounds obtained by replacing H of acids by strontium.* These compounds belong to the type SrX, where X is SO_4, CO_3, $2NO_3$, $\frac{2}{3}PO_4$ &c. The Sr salts are very definite compounds; not many basic salts are known. The chief salts of oxyacids are the following: *bromate* and *hypobromite*, *carbonate*, *chlorate*, *chlorite* and *perchlorate*, *chromate* and *dichromate*, *iodate* and *periodates*, *molybdate*, *nitrate*, *nitrite*, and *hyponitrite*, *selenate* and *selenites*, *sulphate*, *sulphite*, *thiosulphate*, and *thionates* (*v.* Carbonates, nitrates, &c.).

Strontium, selenide of. Obtained as a white solid, rapidly decomposing in air with separation of Se, by heating a small quantity of $SrSeO_4$ in H to dull redness; $[Sr,Se] = 87,160$ (Fabre, *C. R.* 102, 1469).

Strontium, silicofluoride of, $SrSiF_6.2H_2O$. Four-sided prisms; S.G. 2·999; loses $2H_2O$ when gently warmed; prepared by dissolving $SrCO_3$ in H_2SiF_6Aq and evaporating (Berzelius, *Lehrbuch* [5th edit.], 3, 385]. Fresenius (*Fr.* 29, 143) gives S. 3·2 at 15°; S. in alcohol (50 p.c. by vol.) ·06 at 15°.

Strontium, sulphides of. Three sulphides have been isolated: SrS, SrS_4, and SrS_5.

Strontium monosulphide SrS. Formed by heating together Sr and S in the ratio 87:32; also by reducing $SrSO_4$ by charcoal; also by passing CS_2 vapour mixed with H, H_2S, or CO_2 over red-hot $SrCO_3$ (*cf.* Barium monosulphide, vol. i. p. 444). A white powder, which slowly becomes yellowish when exposed to air. Does not phosphoresce (Schöne, *P.* 117, 59). For phosphorescence of SrS mixed with small quantities of other salts *v.* Becquerel (*C. R.* 107, 892). Sabatier (*A. Ch.* [5] 22, 5) gives $[Sr,S] = 49,600$. SrS does not combine with S when heated therewith, but polysulphides are formed by boiling an aqueous solution of SrS with S (Schöne, *P.* 117, 59). SrS dissolves in water; on crystallising SrO_2H_2 separates and SrS_2H_2 remains in solution (H. Rose, *P.* 55, 430).

Strontium tetrasulphide $SrS_4.xH_2O$. The *hexahydrate*, $SrS_4.6H_2O$, is obtained, as a reddish crystalline solid, by boiling 100 parts SrS in water, and evaporating the solution *in vacuo* at a temperature not higher than 16°. From a solution at 20°–25° the *dihydrate* $SrS_4.2H_2O$ separates. An aqueous solution of SrS_4 oxidises in air to the oxysulphide $SrO.SrS_4.12aq$, and then to SrS_2O_3, while S separates and some $SrCO_3$ is formed (Schöne, *P.* 117, 59).

Strontium pentasulphide $SrS_5.xH_2O$. An amorphous, yellowish, hygroscopic solid; formed by evaporating a solution of SrS_4 saturated with S in the cold. After drying at 100°, CS_2 dissolves out $\frac{1}{5}$th of the S, leaving SrS_4 (Schöne, *l.c.*).

Strontium, sulphydrate of; *v.* Strontium hydrosulphide, p. 515.

Strontium, sulphocyanide of; *v.* vol. ii. p. 352.

M. M. P. M.

STROPHANTHIN $C_{31}H_{48}O_{12}$ (A.); $C_{20}H_{34}O_{10}$ (F.). $[\alpha]_D = 30°$. Extracted by alcohol at 70° from the seeds of *Strophanthus hispidus* (Gallois, *C. R.* 84, 261; Fraser, *Ar. Ph.* [3] 3, 229; *Pr. E.* 124, 370; *Ph.* [3] 18, 69; Elborne, *Ph.* [3] 17, 743; 18, 219; Gerrard, *Ph.* [3] 17, 923; Arnaud, *C. R.* 107, 179; Gley, *C. R.* 107, 348). White micaceous crystals, sol. water, v. sol. alcohol, insol. ether. Dextrorotatory. Bitter. Resembles ouabain in toxic effects. Decomposed by boiling dilute acids (even H_2S) into glucose and crystalline strophanthidin, which yields a resin on further boiling with dilute H_2SO_4 (F.). H_2SO_4 and a trace of $FeCl_3$ gives a reddish-brown pp., changing to emerald-green (Helbing, *Ph.* [3] 17, 924).

STRUTHIIN *v.* Saponin.

STRYCHNIC ACID $C_{20}H_{22}NO(NH).CO_2H$. Formed from strychnine, alcohol, and Na at 50°–55° (Tafel, *A.* 264, 50). When heated in a current of H at 190° it changes to strychnine. $K_2Cr_2O_7$ and H_2SO_4 give a brown-red colour or pp.

Nitrosamine $C_{20}H_{22}NO(N.NO).CO_2H$. Gelatinous pp. Exhibits Liebermann's reaction.

Methylo-iodide $C_{20}H_{22}N(MeI)O(NH).CO_2H$. Formed from methyl-strychnine and HI (Tafel, *A.* 264, 55). Colourless needles (containing aq), v. sl. sol. cold alcohol and cold water.—NaA′ aq: v. e. sol. water, m. sol. alcohol. Converted by MeI into crystalline $C_{20}H_{22}N(MeI)(NMe).CO_2Me$.

Methyl-strychnic acid. *Methylo-iodide.* $C_{20}H_{22}N(MeI)O(NMe).CO_2H$. Formed from dimethyl-strychnine and HI (Tafel, *A.* 264, 58). Needles, m. sol. boiling water and hot alcohol.

Deoxystrychnic acid $C_{20}H_{26}N(NH).CO_2H$ aq. Formed by heating deoxystrychnine with alcoholic NaOEt at 180° (Tafel, *A.* 268, 253). Needles (containing aq) (from dilute H_2SO_4) or anhydrous prisms (from alcohol), sl. sol. hot water. Quickly converted by acids into deoxystrychnine. Yields a nitrosamine.

Isostrychnic acid $C_{20}H_{22}NO(NH).CO_2H$. Formed from strychnine, Na, and alcohol at 70°. Got also by heating strychnine with baryta-water at 140° in absence of air. Minute needles. $K_2Cr_2O_7$ and dilute H_2SO_4 form a brown liquid on heating, and a brown pp. with excess of $K_2Cr_2O_7$.—HA'HI aq: prisms, m. sol. cold water and alcohol, insol. ether.

Nitroso-derivative $NO.C_{20}H_{21}NO(NH).CO_2H$ aq. Sol. alkalis, but ppd. by CO_2. Yields a nitrosamine, which gives Liebermann's reaction with phenol and H_2SO_4. —HA'HCl: needles, insol. water.

Methylo-iodide $C_{20}H_{22}N(MeI)O(NH).CO_2H$. Crystalline, m. sol. hot water.—NaA': minute needles. Converted by methyl iodide at 100° into crystalline $C_{20}H_{22}N(MeI)O(NMe).CO_2Me$ 2aq.

Methyl-isostrychnic acid $C_{20}H_{22}NO(NMe).CO_2H$. From isostrychnic acid hydroiodide and MeI at 100° (Tafel, *A.* 268, 240). Small colourless prisms (containing $2\frac{1}{2}$aq). Its alkaline solution is not coloured by air (difference from isostrychnic acid).

Methylo-iodide $C_{20}H_{22}N(MeI)O(NMe).CO_2H$ aq [271°-275°]. Formed from methyl-strychnine methylo-iodide and HI (Tafel, *A.* 264, 77). Needles, m. sol. hot water and hot alcohol, insol. ether.

Nitroso-methyl-isostrychnic acid $NO.C_{20}H_{21}ON(NMe).CO_2H$. Formed from the preceding acid, alcohol, HCl, and amyl nitrite. Green needles (from benzene). When heated with benzoic aldehyde and $ZnCl_2$ it gives a green mass, which dyes like malachite green. Diazo-benzene chloride forms a brownish-orange dye.

STRYCHNINE $C_{21}H_{22}N_2O_2$. Mol. w. 334. [221°] (Blyth); [284°] (Claus a. Glassner, *B.* 14, 773); [268°] (Loebisch a. Schoop, *M.* 6, 858); [269°] (Stoehr). (270° at 5 mm.). S.G. $\frac{18}{4}$ 1·359 (Clarke, *Am.* 2, 174). S. ·015 in the cold; ·04 at 100°. S. ·014 in the cold (Dragendorff, *J.* 1865, 739); ·025 at 14·5° (Crespi, *G.* 13, 175). S. (alcohol) ·3 at 8°; 1·8 at 78°. S. (95 p.c. alcohol) ·936. S. (ether) ·08. S. (benzene) ·607. S. (isoamyl alcohol) ·53 at 12°; 4·3 at 99°. Occurs in nux vomica, in St. Ignatius beans, in the wood of *Strychnos Colubrina*, in *Strychnos Tieuté*, and in other species of *Strychnos* (Pelletier a. Caventou, *A. Ch.* [2] 10, 142; 26, 44; Pelletier a. Dumas, *A. Ch.* [2] 24, 176; Liebig, *A.* 47, 171; 49, 244; Regnault, *A. Ch.* [2] 68, 113; Gerhardt, *Rev. Scient.* 10, 192; Nicholson a. Abel, *C. J.* 2, 241; Henry, *Ph.* 8, 401; Corriol, *Ph.* 11, 492; Robiquet, *Ph.* 11, 580; Henry, jun., *J. Ph.* 16, 752; Berlekom, *Z.* [2] 2, 443; Shenstone, *Ph.* [3] 8, 445). Occurs also in the bark of *Erythrophlœum guineense*, from which the pigmies of Central Africa prepare their arrow-poison (Holmes, *Ph.* [3] 21, 921).

Preparation.—1. The nuts (1 kilo) are softened by steam, dried, powdered, and digested with alcohol (5 kilos of S.G. ·856) acidulated with H_2SO_4 (45 g.). Lime is added to the filtrate; and, after standing, the decanted liquid evaporated; the residue dissolved in dilute acid; and the filtrate ppd. by ammonia. The strychnine is separated from brucine by crystallisation from alcohol (Henry).—2. The dilute alcoholic extract of nux vomica is evaporated to a small bulk and ppd. by lead acetate. The filtrate is mixed with magnesia and left for a few days. The pp. is dissolved in alcohol of 83 p.c. and evaporated to crystallisation. Strychnine is first deposited, and afterwards brucine. The bases are further purified by crystallisation of their nitrates, the nitrate of strychnine separating first.

Properties.—Trimetric prisms, permanent in the air and not altered by light. Lævorotatory, the rotation varying greatly with the nature of the solvent (Hoorweg, *A.* 166, 76; Tykociner, *R. T. C.* 1, 146). The dispersive power is constant (Grimbert, *J. Ph.* [5] 16, 295). At 169° it forms a sublimate of minute needles (Blyth). Very bitter. Alkaline in reaction. Strychnine is a violent poison, acting on the spinal cord and producing convulsions (Lovett, *J. Physiol.* 9, 99). ·03 g. may be fatal. Strychnine dissolves with difficulty in acids, the solubility being greater the more dilute the acid; when a conc. solution of a strychnine salt is slightly acidified a pp. is formed which dissolves in excess of acid, forming a solution which yields a pp. on dilution. Thus H_2SO_4 added to a conc. solution of strychnine sulphate ppts. the acid sulphate $B'H_2SO_4$, the mother-liquor retaining ·113 p.c. of salts. HCl added to a solution of strychnine hydrochloride ppts. B'HCl $1\frac{1}{2}$aq in needles, the mother-liquor retaining ·413 p.c. of salt (Hanriot a. Blarez, *C. R.* 96, 1504). Strychnine is readily soluble in dilute hypophosphorous acid (Jones, *Ph.* [3] 20, 256). KCy added to a solution of a salt of strychnine ppts. the pure base (Flückiger, *N. J. P.* 38, 138; Weith, *B.* 4, 527). A solution of ICl gives a yellow pp. v. sol. HClAq, from which it crystallises on cooling (Dittmar, *B.* 18, 1612).

Reactions.—1. *Dry distillation* yields carbazole, H, C_2H_2, and C_2H_4 (Loebisch a. Schoop, *M.* 7, 614).—2. Distillation with *lime* yields (β)-methyl-pyridine, methyl-indole (scatole), C_2H_4, $NEtH_2$, and NH_3 (Stoehr, *B.* 20, 810, 1108, 2729; *J. pr.* [2] 42, 405).—3. Distillation with *soda-lime* gives carbazole, scatole, and (β)-methyl-pyridine (Loebisch a. Malfatti, *M.* 9, 628).—4. Distillation with KOH gives indole (Goldschmidt, *B.* 15, 1977) and butyric acid (Loebisch a. Schoop, *M.* 7, 93).—5. Distillation with *zinc-dust* at 400° *in vacuo* yields solid $C_{21}H_{22}N_2O$, which dissolves in alcohol with blue fluorescence, and gives no colour with $K_2Cr_2O_7$ and H_2SO_4. Zinc-dust at a red heat gives H, C_2H_4, C_2H_2, NH_3, and carbazole (Loebisch a. Schoop, *M.* 7, 609), and (γ)-lutidine (Scichilone a. Magnanini, *G.* 12, 444).—6. Alkaline $KMnO_4$ yields oxalic acid, CO_2, NH_3, and a crystalline acid [195°] (Hoogewerff a. Van Dorp, *R. T. C.* 2, 181). Half the nitrogen is given off as ammonia (Wanklyn a. Chapman, *C. J.* 21, 161).—7. $KMnO_4$ in dilute acid solutions yields an amorphous acid $C_{11}H_{11}NO_3$ aq (?) (Plugge, *R. T. C.* 2, 270), which yields amorphous $C_{11}H_{10}AgNO_3$ aq (Hanriot, *C. R.* 96, 1671).—8. By treatment with CrO_3 and H_2SO_4 it yields the same oxidation product $C_{14}H_{18}N_2O_4$ as that obtained from brucine under the same treatment (Hanssen, *B.* 18, 1917).—9. PCl_5 (1 pt.) acting on strychnine hydrochloride (8 pts.) under boiling chloroform yields a compound crystallising from benzene in needles [224°], possibly penta-chloro-strychnine (Stoehr, *J. pr.* [2] 42, 414).—10. Boiling HNO_3 forms cacostrychnine and picric acid (Shenstone, *C. J.* 47, 142); nitric acid forms 20 p.c. of di-nitro-di-oxy-quinoline carboxylic acid $C_{10}H_5N_3O_8$, which yields KA′, is reduced by $SnCl_2$ to $C_{10}H_9N_3O_4$ (a body having acid and basic properties), and when heated with water is split up into CO_2 and di-nitro-di-oxy-quinoline (Tafel, *B.* 26, 353).—11. *Baryta water* in sealed tubes at 140° forms two bases, $C_{21}H_{26}N_2O_4$ and $C_{21}H_{28}N_2O_5$, both crystallising from water (Gal a. Etard, *C. R.* 87, 362).—12. *Alloxan* added to a solution of strychnine in a saturated solution of SO_2 forms small colourless prisms of $B'C_4H_2N_2O_4H_2SO_3$ aq (Pellizzari, *A.* 248, 150).—13. *Iodoform* (5 g.) and strychnine (12 g.) dissolved in hot alcohol (500 c.c.) deposit on cooling crystals of B'_3CHI_3, sol. ether and chloroform, but decomposed by light, hot water, and dilute acids (Lextreit, *C. R.* 92, 1057).—14. *Chloro-acetic acid* at 180° forms $C_{23}H_{24}N_2O_4$, a base which crystallises in silky needles, v. sol. hot water and alcohol, insol. ether (Roemer, *Z.* 1871, 435). It yields $(C_{23}H_{21}N_2O_4)_2PtCl_6$.—15. AcCl forms B′AcCl, which gives $(B'AcCl)_2PtCl_4$ (Konrad, *J.* 1874, 876).—16. *Chloro-acetone* at 135° yields $B'C_3H_5ClO$, S. 6·5 at 15°, which yields $(B'C_3H_5ClO)_2PtCl_4$ 2aq and $B'C_3H_5OSO_4H$ 1½aq (Konrad).—17. Aqueous SO_2 and alloxan give colourless prisms of $B'SO_3HC_4H_3N_2O_4$ aq (Pellizzari, *G.* 18, 329).

Detection.—1. H_2SO_4 forms a colourless solution which with $K_2Cr_2O_7$ gives a blue colour, changing through violet and red to yellow (Otto, *A.* 60, 273). A drop of nitric acid and PbO_2 or MnO_2 may be used instead of $K_2Cr_2O_7$ (Marchand, *B. J.* 24, 400; Davy, *A.* 88, 402). $KMnO_4$ and Ag_2O act in like manner (Lyman, *Fr.* 12, 126). The colour with H_2SO_4 and $K_2Cr_2O_7$ is not shown in presence of brucine (Hanriot, *C. R.* 97, 267), and is interfered with by quinine, morphine, and sugar (Brieger, *J.* 1850, 617; Vogel, *J.* 1853, 686; Flückiger, *Fr.* 28, 102).—2. A minute quantity of $KClO_3$ added to a warm solution in dilute HNO_3 gives a scarlet colour, changed by ammonia to brown, and then, on evaporation to dryness, becoming green (C. L. Bloxam, *C. N.* 55, 155).—3. Ammonium vanadate in H_2SO_4 gives a blue colour, turned red by potash (Mandelin, *Fr.* 23, 240).—4. Chlorine water gives a pp.—5. Strychnine can be extracted from beer containing the poison by shaking with animal charcoal, the charcoal being subsequently extracted with alcohol (Graham a. Hofmann, *A.* 83, 39; *cf.* Wagner, *Fr.* 6, 387).—6. Obtained from acid liquids by adding ammonia and immediately shaking with chloroform (Cloetta, *Fr.* 5, 265; Gray, *Fr.* 12, 125).—7. A liquid containing strychnine sulphate may be shaken with benzene without loss of strychnine, but if the liquid be neutralised by magnesia the free strychnine can be extracted by benzene (Dragendorff, *Z.* [2] 2, 27).—8. A 1 p.c. solution of strychnine strongly acidified by HCl is ppd. by K_4FeCy_6 while brucine remains in solution (Holst a. Beckürts). This may be used as a volumetric method. Strychnine and brucine may also be separated by crystallisation of their picrates (Gerock, *Ar. Ph.* [3] 27, 158).

Salts.—$B'HCl$ 1½aq (Regnault, *A.* 26, 17). Trimetric crystals; $a:b:c = ·484:1:·466$ (Stoehr, *J. pr.* [2] 42, 399). Neutral in reaction. S. 2 at 22°. Lævorotatory. $[\alpha]_r = -28°$.—$B'HAuCl_4$. Orange crystals (from alcohol) (Nicholson a. Abel, *C. J.* 2, 241; *A.* 71, 84). Decomposed by boiling water (O. De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2PtCl_6$: golden scales (from alcohol). S.G. $\frac{13·5}{4}$ 1·779 (Clarke, *Am.* 2, 175).—$B'_2H_2PtCl_6$ aq (Schmidt, *A.* 180, 295).—$B'_2H_2ZnCl_4$ aq: prisms (Grafinghoff, *Bl.* [2] 4, 391).—$B'_2H_2CdCl_4$ (Galletly, *N. ed. P. J.* 4, 94).—$B'HHgCl_3$. Crystals (from alcohol).—$B'HgCl_2$: insol. alcohol, water, and ether.—$B'_2H_2SO_4 2HgCl_2$.—$B'_2H_2PdCl_4$: dark-brown needles (from alcohol).—$B'HCl2HgCy_2$: tables (Brandis, *A.* 66, 268).—$B'HgCy_2$: small prisms, sl. sol. water and alcohol, insol. ether.—$B'HBr$ aq: needles, sol. water and alcohol.—$B'HI$ aq: plates or needles, almost insol. cold water.—$B'HI_3$. S. ·007 at 15°. Reddish-brown pp. got by adding a solution of I in HIAq to a salt of strychnine. Crystallises from alcohol in dark-brown needles with bluish metallic lustre. Dichroic (brown and yellow) in polarised light. M. sol. hot alcohol, sl. sol. chloroform, nearly insol. CS_2 (Tilden, *C. J.* 18, 99; Herapath, *Pr.* 8, 149; Bauer, *Ar. Ph.* [3] 5, 289; Jörgensen, *A. Ch.* [4] 9, 115).—$B'HHgI_3$: yellow tables (from alcohol) (Groves, *C. J.* 2, 97).—$B'H_4F_4$ 2aq: prisms (Elderhorst, *A.* 74, 77).—$B'HNO_3$: needles.—$B'HClO_4$ aq: prisms, sl. sol. cold water (Boedeker, *A.* 71, 62).—$B'H_2SO_4$ 2aq: needles.—$B'_2H_2SO_4$. Four-sided prisms. Lævorotatory $[\alpha]_r = -26°$.—$B'_2H_2SO_4$ 5aq: long thin prisms. Got by crystallisation between 109° and 95°.—$B'_2H_2SO_4$ 6aq. Obtained by cooling a conc. solution to 95°–50° (Lextreit, *J. Ph.* [5] 6, 259; Rammelsberg, *B.* 14, 1231; *cf.* Baumhauer, *C. J.* 44, 485).—$B'_2H_2CrO_4$: lemon-yellow needles, sl. sol. water and alcohol.—$B'_2H_2S_2O_3$ 4aq. S. ·3 in the cold. Formed by atmospheric oxidation of a mixture of strychnine, alcohol, and ammonium sulphide (How, *C. N.* 18, 232).—$B'_2H_2S_6$. Formed from strychnine and alcoholic ammonium polysulphide (Hofmann, *B.* 1, 81; 10, 1087) and by atmospheric oxidation of a solution of strychnine in alcoholic H_2S (Schmidt, *B.* 5, 1267; 10, 1288; *A.* 180, 288). Orange needles, insol. water, alcohol, and ether.—$B'H_3PO_4$ 2aq. S. 19. Needles (Anderson, *A.* 66, 56).—$B'_2H_3PO_4$ 9aq: rectangular tables.—$B'H_3AsO_4$ ½aq. S. 7 in the cold; 20 in hot water.—$B'HAsO_3$: efflorescent cubes. S. 3 in the cold; 10 at 100°.—$B'_4H_4FeCy_6$ 4aq. Crystalline powder (Holst a. Beckürts, *Ar. Ph.* [3] 25, 313; *cf.* Brandis, *A.* 66, 257). By atmospheric oxidation in presence of water it is converted into strychnine and the ferricyanide (Beckürts, *B.* 18, 1235).—$B'H_4FeCy_6$: white powder, sol. hot water. Acid in reaction.—$B'_3H_3FeCy_6$ 6aq: golden prisms.—$B'_3(H_3CoCy_6)$ 4aq.—$B'_6(H_2NiCy_4)_3$ 8aq (Lee, *B.* 4, 789).—$B'_2H_2PtCy_4$ 2aq: needles (from alcohol).—Oxalate $B'_2H_2C_2O_4$: flat needles.—$B'_2H_2C_2O_4$ 4½aq.—$B'H_2C_2O_4$.—$B'HSCy$: long silky needles.—$B'HSCyCr(SCy)_3 2NH_3$. Red pp., v. sl. sol. hot water (Christensen, *J. pr.* [2] 45, 367).—$B'_2 2H_2Pt(SCy)_6$. Red crystals (Clarke and Owens, *Am.* 3, 351). — **Cyanurates:** $B'_3H_3O_3C_3N_3$ aq. [287°]. Prisms, sl. sol. water, m. sol. alcohol.—$B'H_3O_3C_3N_3$ aq. [295°]. Needles (Claus, *J. pr.* [2] 38, 228).—**Nitroprusside.** S. ·12 (Davy, *Ph.* [3] 11, 756). **Succinate** $B'_2C_4H_6O_4$ $6\frac{1}{2}$aq (Crespi, *G.* 13, 176).—**Tartrates:** $B'_2C_4H_6O_6$.—$B'_2C_4H_6O_6$ 4aq; white efflorescent needles (Arppe, *J. pr.* 53, 331).—$B'_2C_4H_6O_6$ 7aq (Pasteur, *A. Ch.* [3] 38, 437).—$B'C_4H_6O_6$ 3aq.—$B'C_4H_5(SbO)O_6$. Needles (Stenhouse, *A.* 129, 25).—**Malate** $B'_2C_4H_6O_5$ $3\frac{1}{2}$aq.—**Pyrotartrate** $B'_2C_5H_8O_4$ $3\frac{1}{2}$aq. — **Mucate** $B'_2C_6H_{10}O_8$. Long needles (Ruhemann a. Dufton, *C. J.* 59, 754).

Di-hydrate B'2aq. *Strychnol.* Formed by warming strychnine with alcoholic NaOEt, adding water, and evaporating. The brown oily layer that forms is allowed to solidify, dissolved in water, and ppd. by CO_2. The pp. is dissolved in NH_3Aq and re-ppd. by expelling NH_3 by air (Loebisch a. Schoop, *M.* 7, 83). The same body is got by heating strychnine (15 g.) with BaO_2H_2 (30 g.) for 12 hours at 140° (Tafel, *B.* 23, 2737). Minute wedge-shaped needles, sl. sol. cold water, insol. alcohol and ether. Darkens at 150°. Sol. dilute alcohol and solutions of ammonium salts; sol. acids. Converted into strychnine on warming with dilute acids. Dilute HNO_3 and a little $NaNO_2$ give a crimson colour. Bromine water gives a pale-purple colour. Does not give the strychnine reaction with H_2SO_4 and $K_2Cr_2O_7$. On heating at 100° with NaOMe and MeI it is converted into $C_{21}H_{22}N_2O_2Me_5I$ 2aq, crystallising in needles.

Tri-hydrate v. Reaction 10.

Pentahydrate B'5aq. [215°]. Got by heating strychnine with alcoholic NaOEt (Tafel). Needles, more soluble than the dihydrate. Becomes very hygroscopic when dried *in vacuo*.

Benzoyl derivative $C_{21}H_{21}BzN_2O_2$. V. sl. sol. water (Schützenberger, *A.* 108, 353; *C. R.* 47, 233).

Methylo-iodide B'MeI. S. ·5 in the cold (Stahlschmidt, *P.* 108, 513). Poisonous (Crum Brown a. Fraser, *Tr. E.* 25). Formed by heating with MeI in sealed tubes. Pearly plates. Yields $B'MeI_3$ (Jörgensen, *J. pr.* [2] 3, 157) and the salts B'MeBr, B'MeCl 2aq, $B'_2Me_2PtCl_6$, $B'MeAuCl_4$, $B'_2Me_2SO_4$ 5aq, $B'MeHSO_4$, $B'MeH_2PO_4$ 2aq, $B'MeCl2\frac{1}{2}HgCl_2$, $B'MeNO_3$, and $B'_2Me_2FeCy_4$.

Methylo-hydroxide B'MeOH or $C_{20}H_{22}O(NH){\ll}\genfrac{}{}{0pt}{}{NMe}{CO}{>}O$. Formed from B'MeI by successive treatment with Ag_2SO_4 and baryta (Tafel, *B.* 23, 2733; *A.* 264, 62). Colourless crystals (containing 4aq), v. sol. alcohol, but a product containing less water soon separates. Poisonous. Gives the same colour-reactions as strychnic acid. Alcohol and Na yield a compound [158°]. MeI forms B'MeIMeOH crystallising in plates, decomposed at 280°.

Isomeride of the methylo-hydroxide $C_{22}H_{28}N_2O_3$ 7aq. Formed from the methylo-iodide of isostrychnic acid, Ag, and Ag_2O at 40° (Tafel, *A.* 264, 81). Colourless needles; v. e. sol. hot water and alcohol, insol. ether.

Methyl-strychnine methylo-hydroxide $C_{23}H_{28}N_2O_3$ *i.e.* $C_{20}H_{22}O(NMe){\ll}\genfrac{}{}{0pt}{}{NMe}{CO}{>}O$. Formed from B'MeIMeOH by successive treatment with Ag_2SO_4 and baryta. Got also by the action of Ag_2O on the methylo-iodide of methyl-strychnic acid (Tafel, *B.* 23, 2735; *A.* 264, 66). Prisms (containing 6aq), v. sol. hot water and alcohol, nearly insol. ether. Gives a blood-red colour with HNO_3, CrO_3, or $FeCl_3$. Forms with acids salts which differ from those prepared by the action of silver salts on B'MeIMeOH. Forms a crystalline nitroso-derivative, v. sol. water and warm alcohol, forming a yellow solution changed by NaOH to brownish-red and olive-green. HI yields the methylo-iodide of methyl-strychnic acid. Diazobenzene sulphonic acid gives a brownish-red dye.—**Hydroiodide.** S. 7. Plates.—**Methyloiodide** $C_{24}H_{31}N_2IO_3$. S. 1. Needles.

Isomeride of methyl-strychnine methylo-hydroxide $C_{23}H_{28}N_2O_3$ 3aq. Formed from the methylo-hydroxide of methyl-isostrychnic ether (Tafel, *A.* 264, 82). Crystals, v. sol. hot water and alcohol, insol. ether. Yields a dye with diazo-benzene sulphonic acid.

Ethylo-iodide B'EtI. S. ·6 at 15°; 2 at 100°. Formed by heating strychnine with alcohol and EtI at 100° (How, *A.* 92, 338). Four-sided prisms. Not attacked by KOHAq. Gives the strychnine reaction with $K_2Cr_2O_7$ and H_2SO_4. Converted by moist silver oxide into the base B'EtOH 2aq, which yields the salts $B'EtNO_3$, $B'_2Et_2PtCl_6$, $B'EtHCO_3$, $B'EtHCrO_4$ aq, B'EtCy [105°] (Claus a. Merck, *B.* 16, 2748), and $B'EtI_3$ (Jörgensen, *A. Ch.* [4] 11, 115).

Isoamylo-chloride $B'C_5H_{11}Cl$ $\frac{1}{2}$aq. Formed by heating strychnine with isoamyl chloride (How, *Tr. E.* 21, 1, 27). Prisms. Yields $B'C_5H_{11}OH$, $B'C_5H_{11}I_3$, $B'C_5H_{11}I_5$, crystallising in black prisms (Jörgensen, *J. pr.* [2] 3, 145), and $B'EtHCrO_4$.

Bromo-ethylo-bromide $B'C_2H_4Br_2$. Formed by heating strychnine with ethylene bromide and alcohol (Ménétriès, *J. pr.* 85, 230). White crystals, sl. sol. cold water and alcohol. Converted by $AgNO_3$ into $B'C_2H_4Br.NO_3$ and by Ag_2SO_4 into $B'C_2H_4Br.SO_4H$, whence baryta produces alkaline $B'C_2H_4Br.OH$.—$(B'C_2H_4Br)_2PtCl_6$.—$B'C_2H_4BrI_3$: shining brown laminæ.—Moist Ag_2O converts $B'C_2H_4Br_2$ into $B'C_2H_3OH$, which is alkaline and is converted in aqueous solution by chlorine into $C_{23}H_{21}Cl_3N_2O_2$.—$B'C_2H_3CrO_4H$.—$(B'C_2H_3Cl)_2PtCl_4$.

Chloro-ethylo-hydroxide $B'ClC_2H_4.OH$. Got by heating strychnine with glycolic chlorhydrin at 150° (Messel, *A.* 157, 7). Silky needles (containing aq). Yields $(B'C_2H_4OH)_2SO_4$ 2aq, which is converted by baryta into crystalline $(B'C_2H_4OH)OH$ $2\frac{1}{2}$aq.—$(B'C_2H_4OH)_2PtCl_6$.

Benzylo-chloride $B'C_7H_7Cl$. [263°]. Prisms (containing aq). Yields $(B'C_7H_7Cl)_2PtCl_4$ [216°], $B'C_7H_7NO_3$ [c. 264°], $(B'C_7H_7)_2Cr_2O_7$, and $B'C_7H_7SCy$ [237°] (Garzarolli, *M.* 10, 1).

Benzylo-hydroxide $B'C_7H_7OH$. Plates.

Chlorostrychnine $C_{21}H_{21}ClN_2O_2$. $[\alpha]_D = -105°$. Formed, together with di- and tri-chloro-strychnine, by passing Cl into a solution of strychnine hydrochloride (Laurent, *A. Ch.* [3] 24, 312; *A.* 69, 14; Richet a. Bouchardat, *C. R.* 91, 990). Crystalline, v. sol. alcohol, ether, and chloroform. Chlorostrychnine forms a hydrate $C_{21}H_{21}ClN_2O_2$ 3aq on heating with alcoholic potash.—$B'_2H_2SO_4$ 7aq.

Dichloro-strychnine $C_{21}H_{20}Cl_2N_2O_2$. Needles (from alcohol).

(α)-Tri-chloro-strychnine $C_{21}H_{19}Cl_3N_2O_2$. Formed by saturating a solution of strychnine hydrochloride with Cl. Minute crystals (from alcohol). Yields a trihydrate which is not very poisonous.

(β)-Tri-chloro-strychnine $C_{21}H_{19}Cl_3N_2O_2$. Formed by heating strychnine hydrochloride with PCl_5 and chloroform (Stoehr, *J. pr.* [2] 42, 412; *B.* 20, 813). Microcrystalline powder (from alcohol). Gives the strychnine reaction with $K_2Cr_2O_7$ and H_2SO_4.—B′HCl: plates (from dilute alcohol).—$B'H_2SO_4$. Plates, m. sol. water.

Bromo-strychnine $C_{21}H_{21}BrN_2O_2$. [222°]. Formed by adding Br (2 at.) to a solution of strychnine hydrochloride (1 mol.), ppg. by alkali, and recrystallising from alcohol (Shenstone, *C. J.* 47, 139; Beckürts, *B.* 18, 1236; Loebisch a. Schoop, *M.* 6, 855). Trimetric crystals; $a:b:c = 1·459:1:1·195$ (Miers, *C. J.* 47, 144).—B′HCl.—B′HBr.—$B'HNO_3$.—$B'_2H_2SO_4$7aq.

Methylo-iodide B′MeI. Pearly plates, sol. alcohol. Converted by moist Ag_2O into B′MeOH4aq.

Dibromide $C_{21}H_{21}Br_3N_2O_2$. Got by adding Br to a solution of strychnine at 40°. Bright yellow crystalline powder.

Di-bromo-strychnine $C_{21}H_{21}Br_2N_2O_2$. Got by adding Br to strychnine in chloroform. Trimetric crystals, v. sol. chloroform and dilute alcohol.—B′HCl: needles.

Nitro-strychnine $C_{21}H_{21}(NO_2)N_2O_2$. [225°]. Formed by adding strychnine nitrate to H_2SO_4 (Loebisch a. Schoop, *M.* 6, 845; 7, 59). Golden plates (from alcohol). Gives no colour with H_2SO_4 and $K_2Cr_2O_7$. Dissolves in acids and alkalis. On heating with alcoholic potash it is converted into xanthostrychnol $C_{21}H_{21}N_3O_4$, which forms ruby-red crystals (containing 2aq) and gives salts with acids and bases.—B′HCl.—$B'_2H_2PtCl_6$.—B′2KOH: red deliquescent needles.—$B'_2BaO_2H_2$ 2aq.—$Ag_2C_{21}H_{19}N_3O_4$: unstable pp.

(α)-Di-nitro-strychnine $C_{21}H_{20}(NO_2)_2N_2O_2$. [226°]. Formed by passing nitrous acid gas into an alcoholic solution of strychnine nitrate (Claus a. Glassner, *B.* 14, 774). Orange-yellow plates. Converted by dilute HNO_3 into cacostrychnine.—$B'HNO_3$: yellow nodules (from acetone), v. sl. sol. hot water.

(β)-Di-nitro-strychnine. Formed by dissolving strychnine (60 g.) in fuming HNO_3 (300 g.) at −10° (Hanriot, *C. R.* 96, 585). Transparent amber-yellow prisms (from chloroform-alcohol), sol. hot water and alcohol, v. sol. chloroform. Decomposes at about 202°.—B′HCl.—*Nitrate*: plates (from hot water).

Amido-strychnine *v.* vol. i. p. 184.

Di-amido-strychnine, *ibid.*

Cacostrychnine *v.* vol. i. p. 654.

Deoxystrychnine $C_{21}H_{26}N_2O$ *i.e.* $C_{20}H_{26}N{<}\begin{smallmatrix}N\\CO\end{smallmatrix}$. [172°]. Formed by boiling strychnine with HI and P (Tafel, *A.* 268, 245). Crystalline mass (containing 3aq), almost insol. water, sl. sol. ether and benzene, v. sol. alcohol. Melts, when hydrated, at 75°. Poisons like strychnine. Very bitter. Very little produces vomiting. Lævorotatory, a 10 p.c. solution rotating 1·6° in a 100 mm. tube. Its solution in H_2SO_4 is coloured bluish-violet by $K_2Cr_2O_7$, quickly becoming brown. Its salts are more soluble than those of strychnine.—B′HI aq. Groups of prisms.—$B'_2H_2Cr_2O_7$. Thin yellow needles.—$B'_2H_2PtCl_6$.

Methylo-iodide B′MeI. Crystals. S. c. 10 at 100°.

Strychnine sulphonic acid $C_{21}H_{21}(SO_3H)N_2O_2$. Formed by dissolving dry strychnine sulphate in fuming H_2SO_4 (containing 30 p.c. anhydride extra) in the cold and allowing to stand a fortnight (Loebisch a. Schoop, *M.* 6, 857). Deliquescent mass. Does not give the strychnine reaction with $K_2Cr_2O_7$ and H_2SO_4.

Strychnine sulphonic acid. Formed by heating strychnine with H_2SO_4 (2 pts.) at 100° (Stoehr, *B.* 18, 3429; Guareschi, *G.* 17, 109). Amorphous powder, v. sl. sol. water and alcohol, sol. dilute acids and alkalis. Does not give a colour with $K_2Cr_2O_7$ and H_2SO_4. Not poisonous.—NH_4A': v. sol. water, insol. alcohol.—KA′: m. sol. water.—BaA'_2: amorphous pp.

Strychnine disulphonic acid $C_{21}H_{20}(SO_3H)_2N_2O_2$. Got by heating strychnine with H_2SO_4 and SO_3 at 150°. Amorphous, v. sol. water, v. sl. sol. benzene, insol. alcohol and ether.—Na_2A'' 6aq.—BaA″: plates, sol. water.—BaA″7aq.—$Ba(HA'')_2$: yellow powder.

STRYPHNIC ACID $C_4H_3N_5O_2$. Got by adding HOAc to a mixture of uric acid and KNO_2 and evaporating (Gibbs, *B.* 2, 341). Small pale-yellow crystals, sol. hot water. Sodium-amalgam forms crimson crystals. — KA′ 1½aq: yellow needles.—MgA'_2 6aq.—CaA'_2 2aq.—SrA'_2 6aq.—BaA'_2 2aq.—PbA'_2.—$Pb_2A'_2O$ 3aq.

STYCERIC ACID *v.* PHENYL-GLYCERIC ACID.

STYCERIN CHPh(OH).CH(OH).CH_2OH. Formed by heating CHPhBr.CH_2Br.CH_2OH (*v.* DI-BROMO-PHENYL-PROPYL ALCOHOL) with 30 pts. water and some AgOAc at 150°–165° (Grimaux, *J.* 1873, 404). Yellow gummy mass with bitter taste. V. sol. Aq and alcohol, nearly insol. ether.

STYPHNIC ACID *v.* TRI-NITRO-RESORCIN.

STYRACIN *v.* *Cinnamyl ether* of CINNAMIC ACID.

STYRENE C_8H_8 *i.e.* C_6H_5.CH:CH_2. *Styrol. Styrolene. Cinnamene. Phenyl-ethylene.* Mol. w. 104. (144°) (Schiff, *A.* 220, 93). S.G. $^{20}_{4}$ ·9074. $\mu_D = 1·541$ (Madan, *C. J. Proc.* 1, 107). S.V. 131 (Schiff). R_∞ 58·1 (Nasini a. Bernheimer, *G.* 1, 93). Occurs in liquid storax (Bonastre, *J. Ph.* 17, 338; Simon, *A.* 31, 265; Blyth a. Hofmann, *A.* 53, 293, 325) and in coal tar (Berthelot, *A. Suppl.* 3, 368; Krämer a. Spilker, *B.* 23, 3282).

Formation.—1. By distilling cinnamic acid alone or with lime or baryta (Gerhardt a. Cahours, *A. Ch.* [3] 1, 96; Kopp, *C. R.* 53, 634; Howard, *C. J.* 13, 135; Kraemer, Spilker, a. Eberhardt, *B.* 23, 3269).—2. By distilling cupric cinnamate (Hempel, *A.* 59, 316).—3. By distilling balsam of Peru with pumice (Scharling, *A.* 117, 184).—4. By distilling dragon's blood alone or with zinc-dust (Glénard a. Bondault, *A.* 53, 325; Bötsch, *M.* 1, 610).—5. By heating acetylene at a dull-red heat (Berthelot, *C. R.* 62, 905, 947; *A.* 141, 181).—6. By passing ethylene alone or mixed with benzene or diphenyl through a red-hot tube (Berthelot, *Z.* [2] 4, 384; *A.* 142, 257; Barbier, *C. R.* 79, 660; Ferko, *B.* 20, 660).—7. By passing ethyl-benzene through a red-hot tube (Berthelot, *Z.* [2] 4, 589).—8. By heating C_6H_5.CH_2.CH_2Br alone or with alcoholic potash at 180° (*B.*; Thorpe, *Z.* 1871, 130).—9. By heating C_6H_5.CHBr.CH_3 with alcoholic KCy (Radziszewski, *B.* 7, 140).—10. By distilling C_6H_5.CH(OAc).CH_3 (R.). — 11. By heating C_6H_5.CH(OH).CH_3 (derived from acetophenone) with $ZnCl_2$ (Emmerling a. Engler, *B.* 4, 147).—12. By the action of acetylene on benzene in presence of $AlCl_3$ (Varet a. Vienne, *Bl.* [2] 47, 918; *C. R.* 104, 1375).—13. From phenyl-acetylene, zinc, and HOAc (Aronstein a. Hollemann, *B.* 22, 1184).

Properties.—Oil, with aromatic odour. Inactive to light (Van't Hoff, *Bl.* [2] 25, 175). Miscible with alcohol and ether. Changes on keeping, or on heating in a sealed tube at 300°, to solid metastyrene. Combines with Cl_2 and Br_2. HBr forms C_6H_5.CHBr.CH_3. HCl forms PhCHCl.CH_3 only (Schramm, *B.* 26, 1709). Potash has no action. Fuming HNO_3 forms nitro-styrene. Chromic acid mixture forms benzoic acid. Conc. H_2SO_4 changes it to metastyrene. On heating with aqueous $NaHSO_3$ at 120° styrene forms the compound $C_8H_8NaHSO_3$ [306°] (W. von Miller, *N. R. P.* 24, 31). Condenses, in presence of H_2SO_4, with toluene and xylene, forming di-phenyl-propane and phenyl-tolyl-propane respectively (Kraemer a. Spilker, *B.* 23, 3169).

Metastyrene $(C_8H_8)_x$. S.G. $\frac{13}{}$ 1·054. μ_D 1·593 (Madan, *C. J. Proc.* 1, 107). Occurs in liquid storax (Kovalevsky, *A.* 120, 66). Formed from styrene on keeping or on heating in a sealed tube at 200°. Formed also by heating styrene with aqueous $NaHSO_3$ at 110° (Miller, *A.* 189, 341). Transparent solid without taste or smell, becomes sticky when warmed. Highly refractive. Insol. water and alcohol, sl. sol. ether. Inactive to light (Van't Hoff, *B.* 9, 1339; *cf.* Berthelot, *C. R.* 85, 1191). Changes to styrene on distillation. Cl and Br act slowly, forming the same compounds as with styrene.

Di-styrene $C_{16}H_{16}$ *i.e.* Ph.CH:CH.CHMe.Ph(?). (c. 315° i.V.). S.G. $\frac{0}{}$ 1·027; $\frac{15}{}$ 1·016. V.D. 7·07 (calc. 7·2). Got by boiling cinnamic acid with H_2SO_4 (1 vol.) and water ($1\frac{1}{2}$ vols.) (Erlenmeyer, *A.* 135, 122; Fittig a. Erdmann, *A.* 216, 187). Liquid, with blue fluorescence, which slowly disappears. Inactive to light. If kept boiling for a long time it decomposes, forming toluene, styrene, high boiling products, and probably iso-propyl-benzene.

Reactions.—1. Chromic mixture gives benzoic acid.—2. Bromine gives the di-bromide $C_{16}H_{16}Br_2$ [102°], crystallising from ether in needles. V. e. sol. CS_2, ether or benzene, v. sol. hot alcohol.

Solid distyrene $C_{16}H_{16}$. [119°]. A product of the distillation of cinnamic acid or of its Ca salt (Engler a. Leist, *B.* 6, 256; Miller, *A.* 189, 340). Formed also by passing $C_6H_5.C_2H_3Br_2$ over red-hot lime (Radziszewski, *B.* 6, 494). Tables. Yields a dibromide $C_{16}H_{16}Br_2$ [238°], crystallising from benzene in needles (Liebermann, *B.* 22, 2256).

References.—Amido-, Bromo-, Bromo-amido-, Bromo-nitro-, Chloro-, Chloro-nitro-, Nitro-, and Nitro-amido- Styrene.

STYRENE DIBROMIDE *v.* Di-bromo-ethyl-benzene.

STYRENE DICARBOXYLIC ACID $C_{10}H_8O_4$ *i.e.* [1:2] $CO_2H.C_6H_4$.CH:CH.CO_2H. *o-Carboxy-cinnamic acid.* [175°]. Formed by heating the salts of oxy-carboxy-phenyl-propionic acid (Gabriel a. Michael, *B.* 10, 1558, 2200). Slender needles (from water). Changed on fusion into the lactone of oxy-carboxy-phenyl-propionic acid.—PbA″.—Ag_2A'': sticky pp.

Isomeride *v.* *p*-Carboxy-cinnamic acid, vol. ii. p. 190.

STYRENE DICHLORIDE *v.* *ωa*-Di-chloro-di-ethyl-benzene.

STYRENE DI-IODIDE *v.* Di-iodo-ethyl-benzene.

STYRENE DISULPHOCYANIDE $C_8H_8(SCN)_2$. [102°]. Formed by heating C_6H_5CHBr.CH_2Br with potassium sulphocyanide in alcohol (Nagel, *A.* 216, 323). Pale-yellow needles, v. sol. ether, hot benzene, and toluene. Crystallises from benzene as $C_{10}H_8S_2N_2C_6H_6$ [62°]. Alcoholic ammonium sulphide at 100° forms $(C_8H_8)_2S$ [151°]. Cold fuming HNO_3 gives rise to the compound [1:4] $C_6H_4(NO_2)$.CH(SCy)CH_2(SCy) [112°] crystallising from alcohol in needles.

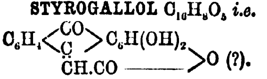
DI-STYRENIC ACID $C_{17}H_{16}O_2$ *i.e.* Ph.CH:CH.CPhH.CH_2.CO_2H or Ph.CH:CH.CH(CO_2H).CH_2Ph. Formed by boiling cinnamic acid with H_2SO_4 (1 vol.) diluted with water (1 vol.) (Fittig a. Erdmann, *A.* 216, 182). White amorphous powder. V. sl. sol. water, v. e. sol. ether, alcohol, or glacial acetic acid. It melts below 50°. May be distilled almost undecomposed.

Reactions.—1. *Sodium amalgam* has no action.—2. Br in CS_2 forms no bromide.—3. Boiling H_2SO_4 (1 vol.) mixed with water ($1\frac{1}{2}$ vols.) does not affect it.—4. Chromic mixture gives only benzoic acid.

Salts.—$Ca(C_{17}H_{15}O_2)_2$.—BaA'_2.—AgA′.

Ether.—EtA′. Liquid.

STYROGALLOL $C_{16}H_8O_5$ *i.e.*



$$\begin{array}{l}C_6H_4\left<\begin{array}{c}CO\\ C\end{array}\right>C_6H(OH)_2\\ \qquad\quad \overset{\|}{C}H.CO\text{ ——— }>O\ (?)\end{array}$$

Formed from cinnamic acid, gallic acid, and conc. H_2SO_4 at 50° (Jacobsen a. Julius, *B.* 20, 2588; von Kostanecki, *B.* 20, 3137). Yellow needles, which may be sublimed; sl. sol. hot alcohol. Not melted at 350°. With mordants it dyes like nitro-alizarin.

STYROLENE ALCOHOL *v.* Di-oxy-ethyl-benzene.

STYRONE *v.* Cinnamyl alcohol.

STYRONE DIBROMIDE *v.* (*di*)-Bromo-phenyl-propyl alcohol.

STYRYL-ACRYLIC ACID *v.* Phenyl-pentinoic acid.

STYRYL AMYL KETONE CARBOXYLIC ETHER $C_{17}H_{22}O_3$ *i.e.* C_6H_5.CH:CH.CO.CEt_2.CO_2Et. [102°]. Formed from di-ethyl-acetoacetic ether, benzoic aldehyde, and HCl in the cold (Claisen a. Matthews, *A.* 218, 184). Triclinic prisms (from ligroïn). Yields $C_{17}H_{22}Br_2O_3$ [55°] crystallising in small prisms.

STYRYL-ANGELIC ACID $C_{13}H_{14}O_2$ *i.e.* C_6H_5CH:CH.CH:CEt.CO_2H. [127°]. Formed by heating cinnamic aldehyde with butyric anhydride and sodium butyrate at 165° (Perkin, *C. J.* 31, 413). Crystals, v. sol. alcohol.—AgA′.

STYRYL BUTENYL KETONE $C_{13}H_{14}O$ *i.e.* C_6H_5.CH:CH.CO.CH:CMe_2. (179° at 14 mm.). Formed by passing HCl into a mixture of benzoic aldehyde and mesityl oxide (Claisen a. Claparède, *B.* 14, 351). Yellowish liquid, smelling like strawberries. Yields $C_{13}H_{14}Br_4O$ [180°].

STYRYL-CROTONIC ACID $C_{12}H_{12}O_2$. [158°]. Formed by heating cinnamic aldehyde with propionic anhydride and sodium propionate (Perkin, *C. J.* 31, 413). Prisms (from ligroïn). —AgA′: white pp., sl. sol. cold water.

STYRYL ETHYL KETONE CARBOXYLIC ACID $C_6H_5.CH:CH.CO.CH_2.CH_2.CO_2H$. *Cinnamoyl-propionic acid. Benzylidene-levulic acid.* [120°]. Formed from *β*-acetyl-propionic acid, benzoic aldehyde, and dilute KOHAq (Erdmann, *A.* 258, 130). Leaflets (from water). May be reduced to $C_6H_5.CH_2.CH_2.CO.CH_2.CH_2.CO_2H$ [88°].

Oxim $C_{12}H_{13}NO_3$. [149°].

STYRYL ETHYL OXIDE $C_{10}H_{12}O$ *i.e.* $C_6H_5.CH:CH.O.C_2H_5$. (217°). S.G. $\frac{0}{0}$ ·981. Formed from *ω*-chloro-styrene and NaOEt at 180° (Erlenmeyer, *B.* 14, 1868). Aromatic liquid. Converted by heating with water into alcohol and phenyl-acetic aldehyde.

STYRYL-ETHYL-PYRIDINE $C_{15}H_{15}N$ *i.e.* $C_6H_5.CH:CH.C\left\langle\begin{matrix}N.CH\\CH:CH\end{matrix}\right\rangle CEt$. *Ethyl-stilbazole.* [58°]. (356° cor.). Formed by heating methyl-ethyl-pyridine with benzoic aldehyde and $ZnCl_2$ at 220° (Plath, *B.* 21, 3087). Needles or plates, insol. water, v. sol. alcohol and ether, sl. sol. ligroïn. Bromine yields the dibromide $C_6H_5.CHBr.CHBr.C_5H_3EtN$. [128°]. — B′HCl. [193°]. — $B'_2H_2PtCl_6$ 2aq. [188°]. Needles.— $B'HAuCl_4$. [168°].—$B'HSnCl_3$ 3aq. [246°].— $B'HHgCl_3$. [196°].—$B'C_6H_3N_3O_7$. [203°].

STYRYL-GLYOXAL. *Oxim* $C_{10}H_9NO_2$ *i.e.* $C_6H_5CH:CH.CO.CH:N.OH$. [144°]. Formed from nitroso-acetone, benzoic aldehyde, and alcoholic NaOEt (Claisen a. Manasse, *B.* 22, 529). Crystals (from water or benzene). Gradually decomposes, with evolution of HCy.

STYRYL-GLYOXYLIC ACID $C_{10}H_8O_3$ *i.e.* $C_6H_5.CH:CH.CO.CO_2H$. Formed by saponification of its amide by conc. HClAq, and also by saturating a mixture of benzoic aldehyde and pyruvic acid with HCl (Claisen, *B.* 13, 2124; 14, 2472). Gummy mass, sol. water. Split up by alkalis, even in the cold, into benzoic aldehyde and pyruvic acid.—AgA′: pp.

Amide $CHPh:CH.CO.CO.NH_2$. [130°]. Prepared by the action of conc. HClAq and HOAc on the nitrile of cinnamic acid. Flat prisms or plates. Sol. ether and hot water.

Reference.—Nitro-styryl-glyoxylic acid.

STYRYL-HYDANTOIC ACID $C_{11}H_{12}N_2O_3$. [185°]. Formed by boiling styryl-hydantoïn with baryta water (Pinner a. Spilker, *B.* 22, 692). White plates, sol. alcohol and hot water. Boiling HClAq converts it into styryl-hydantoïn.—AgA′.

STYRYL-HYDANTOÏN *v.* Di-oxy-styryl-*m*-pyrazole.

STYRYLIDENE-THIO-GLYCOLLIC ACID *v.* Cinnamylidene-thio-glycollic acid.

DI-STYRYL-KETONE *v.* Di-benzylidene-acetone and Nitro- and Oxy- di-styryl-ketone.

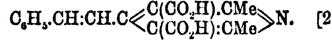
STYRYL-DI-METHYL-GLYOXALINE $C_{13}H_{14}N_2$ *i.e.* $C_6H_5CH:CH.C\left\langle\begin{matrix}NH.CMe\\N-CMe\end{matrix}\right.$. [202°]. Formed from di-methyl di-ketone, cinnamic aldehyde, and alcoholic ammonia at 100° (Wadsworth, *C. J.* 57, 11). Crystals, v. sol. alcohol.—$B'_2H_2PtCl_6$: minute yellow needles.

STYRYL METHYL KETONE *v.* Benzylidene-acetone and Nitro- and Oxy- styryl methyl ketone.

STYRYL METHYL KETONE CARBOXYLIC ETHER *v.* Benzylidene-acetoacetic ether, vol. i. p. 24.

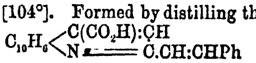
STYRYL-METHYL-OXAZOLE DIHYDRIDE $C_6H_5CH:CH.C\left\langle\begin{matrix}O.CHMe\\N.CH_2\end{matrix}\right.$. [81°]. Formed from *β*-bromo-propylamine hydrobromide, cinnamoyl chloride, and alcoholic potash (Elfeldt, *B.* 24, 3226). Transparent crystals. — $B'_2H_2PtCl_6$. [198°].—$B'C_6H_3N_3O_7$. [183°]. Needles.

STYRYL-METHYL-PYRIDINE $C_{14}H_{13}N$ *i.e.* $C_6H_5.CH:CH.C_5H_3MeN$. *Methyl-stilbazole.* (c. 323°). S.G. $\frac{0}{4}$ 1·0717. Formed by heating benzoic aldehyde with (*αγ*)-di-methyl-pyridine and $ZnCl_2$ at 215° (Bachér, *B.* 21, 3072). Oil, v. sol. alcohol and ether. Gives $C_{14}H_{13}Br_2N$. [140°]. May be reduced to $C_{14}H_{15}N$ (c. 293°) and $C_{14}H_{21}N$ (c. 288°).—Hydroiodide. [211°]. B'_2H_2PtCl6aq. [183°].—$B'HAuCl_4$. [142°].— $B'HHgCl_3$.—$B'C_6H_3N_3O_7$. [193°]. Yellow needles.

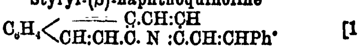
STYRYL-DI-METHYL-PYRIDINE DICARBOXYLIC ACID $C_{17}H_{15}NO_4$ *i.e.*  $C_6H_5.CH:CH.C\left\langle\begin{matrix}C(CO_2H).CMe\\C(CO_2H):CMe\end{matrix}\right\rangle N$. [241°]. Formed from its ether, which is got by the action of nitrous acid gas on an alcoholic solution of the dihydride $C_{21}H_{23}NO_4$ [149°], obtained from cinnamic aldehyde, acetoacetic ether, and alcoholic NH_3 (Epstein, *A.* 231, 1). Minute colourless tablets (containing 2aq), sl. sol. water, sol. alcohol. Melts at 219° when hydrated. Converted by hypochlorous acid into $C_{17}H_{13}NO_4$ 2aq (Messinger, *B.* 19, 196).—K_2A'' 3aq. —$(H_2A'')_2H_2PtCl_6$.—$H_2A''HCl$. Decomposed by water.

Ethyl ether Et_2A''. [39°]. Yields the salt $(Et_2A'')_2H_2PtCl_6$ [195°].

STYRYL-METHYL-THIO-GLYCOLLIC ACID *v.* Cinnamyl-thio-glycollic acid.

STYRYL-(*α*)-NAPHTHOQUINOLINE $C_{21}H_{15}N$ *i.e.* $C_6H_4\left\langle\begin{matrix}CH:CH.C.CH:CH\\\text{———}C.\ N\ :C.CH:CHPh\end{matrix}\right.$. [104°]. Formed by distilling the carboxylic acid  $C_{10}H_6\left\langle\begin{matrix}C(CO_2H):CH\\N=\!=\!=C.CH:CHPh\end{matrix}\right.$ [256°], which is got by the action of (*α*)-naphthylamine on cinnamic aldehyde and pyruvic acid (Döbner a. Peters, *B.* 23, 1233). Concentric groups of yellowish needles, sl. sol. alcohol.—$B'_2H_2PtCl_6$ 2aq: orange-yellow pp. — $B'_2H_2Cr_2O_7$. — $B'C_6H_3N_3O_7$. [230°]. Golden needles.

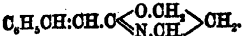
Carboxylic acid $C_{22}H_{15}NO_2$. [256°]. Yields BaA'_2 2aq, CuA'_2 aq, and AgA′.

Styryl-(*β*)-naphthoquinoline  $C_6H_4\left\langle\begin{matrix}\text{———}C.CH:CH\\CH:CH.C.\ N\ :C.CH:CHPh\end{matrix}\right.$. [175°]. Formed in like manner from (*β*)-naphthylamine. White silky needles or pearly plates.—Salts: $B'_2H_2PtCl_6$ 2aq. — $B'_2H_2Cr_2O_7$. — $B'C_6H_3N_3O_7$. [254°]. Golden needles, sl. sol. ether.

Carboxylic acid $C_{22}H_{15}NO_2$. [305°]. Lemon-yellow needles, sl. sol. hot alcohol.

STYRYL-OXAZOLE DIHYDRIDE $C_{11}H_{11}NO$ *i.e.* $C_6H_5CH:CH.C\left\langle\begin{matrix}O.CH_2\\N.CH_2\end{matrix}\right.$. [53°]. Formed from $CH_2Br.CH_2.NH.CO.CH:CHPh$ and alcoholic potash (Elfeldt, *B.* 24, 3225).—$B'_2H_2PtCl_6$. [194°]. Orange-yellow powder.—$B'C_6H_3N_3O_7$. [189°]. Yellow needles.

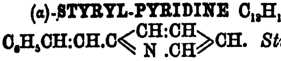
STYRYL-PENTOXAZOLE DIHYDRIDE



$C_6H_5CH{:}CH.C\Big\langle\begin{smallmatrix}O.CH_2\\ N.CH_2\end{smallmatrix}\Big\rangle CH_2$. [56°]. Formed by the action of alcoholic potash on the γ-bromo-propyl-amide of cinnamic acid (Elfeldt, *B.* 24, 3227). Needles.—$B'_2H_2PtCl_6$. Decomposes at 193°.—$B'C_6H_3N_3O_7$. [196°].

STYRYL-PHENOL *v.* OXY-DI-PHENYL-ETHYLENE.

(*a*)-**STYRYL-PYRIDINE** $C_{13}H_{11}N$ *i.e.*



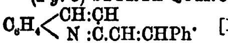
$C_6H_5CH{:}CH.C\Big\langle\begin{smallmatrix}CH{:}CH\\ N\ .CH\end{smallmatrix}\Big\rangle CH$. *Stilbazole.* [91°]. (325° cor.). Formed by heating benzoic aldehyde with methyl-pyridine and $ZnCl_2$ at 220° (Baurath, *B.* 20, 2719; 21, 818). Crystals, m. sol. alcohol.

Reactions.—1. Br forms $C_{13}H_{11}Br_2N$ [167°]. 2. HIAq reduces it to $C_{13}H_{13}N$ [−3°].—3. Na and HOEt reduce it to $C_{13}H_{19}N$ (288° cor.).

Salts.—B'HCl 4aq: needles. Melts at 177° when anhydrous.—$B'_2H_2PtCl_6$ 2aq. [188°]. Red needles.—$B'HAuCl_4$. [185°]. — $B'HHgCl_3$ aq. [183°].—$B'HI_3$. [159°]. Prisms, with blue reflex.

Reference.—OXY-STYRYL-PYRIDINE.

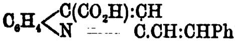
(*Py.* 3)-**STYRYL-QUINOLINE** $C_{17}H_{13}N$ *i.e.*



$C_6H_4\Big\langle\begin{smallmatrix}CH{:}CH\\ N\ {:}C.CH{:}CHPh\end{smallmatrix}$ [100°]. Formed by distilling its carboxylic acid (Doebner a. Peters, *B.* 22, 3008). Got also by heating (*Py.* 3)-methyl-quinoline with benzoic aldehyde and $ZnCl_2$ (Wallach, *B.* 16, 2008; Jacobsen a. Reimer, *B.* 16, 2606). Crystals. Yields $C_{17}H_{13}Br_2N$ [174°].—**Salts:** $B'_2H_2PtCl_6$ 2aq.—$B'H_2Cr_2O_7$ $2\frac{1}{2}$aq.

References.—NITRO- and OXY- STYRYL-QUINOLINE.

STYRYL-QUINOLINE CARBOXYLIC ACID



$C_6H_4\Big\langle\begin{smallmatrix}C(CO_2H){:}CH\\ N\ \text{———}\ C.CH{:}CHPh\end{smallmatrix}$ [295°]. Formed from cinnamic aldehyde, pyruvic acid, and aniline in alcohol (Doebner a. Peters, *B.* 22, 3006). Yellow needles, insol. water, sl. sol. ether.—MgA'_2: concentric groups of needles.

STYRYL-QUINOLINE SULPHONIC ACID $C_9H_5(SO_3H)N.CH{:}CHPh$. Formed by heating (*Py.* 1)-methyl-quinoline (*B.* 2)-sulphonic acid with benzoic aldehyde and $ZnCl_2$ for six hours at 170° (Busch a. Koenigs, *B.* 23, 2682). Crystals (containing 2aq). V. sol. 50 p.c. acetic acid.

STYRYL THIENYL KETONE $C_{13}H_{10}SO$ *i.e.* $C_6H_5CH{:}CH.CO.C_4H_3S$. [80°]. Formed by passing HCl into a mixture of thienyl methyl ketone and benzoic aldehyde (Brunswig, *B.* 19, 2895). Needles. Yields a dibromide $C_{13}H_{10}Br_2SO$ [157°] crystallising from alcohol in plates.

DI-STYRYL-DI-VINYL KETONE *v.* DI-PHENYL-DI-BUTINYL KETONE.

STYRYL-VINYL METHYL KETONE *v.* PHENYL-BUTINYL METHYL KETONE.

SUBERCOLIC ACID $C_6H_8(CO_2H)_2$. Formed in small quantity by the action of alcoholic potash on di-bromo-suberic acid (Hell a. Rempell, *B.* 18, 820). White powder, yielding at 225°–230° a sublimate of slender white needles.—BaA''.—CaA''.—MgA'' 2aq.—Ag_2A'': white pp.

SUBERCONIC ACID. [165°–170°]. A crystalline product of the action of alcoholic potash on bromo-suberic acid (Ganttner a. Hell, *B.* 15, 149).

SUBERENE CARBOXYLIC ACID $C_8H_{12}O_2$. [54°]. Formed by boiling chloro-suberonic acid $C_8H_{13}ClO_2$ with NaOHAq (Spiegel, *A.* 211, 119). Pearly plates, volatile with steam. Reduced by sodium-amalgam to suberane carboxylic acid $C_8H_{14}O_2$.

SUBERIC ACID $C_8H_{14}O_4$. Mol. w. 174. [140°]. (c. 300°). (279° at 100 mm.) (Krafft, *B.* 22, 816). S. ·142 at 15°. S. (ether) ·8 at 15°. H.C.p. 992,409 (Louguinine, *C. R.* 107, 597); 985,600 (Stohmann, *J. pr.* [2] 40, 215). H.F. 249,400 (S.).

Formation.—1. By the action of nitric acid upon cork (Brugnatelli, *Crell. Ann.* 1787, i. 145; Bouillon-Lagrange, *A. Ch.* 23, 2; *J. Ph.* 8, 107; Chevreul, *A. Ch.* 62, 323; 96, 182; Brandes, *S.* 32, 393; 33, 83; 36, 263; *A.* 9, 295; Bussy, *J. Ph.* 8, 107; 19, 425; Boussingault, *J. pr.* 7, 211; Harff, *N. Br. Arch.* 5, 303).—2. By the action of nitric acid upon oleïc and stearic acids (Laurent, *A. Ch.* [2] 66, 157; Bromeis, *A.* 35, 89), upon castor oil (Tilley, *A.* 39, 166; Dale, *A.* 132, 244; 199, 145; Grote, *A.* 130, 208), upon linseed oil (Saco, *A.* 51, 222), upon cocoa-nut oil (Wirtz, *A.* 104, 261), upon almond oil, upon spermaceti (Arppe, *A.* 120, 292; 124, 89), upon palmitolic acid (Schröder, *A.* 143, 33), upon paraffin (Pouchet, *C. R.* 79, 320), upon palm oil (Ganttner a. Hell, *B.* 13, 1165; 14, 1549), and upon myristic acid (Noerdlinger, *B.* 19, 1896).—3. Occurs among the products of the distillation of crude fatty acids in superheated steam (Cahours, *C. R.* 94, 610).—4. From di-oxy-stearic acid and alkaline $KMnO_4$ (Spiridonoff, *J. pr.* [2] 40, 250).—5. Suberic ether is formed by the electrolysis of $CO_2Et.CH_2.CH_2.CH_2.CO_2K$, the yield being 28 p.c. of the theoretical amount (Crum Brown a. Walker, *A.* 261, 120).

Properties.—Long needles (from water) or tables. May be sublimed in needles. Not volatile with steam.

Reactions.—1. Yields hexane when distilled with *baryta.*—2. Forms suberone on distilling with *lime.*—3. *Bromine* at 160° forms bromo- and di-bromo-suberic acids, which when boiled with potash yield oxy- and di-oxy- suberic acids (Gal a. Gay-Lussac, *C. R.* 70, 1175).

Salts.—K_2A''. S. 85 at 14°.—Na_2A'' $\frac{1}{2}$aq. S. (of Na_2A'') 50 at 14°.—NaHA''.—$(NH_4)_2A''$. S. 38 at 25°.—BaA'': crystalline powder, less sol. hot water than cold. S. 2·2 at 7·5°; 1·8 at 100°.—SrA''. S. 2·9 at 14°; 1·9 at 100°.—CaA'' aq. S. ·62 at 14°; ·42 at 100°.—MgA'' 2aq. S. 13·5 at 20°.—ZnA''. S. ·041 at 14°.—CuA'' aq: blue pp. —CuA'' 2aq. S. (of CuA'') ·024 at 16°.—CdA'' aq. S. (of CdA'') ·08 at 17°.—HgA''. S. ·012 at 7·5°.—$Al_2OA''_2$. S. ·0094 at 6·5°.—PbA''. S. ·008 at 16°.—$Pb_3A''O_2$.—MnA'' 3aq. S. 1·08 at 13°.—$Fe_4A''_5O$. S. ·0015 at 9°.—CoA'' 4aq.—CoA'' 2aq. S. (of CoA'') 1·16 at 14°; ·85 at 100°. —NiA'' 4aq. S. (of NiA'') ·79 at 7·5°.—Ag_2A''. S. ·0075 at 8°.

Methyl ether Me_2A''. S.G. $\frac{18}{}$ 1·014.

Ethyl ether Et_2A''. (282°). S.G. $\frac{15}{15}$ ·9852; $\frac{25}{25}$ ·9783 (Perkin, *C. J.* 45, 517). M.M. 12·461 at 14°.

Amide $C_8H_{16}N_2O_2$. Crystalline.

Amic acid $C_6H_{12}(CONH_2).CO_2H$. [c. 170°]. Formed by distilling ammonium suberate. Crystalline, v. sol. hot water.

Anilide $C_6H_{12}(CO.NHPh)_2$. [183°]. Formed by heating suberic acid (1 pt.) with aniline

(1 pt.) (Gerhardt a. Laurent, *A. Ch.* [3] 24, 185). Pearly plates (from alcohol), v. sol. ether.

Phenylamic acid $C_6H_{12}(CO.NHPh).CO_2H$. Formed at the same time as the anilide. Minute laminæ, sl. sol. hot water.—AgA′: white pp.

References.—Bromo-, Chloro-, and Oxy-suberic acid.

Isosuberic acid is Di-ethyl-succinic acid (Hell, *B.* 22, 67).

SUBERIC ALDEHYDE $C_8H_{14}O_3$. (202°). A product of the action of fuming HNO_3 on palmitolic acid (Schröder, *A.* 143, 34). Oil, partially decomposed by distillation. Oxidised by bromine water to suberic acid.

SUBEROCARBOXYLIC ACID *v.* Hexane tricarboxylic acid.

SUBEROMALIC ACID *v.* Oxy-suberic acid.

SUBERONE $C_7H_{12}O$. Mol. w. 112. (180° i.V.). V.D. 3·73 (calc. 3·89). Formed, together with hexane, by distilling suberic acid with lime (Boussingault, *A.* 19, 308; Tilley, *A.* 39, 167; Dale a. Schorlemmer, *C. J.* 27, 935; *A.* 199, 147; Wislicenus, *A.* 275, 356). Colourless liquid, smelling like peppermint. Oxidised by HNO_3 (S.G. 1·4) to *n*-pimelic acid [102°]. Does not reduce $AgNO_3$ or Fehling's solution. Combines with bromine, forming a product which, when distilled over KOH, gives $C_7H_{12}O$ (Ladenburg, *B.* 14, 2406). Combines with HCy yielding $C_7H_{12}(OH)CN$, which is converted by HCl into suberyl-glycollic acid $C_7H_{12}(OH).CO_2H$ [80°], from which conc. HClAq at 130° produces chloro-suberane carboxylic acid $C_7H_{12}Cl.CO_2H$, a thick oil, converted by KOH into suberene carboxylic acid $C_7H_{11}.CO_2H$ [54°], which may be reduced by sodium-amalgam to suberane carboxylic acid $C_7H_{13}.CO_2H$, and this may be oxidised by HNO_3 to a dibasic acid $C_8H_{14}O_4$ or $C_8H_{12}O_4$ (Dale a. Schorlemmer, *C. J.* 39, 539; Spiegel, *A.* 211, 117). Suberone is reduced in alcoholic solution by sodium to $C_7H_{14}O$, a colourless liquid, with mouldy smell (185°), S.G. $\frac{15}{15}$ ·9595, which unites with phenyl cyanate forming $C_7H_{13}O.CO.NHPh$ [85°], and also with HI forming a compound which is converted by alcoholic potash into suberonylene C_7H_{12} [114·5°] and a little $C_7H_{13}OEt$. The compound $C_7H_{14}O$ is reduced by conc. HIAq at 250° to C_7H_{14}. Suberonylene combines with bromine (Markownikoff, *C. R.* 110, 466).

Oxim C_7H_{12}:NOH. Liquid, smelling like peppermint, sol. alcohol, ether, alkalis, and acids (Nägeli, *B.* 16, 497). Reduced by sodium-amalgam to $C_7H_{13}.NH_2$.

SUBERO-TARTARIC ACID *v.* Di-oxy-suberic acid.

SUBERYL-GLYCOLIC ACID *v.* Oxy-suberanic acid.

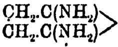
SUBLIMATION. The passage of a solid body, when heated, to the state of vapour without melting. The temperature of sublimation is definite for every solid, and is dependent on the pressure. There is a definite pressure for each definite solid below which the substance cannot exist as a stable liquid, so that if heated below this pressure it passes from the solid directly to the gaseous state; but if heated under pressures greater than this pressure the substance first liquefies and then vaporises. As the definite pressure is considerably below that of the atmosphere for most substances, but few bodies undergo sublimation, properly so called, when heated under ordinary conditions. Sublimation is treated fairly fully in Thorpe's Dictionary of Applied Chemistry (vol. iii. p. 609), and instances are given where the process is made use of in manufacturing operations. M. M. P. M.

SUBSTITUTION. The replacement of one element in a compound by another element is the primary meaning given to the term 'substitution.' As our ways of looking at composition, and changes of composition, are saturated with the conceptions of the molecular and atomic theory, substitution is better described as the replacement of an atom in a molecule by another atom. But the term must be widened to include cases wherein an atom is replaced by a group of atoms, which group is regarded in that reaction as if it were a single atom. The moment attention is paid to the number of atoms that can be substituted for some specified atom in a molecule the conception of chemical equivalency is found necessary to give a common foundation to the facts that are observed (*v.* Equivalency, vol. ii., especially pp. 449-451). The properties of a molecule are changed by the substitution of an atom or atomic group in the place of one, or more, of the atoms in the original molecule; the prosecution of the inquiry into the connections between the properties of molecules derived, by substitution, from some parent molecule leads to the hypothesis of types, which is afterwards merged in the wider subject of chemical classification (*v.* Classification, Chemical, vol. ii. p. 196; Equivalency, vol. ii. pp. 450-451; Types, in this vol.).

Experiments show that the substitution of a more positive by a less positive atom, or atomic group, is accompanied by a change of properties in the direction that the substitution-product is more acidic than the parent substance. This field of inquiry has been cultivated systematically in recent years, and measurements have been made of the effects of substitution-changes of the kind indicated on the affinities of many acids. The results obtained have led, and are leading, to new conceptions of the nature of affinity, and of the constitutions of molecules (*v.* Physical methods, section *Electrical methods*, pp. 197-207 in this vol.).

M. M. P. M.

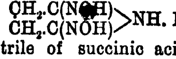
SUCCINAMIDINE $C_4H_9N_3$ *i.e.*



$\left.\begin{matrix}CH_2.C(NH_2)\\CH_2.C(NH_2)\end{matrix}\right>NH$. Formed by the action of ammonia on succinic-di-imido-di-ethyl ether $C_2H_4(C(OEt):NH)_2$ (Pinner, *B.* 16, 362, 924, 1643, 1655). The salt B″2HCl forms minute needles, dissolving in water with formation of NH_4Cl and succinimidine $C_2H_4(NH)_3$.

SUCCINAMIDOXIM $C_2H_4(C(NH_2):NOH)_2$. *Succinene diamidoxim.* [188°]. Formed by adding hydroxylamine hydrochloride and Na_2CO_3Aq to an alcoholic solution of the nitrile of succinic acid (Sembritzki, *B.* 22, 2958). Crystals, sol. hot water, sl. sol. hot alcohol, insol. ether. Coloured reddish-brown by $FeCl_3$. Fehling's solution gives a dirty green pp. Ac_2O forms $C_2H_4(C(NH_2):NOAc)_2$ [168°]. NaOEt and EtI form $C_2H_4(C(NH_2):NOEt)_2$ [119°]. BzCl and NaOH produce the benzoyl derivative $C_2H_4(C(NH_2):NOBz)_2$ [192°], crystallising in needles, converted by heating with water at

159° into $C_2H_4(C\langle{}^{N.O}_{N}\rangle CPh)_2$ [159°]. Aqueous potassium cyanate and HCl form $C_2H_4(C(NOH).NH.CO.NH_2)_2$ [164°].

Succinimidoxim 
$\begin{array}{l} CH_2.C(NOH) \\ CH_2.C(NOH) \end{array}\Big> NH$. Formed by heating the nitrile of succinic acid with hydroxylamine at 65° (Sembritzki, *B.* 22, 2964). Prisms (containing 2aq). Sol. hot water, insol. alcohol. Alcoholic NaOH forms a blue solution turning green. $FeCl_3$ gives a dark-violet colour.—$Ag_2C_4H_5N_3O_2$: pearly plates.

Di-acetyl derivative $C_4H_5Ac_2N_3O_2$. [171°]. Crystalline powder, sol. water.

Di-benzoyl derivative $C_4H_5Bz_2N_3O_2$. [189°]. Crystals, insol. water, sol. hot alcohol.

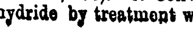
SUCCINIC ACID $C_4H_6O_4$ *i.e.* $CO_2H.CH_2.CH_2.CO_2H$. Mol. w. 118. [182°] (Krafft a. Noerdlinger, *B.* 22, 816; Reissert, *B.* 23, 2245); [185°] (Davidoff, *B.* 19, 406). (261°). S.G. 1·55. S. 2·88 at 0°; 5·14 at 14·5°; 121 at 100° (Bourgoin, *Bl.* [2] 21, 110; 29, 243; Miczynski; *M.* 7, 263). S. (alcohol) 7·5 at 15°. S. (ether) 1·25 at 15°. H.C.v. 357,100. H.C.p. 356,800. H.F. 226,200 (Stohmann, *J. pr.* [2] 40, 207); 229,000 (von Rechenberg). S.H. ·290 (from 0°–50°); ·365 (0°–150°) (Hess, *A. Ch.* [2] 35, 410). *Heat of Neutralisation*: Gal a. Werner, *C. R.* 103, 871.

Occurrence.—In amber (Agricola; Berzelius, *A. Ch.* 94, 187; Lecanu a. Serbat, *J. Ph.* 8, 541; 9, 89; Liebig a. Wöhler, *P.* 18, 162; D'Arcet, *P.* 36, 80), in turpentine from several species of pine, in *Chelidonium majus* (Walz, *N. J. P.* 15, 22; Zwenger, *A.* 114, 350), in lettuce (Köhnke, *B. J.* 25, 443), in *Papaver somniferum*, in unripe grapes (Brunner a. Brandenburg, *B.* 9, 982), in exudations from the bark of mulberry trees (Goldschmiedt, *M.* 3, 136), in beet juice (von Lippmann, *B.* 24, 3299), and in rhubarb (Brunner, *B.* 19, 595). Occurs also in the thymus gland of the calf, the spleen of the ox (Gorup-Besanez, *A.* 98, 28), in certain pathological exudations (Heintz, *A.* 76, 369; Brieger, *H.* 5, 368), in the urine of rabbits fed on carrots (Meissner a. Jolly, *J.* 1865, 675; *cf.* Salkowski, *Pf.* 4, 91), and in human urine after eating asparagus (Hilger, *A.* 171, 208).

Formation.—1. By the action of HNO_3 on many organic substances, including fats, fatty acids from butyric acid upwards, wax, spermaceti, sebacic acid, and azelaïc acid (Bromeis, *A.* 35, 90; 37, 292; Sthamer, *A.* 43, 346; Ronalds, *A.* 43, 356; Radcliff, *A.* 43, 351; Arppe, *A.* 95, 242; Dessaignes, *A.* 70, 102; 74, 361; Erlenmeyer, *B.* 7, 696; Noerdlinger, *B.* 19, 1895).—2. In the alcoholic fermentation of sugar (Pasteur, *Bl.* 1852, 52; *A.* 105, 264).—3. In the fermentation of asparagine (Piria, *A.* 68, 343), of calcium malate (Dessaignes; Liebig, *A.* 104, 363), of ammonium tartrate (König, *B.* 14, 211), and of flesh (Salkowski, *B.* 12, 649).—4. By reducing fumaric and maleïc acids with sodium-amalgam (Kekulé, *A. Suppl.* 1, 133).—5. By reducing malic and tartaric acids with HI (R. Schmitt, *A.* 114, 106; Dessaignes, *A.* 115, 120; 117, 134).—6. By heating its nitrile (ethylene cyanide) with alcoholic potash at 100° (Maxwell Simpson, *A.* 118, 373), or by treating it with dilute nitric acid (Jungfleisch, *Bl.* [2] 19, 197).—7. From bromo-acetic acid and reduced silver at 130° (Steiner, *B.* 6, 184).—8. From β-chloro-propionic ether by successive treatment with KCy and potash (Wichelhaus, *Z.* [2] 3, 247).—9. From sodium acetoacetic ether by treatment with chloro-acetic ether and saponification of the product (Wippermann, *B.* 3, 337; Noeddecke, *A.* 149, 224).—10. By heating ethane tricarboxylic acid at 160° (Bischoff, *B.* 13, 2162).—11. By potash-fusion from gum arabic, milk sugar, and carminic acid (Hlasiwetz, *A.* 138, 76; 141, 340).—12. By reducing acetylene dicarboxylic acid with zinc and HOAc at 60° (Aronstein a. Hollemann, *B.* 22, 1183).—13. Its ether is formed by electrolysis of $CO_2Et.CH_2.CO_2K$ in aqueous solution; the yield being 60 p.c. of the theoretical (Crum Brown a. Walker, *A.* 261, 115).

Preparation.—1. By distilling amber, heating the watery distillate, filtering, and allowing to crystallise. The product is freed from oils by treatment with nitric acid.—2. By neutralising tartaric acid (2 kilos) with NH_3Aq, adding to the aqueous solution (40 litres) K_2HPO_4 (20 g.), $MgSO_4$ (10 g.) and a little $CaCO_3$. Fermentation is started by diluting a little (5 c.c.) of the solution with water (25 c.c.) and exposing it to the air for a few days. When fermentation has set in, the liquid is returned to the main quantity, and the whole kept at 25°–30° for seven weeks. The liquid is evaporated somewhat, clarified by white of egg, and boiled with lime. After cooling, the calcium succinate is collected and decomposed by H_2SO_4. The yield is good (500 g.) (Koenig, *B.* 15, 172).

Properties.—Monoclinic prisms, permanent in air, acid in taste. V. sol. water, m. sol. alcohol, sl. sol. ether. Resolved on boiling into water and anhydride; the lactone $C_7H_8O_4$ being also formed. $BaCl_2$ completely ppts. hot neutral solutions (Schmitt a. Hiepe, *Fr.* 21, 536). $BaCl_2$ followed by NH_3Aq and alcohol ppts. succinic (but not benzoic) acid. $FeCl_3$ gives in neutral solutions a reddish-brown pp. $PbAc_2$ gives a pp. sol. excess.

Reactions.—1. Not attacked by HNO_3, CrO_3, or chlorine water. MnO_2 and H_2SO_4 yield acetic acid. $KMnO_4$ in neutral solution oxidises it to oxalic acid and CO_2; and, in acid solution, to CO_2 (Berthelot, *Bl.* [2] 8, 390; Sorokin, *J. R.* 11, 383).—2. Yields ethylene and CO_2 when decomposed in alkaline solution by an electric current (Kekulé, *A.* 131, 79; Bourgoin, *A. Ch.* [5] 20, 80; *cf.* Kolbe, *A.* 113, 244). In perfectly neutral solution only CO_2, CO, and O are given off at the positive pole.—3. *Potash-fusion* yields oxalic acid.—4. PCl_5 forms successively: succinic anhydride $C_2H_4(CO)_2O$, succinyl chloride $C_2H_4(COCl)_2$, fumaryl chloride $C_2H_2(COCl)_2$, chloro-fumaryl chloride $C_2HCl(COCl)_2$, di-chloro-maleyl chloride $C_2Cl_2(COCl)_2$, two tetra-chlorinated di-chloro-maleyl chlorides, viz.: $C_2Cl_2(CCl_3)(COCl)$ and $C_2Cl_2(CCl_2)_2O$ (*v.* DI-CHLORO-MALEIC ACID), and finally per-chloro-ethane, $2C_2Cl_6$ (Kander, *J. pr.* [2] 31, 1).—5. On long boiling it yields the dilactone of diethyl ketone s-di-ω-carboxylic acid 
$\begin{array}{l} CO\ .O \qquad\qquad O.CO \\ CH_2.CH_2.C.CH_2.CH_2 \end{array}$ [75°] (c. 203° at 15 mm.), crystallising from alcohol in plates, converted by HClAq into hydrochelidonic acid $CO(CH_2.CH_2.CO_2H)_2$ [143°], which yields an oxim [129°] (Volhard, *A.* 253, 206).—6. Converted into succinic anhydride by treatment with

P_2O_5, AcCl, BzCl, Ac_2O, or succinyl chloride (Anschütz, *B.* 10, 325, 1881).—7. A solution containing 5 p.c. succinic acid and 1 p.c. uranium succinate when exposed to sunlight turns green and gradually gives off CO_2, leaving propionic acid in solution (Seekamp, *A.* 133, 253). Barium succinate (1 mol.) heated with NaOMe (1 mol.) for 3 hours at 300° yields propionic acid (Mai, *B.* 22, 2133).—8. Heated with a large excess of lime it yields ethane as chief product (Hanriot, *Bl.* [2] 45, 79).—9. The salts on distillation yield a liquid product (160°-250°) which yields benzene when distilled over zinc-dust (Von Richer, *J. pr.* [2] 20, 206; *cf.* Fumaro, *G.* 11, 273). Hydroquinone is also a product of the distillation of succinates.—10. The sodium salt heated with P_2S_5 yields thiophene (Volhard a. Erdmann, *B.* 18, 454).—11. The Na salt heated with aldehydes and NaOAc forms oxyacids of the form $R.CH(OH).CH(CO_2H).CH_2.CO_2H$ (Fittig, *B.* 18, 2523).—12. By heating with phthalic anhydride and NaOAc at 250°, exhausting the product with water and alcohol, and boiling the residue with aniline, there is got 'diphthalsuccinanilide' $C_{30}H_{24}N_2O_4$ [267°] converted by boiling with HOAc and HCl into 'diphthalsuccindehydranilide' $C_{30}H_{20}N_2O_2$, crystallising from HOAc in small yellow prisms, not liquid at 280° (Roser, *B.* 18, 3122).—13. By heating with *glycerin* at 200° it yields 'succinin' $C_3H_5(OH)A''$, a gummy mass, insol. cold water, alcohol, and ether (Fumaro a. Danesi, *G.* 10, 58). Alkalis and acids split it up into glycerin and succinic acid.—14. *a-Chloro-propionic ether* and alcoholic potash give $C_2H_4(CO.O.CHMe.CO_2Et)_2$ (c. 302° at 730 mm.) (Wurtz a. Friedel, *A. Ch.* [3] 63, 101; Wislicenus, *A.* 133, 262).

Salts.—$(NH_4)_2A''$. Hexagonal prisms, v. sol. water and alcohol. Yields succinamide when heated.—$(NH_4)HA''$. Triclinic crystals, v. sol. water and alcohol (Brooke, *Ann. Phil.* 22, 286). Formed by evaporating a solution of the neutral salt.—K_2A'' 2aq. Deliquescent crystals, sol. alcohol, insol. ether.—K_2A'' 3aq. Trimetric crystals (Salzer, *B.* 16, 3025).—KHA'' 2aq. Efflorescent six-sided prisms.—$KH_3A''_2$.—Na_2A'' 6aq: monoclinic prisms.—$NaHA''$. Triclinic prisms.—$NaHA''$ 3aq: monoclinic crystals.—BaA''. Sl. sol. water, insol. NH_3Aq and alcohol. S. ·42 at 8°; ·43 at 12°; ·28 at 67° (Miczynski).—CaA'' 3aq: small needles, deposited gradually on mixing cold conc. solutions of sodium succinate and $CaCl_2$. On mixing the hot solutions CaA'' aq is ppd. S. 1·1 at 0°; 1·3 at 24°; ·8 at 68° (Miczynski, *M.* 7, 266).—$CaH_2A''_2$ 2aq.—SrA'': monoclinic prisms.—BeA'' 2aq (Atterberg, *Bl.* [2] 21, 162).—$Be_2(OH)_2A''$ 2aq.—MgA'' 6aq. Prisms (Fehling, *A.* 49, 154).—$MgK_2A''_2$.—$Mg_6A''_2O_4$ aq.—CrA'' aq: scarlet pp.—CuA'' (dried at 200°).—$CuA''2NH_3$.—$CuA''4NH_3$ (Schiff, *A.* 123, 45).—$Fe(OH)A''$: brownish-red pp.—NiA'' 4aq.—MnA'' 4aq. Triclinic prisms (Handl, *Sitz. W.* 32, 254).—PbA'' (dried at 100°). White powder, sl. sol. water, v. sol. KOHAq and HNO_3.—$Pb_3OA''_2$: sticky pp., got by adding lead subacetate to sodium succinate.—$Pb_4O_2A''_2$ (dried at 200°): white powder.—ZnA'' (dried at 200°). Crystalline powder.—$ZnA''3NH_3$ (Lutschak, *B.* 5, 30).—CdA''.—$(UrO)_2A''$ aq.—$K(UrO)A''$ ½aq.—$Na(UrO)A''$ ½aq.—Ag_2A''. White amorphous pp.—**Quinine salt** $(C_{20}H_{24}N_2O_2)_2H_2A''$ aq. Prisms. S. ·11 at 10° (Hesse, *A.* 135, 331).—**Cinchonine salt** $(C_{20}H_{24}N_2O)_2H_2A''$ aq. Thick crystals (Hesse, *A.* 122, 226).—**Cinchonidine salt** $(C_{20}H_{24}N_2O)_2H_2A''$ 6aq. Silky prisms. S. ·4 at 10° (Hesse, *A.* 135, 342).—**Urea salt** $(CON_2H_4)_2H_2A''$. Six-sided monoclinic prisms; $a:b:c = 1·483:1:1·365$; $\beta = 83°\ 28'$ (Lischmidt, *Sitz. W.* 52, ii. 238).—**Ethylene-diamine salt** $C_2H_4(NH_2)_2H_2A''$. [182°]. Thick white prisms, v. sol. water, insol. ether (Mason, *C. J.* 55, 10).—**Benzylamine salts** $(C_7H_7NH_2)_2H_2A''$. [145°]. Thin plates, sol. alcohol (Werner, *C. J.* 55, 628).—$(C_7H_7NH_2)H_2A''$. [117°]. Rectangular prisms (containing aq), v. sol. water.

Methyl ether Me_2A''. [19°]. (195° cor.). S.G. $\frac{20}{4}$ 1·1209 (Emery, *B.* 22, 3185); $\frac{15}{15}$ 1·1261; $\frac{25}{25}$ 1·0383 (Perkin, *C. J.* 45, 516). M.M. 6·232 at 18·2°. S.V. 159·7 (Lossen, *A.* 254, 64). H.C. (solid) 703,600. H.C. (liquid) 708,500. H.F. (solid) 205,400 (Stohmann, *J. pr.* [2] 40, 353). Formed from succinic acid, MeOH, and gaseous HCl (Fehling, *A.* 49, 195). Formed also from succinyl chloride and NaOMe in ether, and from Ag_2A'' and MeI. Crystalline, sol. alcohol.

Methyl ethyl ether $MeEtA''$. (208° cor.). C.G. ^{0} 1·093. S.V. 184·6. Formed by the action of $EtAgA''$ on MeI (Köhler, *A.* 221, 88). On saponification by baryta it yields H_2A'', $HMeA''$, and $HEtA''$ (Lossen a. Köhler, *A.* 262, 200).

Mono-ethyl ether $HEtA''$. Formed by boiling succinic anhydride with alcohol (Heintz, *J.* 1859, 280). Syrup, miscible with water, alcohol and ether.—$AgEtA''$: amorphous, sl. sol. water.—The salt $NaEtA''$ is converted by $POCl_3$ into $CO_2Et.C_2H_4.COCl$ (144° at 90 mm.), which is split up by distillation into EtCl and succinic anhydride, and is converted by phenyl hydrazine into $CO_2Et.C_2H_4.CO.NH.NHPh$ [107°], crystallising in white needles, itself converted into $O(CO.C_2H_4.CO.N_2H_2Ph)_2$ [137°] by successive treatment with HOH and HCl (Michaelis a. Hermans, *B.* 25, 2748). The salt $NaEtA''$ is converted by *a*-chloro-propionic ether into $CO_2Et.C_2H_4.CO.CHMe.CO_2Et$ (280°) S.G. ^{0} 1·119, which is split up by boiling with baryta water into succinic and lactic acids (Wurtz a. Friedel, *J.* 1861, 378).

Ethyl ether Et_2A''. (216·5° cor.). S.G $\frac{15}{15}$ 1·0465; $\frac{25}{25}$ 1·0383. M.M. 8·380 at 17·8° (Perkin). S.V. 209·4. Formed by boiling succinic acid (20 pts.) with alcohol (3 pts.) and H_2SO_4 (1 pt.) (Eghis, *B.* 6, 1178; *cf.* D'Arcet, *A. Ch.* [2] 58, 291). It is also produced by heating $C_2H_4Br_2$ in alcohol with potassium succinate in sealed tubes (Davidoff, *Bl.* [2] 46, 818; 19, 406). Oil. Converted by Na into the dihydride of dioxyterephthalic ether. Not attacked by hydroxylamine (Jeaurenaud, *B.* 22, 1273). Succinic ether (40 g.) treated with cyanamide (20 g.) and an alcoholic solution of K (18 g.) for 5 hours with inverted condenser yields $C_2H_4(CO.NKCy)_2$ and $C_2H_4(CO_2K)(CO.NKCy)$. These bodies may be converted by $AgNO_3$ into Ag salts, which may be separated by HNO_3, in which silver 'succincyanamate' dissolves, while silver 'succinyl-di-cyan-di-amide' is insoluble. The Ag salts may then be suspended in alcohol and decomposed by H_2S (Möller, *J. pr.* [2] 22, 214). Succinyl-di-cyan-di-amide $C_2H_4(CO.NHCy)_2$ [105°] crystallises in monoclinic pyramids (containing 2aq), decomposed by warm water into succinic

acid and cyanamide. It may also be prepared by the action of NaNH.Cy on succinyl chloride, and by warming $C_2H_4(CO)_2NCy$ with cyanamide. The salt $C_2H_4(CO.NAgCy)_2\frac{1}{2}aq$ crystallises in plates, sol. NH_3Aq.—$Et_2A''5TiCl_4$ (Demarçay, *C. R.* 70, 1414).—$Et_2A''2TiCl_4$.—$Et_2A''TiCl_4$.

Ethyl propyl ether EtPrA″. (231°). S.G. $\frac{0}{0}$ 1·0387. S.V. 230·2 (Wiens, *A.* 253, 300). Yields, on saponification by baryta, salts of EtHA″, PrHA″, and H_2A'' (Lossen a. Köhler, *A.* 262, 201).

Ethyl butyl ether $Et(C_4H_9)A''$ (247°). S.G. $\frac{0}{0}$ 1·0218. S.V. 255·9 (W.).

Ethyl heptyl ether $Et(C_7H_{15})A''$. (291·4°). S.G. $\frac{0}{0}$ ·9850. S.V. 332·9 (W.).

n-Propyl ether Pr_2A'' (247·1°). (Wiens, *A.* 253, 300); (250·8°) (Perkin, *C. J.* 53, 561). S.G. $\frac{0}{0}$ 1·0189 (W.); $\frac{4}{4}$ 1·0157; $\frac{15}{15}$ 1·0062; $\frac{25}{25}$ ·9986 (P.). S.V. 257·8. Formed by passing HCl into succinic acid in propyl alcohol.

Isopropyl ether Pr_2A''. (228°). S.G. $\frac{0}{}$ 1·009 (Silva, *A.* 154, 255).

Propyl butyl ether $Pr(C_4H_9)A''$. (258·7°). S.G. $\frac{0}{0}$ 1·0106. S.V. 277·8 (Wiens, *A.* 253, 300).

Isobutyl ether $(PrCH_2)_2A''$. (265° cor.). S.G. $\frac{15}{15}$ ·9737; $\frac{25}{25}$ ·9667. M.M. 12·707 at 14·5° (Perkin, *C. J.* 45, 519).

Isoamyl ether $(C_5H_{11})_2A''$. (290° cor. at 728 mm.). S.G. ^{13} ·961. Formed from Ag_2A'' and isoamyl bromide (Del Zanna a. Guareschi, *Atti Real. Instit. Veneto* [5] 6; *B.* 12, 1699).

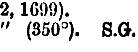
Heptyl ether $(C_7H_{15})_2A''$ (350°). S.G. $\frac{0}{0}$ ·9519. S.V. 459·6 (Wiens).

Cetyl ether $(C_{16}H_{33})_2A''$. [58°]. Formed by heating the acid with cetyl alcohol (Tütscheff, *Rep. Chim. pure*, 2, 463). Plates, sl. sol. alcohol, v. sol. ether.

Ethylene ether C_2H_4A''. [c. 90°]. By heating succinic acid with glycol at 170° there is formed crystalline $(CO_2H.C_2H_4.CO_2)_2C_2H_4$ melting below 100°, which at 300° yields C_2H_4A'' (Lourenço, *A.* 115, 358). Crystalline, insol. water and ether, sol. hot alcohol. Decomposed by distillation.

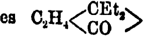
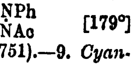
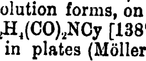
Di-phenyl ether $C_2H_4(CO_2Ph)_2$. [119°]. (330°). Formed from succinic acid, phenol and $POCl_3$ (Rasiński, *J. pr.* [2] 26, 63). Got also from succinyl chloride and phenol (Weselsky, *B.* 2, 519). Completely decomposed by slowly heating (Anschütz, *C. J.* 47, 898). NaSEt gives di-thio-succinic ether. Pearly plates (from alcohol).

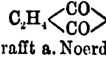
Di-benzyl ether $(CH_2Ph)_2A''$. [42°]. Formed from Ag_2A'' and benzyl bromide (Zanna a. Guareschi, *G.* 11, 255). Laminæ.

Chloride $C_2H_4(CO.Cl)_2$ or  $C_2H_4<{\begin{matrix}CCl_2\\CO\end{matrix}}>O$. Mol. w. 155. (190°–200°). S.G. 1·39. Formed from succinic anhydride and PCl_5 (Gerhardt a. Chiozza, *A.* 87, 293).

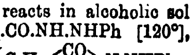
Preparation.—Succinic acid is heated with PCl_5 for two days with an inverted condenser in an oil bath. The $POCl_3$ is distilled off (below 120°) and the residue shaken with benzoline that has been dried over lime. The benzoline dissolves the rest of the $POCl_3$ and the succinyl chloride separates as a lower layer. The operation is repeated until the oil no longer forms phosphoric acid when mixed with water (H. Möller, *J. pr.* [2] 22, 208).

Properties.—Solidifies at 0°.

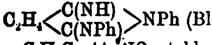
Reactions.—1. Reduced to butyrolactone by *sodium amalgam* (3 p.c. Na) acting upon its ethereal solution mixed with glacial acetic acid.—2. *Benzene* and aluminium chloride give $C_2H_4<{\begin{matrix}CPh_2\\CO\end{matrix}}>O$ [90°], $C_2H_4(CO.C_6H_5)_2$ [184°], and a little β-benzoyl-propionic acid (Auger, *A. Ch.* [6] 22, 312; *Bl.* [2] 49, 345).—3. $ZnEt_2$ gives  $C_2H_4<{\begin{matrix}CEt_2\\CO\end{matrix}}>O$.—4. Na_2S gives succinyl sulphide.—5. PCl_5 at 230° gives off HCl and the product, after treatment with water, contains C_4Cl_6O (199°–215°) which solidifies below 0°. Hot conc. H_2SO_4 dissolves C_4Cl_6O and the product, diluted with water, yields on evaporation hygroscopic crystals, which on sublimation give non-hygroscopic plates of $C_4Cl_2O_3$ [120°] (Kauder, *J. pr.* [2] 28, 191). Di-chloro-maleïc chloride is also a product of the action of PCl_5 on succinyl chloride.—6. *Chlorine* passed into boiling succinyl chloride forms chlorides of fumaric, chloro-fumaric, and di-chloro-maleïc acids (Kauder, *J. pr.* [2] 31, 24).—7. $C_6H_5.SO_2NBzAg$ forms $C_2H_4(CO.NBz.SO_2.C_6H_5)_2$ [146°] (G. a. C.).—8. *Phenyl-hydrazine* forms the compound $C_2H_4(CO.NH.NHPh)_2$ [218°] (Freund, *B.* 21, 2462; Fischer, *B.* 22, 2728), whence phosgene produces $C_2H_4(CO.N_2Ph:CO)_2$ [225°]. Sodium phenyl-hydrazine in benzene forms  $C_2H_4<{\begin{matrix}CO.NPh\\CO.NH\end{matrix}}$ [199°], which gives  $C_2H_4<{\begin{matrix}CO.NPh\\CO.NAc\end{matrix}}$ [179°] (Michaelis a. Hermans, *B.* 25, 2751).—9. *Cyanamide* in ethereal solution forms, on warming, succin-cyanimide $C_2H_4(CO)_2NCy$ [138°] crystallising from alcohol in plates (Möller, *J. pr* [2] 22, 207).—10. *Cyano-acetic ether* in Et_2O at 100° forms $C_2H_4:C_2O_2:CCy.CO_2Et$ [126°] (Muller, *C. R.* 112, 1140).—11. *Urea* at 65° forms the compound $C_2H_4(CO.NH.CO.NH_2)_2$, a powder, v. sl. sol. hot water (Conrad, *J. pr.* [2] 9, 301).

Anhydride  $C_2H_4<{\begin{matrix}CO\\CO\end{matrix}}>O$. Mol. w. 100. [119°]. (261°) (Krafft a. Noerdlinger, *B.* 22, 816).

Formation.—1. By rapidly boiling succinic acid. 2. By distilling the acid with P_2O_5 (D'Arcet, *A. Ch.* [2] 58, 282), with PCl_5 (Gerhardt a. Chiozza, *C. R.* 36, 1050), or with BzCl (Kraut, *A.* 137, 254).—3. By warming succinyl chloride with dry oxalic acid (Anschütz, *A.* 226, 16).—4. By heating succinic acid (100 g.) with $POCl_3$ (65 g.) at 120° (Volhard, *A.* 242, 150).—5. By distilling succinyl chloride (180 g.) with succinic acid (137 g.), and crystallising from alcohol (H. Möller, *J. pr.* [2] 22, 194).—6. By the action of dry $Pb(NO_3)_2$ (also nitrates of other heavy metals) upon succinyl chloride; $PbCl_2$ is produced, and N_2O_4 and oxygen evolved; yield c. 60 p.c. of theoretical (Lachowicz, *B.* 18, 2990).

Properties.—Long trimetric needles (from alcohol); $a:b:c = {\cdot}595:1:{\cdot}462$ (Bodewig, *B.* 14, 2788). Sl. sol. water, v. sl. sol. ether. Converted by dry NH_3 into succinimide. Slowly converted by boiling alcohol into succinic ether. Phenyl-hydrazine reacts in alcoholic solution, forming $CO_2H.C_2H_4.CO.NH.NHPh$ [120°], converted by heat into  $C_2H_4<{\begin{matrix}CO\\CO\end{matrix}}>N.NHPh$ [155°] (Auger, *A. Ch.* [6] 22, 339; *cf.* this vol. p. 45) or [158°] (Michaelis, *B.* 25, 2750). Potassium cyanamide forms 'succincyanamic' acid, the compound $CO_2H.C_2H_4.CO.NHCy$ [128°], which is v. e. sol. water, v. sol. alcohol and ether, is split up by dilute acids into succinic acid and cyanamide, and yields the following six salts Na_2A'' 5aq, K_2A''aq, CaA''4aq, BaA''2aq, $AgHA''$, and Ag_2A'' (Möller, *J. pr.* [2] 22, 193). Urea heated with succinic anhydride at 125° forms succinuric acid $CO_2H.C_2H_4.CO.NH.CO.NH_2$ [205°] (Pike, *B.* 6, 1104).

Nitrile $C_2H_4(CN)_2$. *Ethylene cyanide.* Mol. w. 80. [55°]. (147° at 10 mm.) (F.); (185° at 60 mm.) (Biltz, *B.* 25, 2541). H.C.p. 546,100. H.F. (from diamond) −32,000 (Berthelot a. Petit, *C. R.* 108, 1217). Formed by boiling ethylene bromide (300 g.) with alcohol (500 g.) and KCy (200 g.) for two hours with inverted condenser (Maxwell Simpson, *Pr.* 10, 574; Geuther, *A.* 120, 268; Fauconnier, *Bl.* [2] 50, 214; Nevolé a. Tscherniak, *C. R.* 86, 1411). Amorphous, sometimes crystalline, solid, v. sol. water, alcohol, and chloroform; sl. sol. ether. Decomposed by distillation under atmospheric pressure. Converted into succinic acid by boiling alcoholic potash. Aniline hydrochloride at 200° reacts, forming di-phenyl-succinimidine

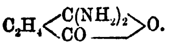


$C_2H_4{<}\begin{matrix}C(NH)\\C(NPh)\end{matrix}{>}NPh$ (Blochmann, *B.* 20, 1856). —$C_2H_4Cy_2 4AgNO_3$: tables, sol. water and alcohol, insol. ether.

Amide-nitrile $CN.C_2H_4.CO.NH_2$. Formed by heating the nitrile with alcoholic potash at 110° (Drouin, *C. R.* 108, 675). Crystals, sl. sol. alcohol, insol. ether. Slowly decomposes at 210°–220°.

Amide $C_2H_4(CO.NH_2)_2$. *Succinamide.* Mol. w. 116. [243°]. S. ·625 at 9° (Henry, *C. R.* 100, 943); 11 at 100° (F.). Formed by the action of aqueous NH_3 on the ether and on the chloride (D'Arcet, *A.* 16, 215; Fehling, *A.* 49, 196). Formed also by warming succinimide with alcoholic NH_3 (Menschutkin, *A.* 162, 165, 187). Needles, insol. ether and alcohol. Decomposed at 200° into NH_3 and succinimide or by saturating at −15° with gaseous NH_3, and heating to 150° in sealed tubes (Roubtzoff, *Bl.* [2] 45, 250).—$HgC_4H_6N_2O_2 1\frac{1}{2}$aq. White powder, deposited on cooling from a solution of HgO in hot aqueous succinamide.

Iso-amide



$C_2H_4{<}\begin{matrix}C(NH_2)_2\\CO\end{matrix}{>}O$. [c. 95°]. Formed to the extent of 8 p.c. in the preparation of the amide from succinyl chloride and NH_3Aq (Auger, *A. Ch.* [6] 22, 312). Hygroscopic mass. Its aqueous solution gives with $AgNO_3$ a pp. of $C_2H_4(CO)_2NAg$.

Methylamide $C_2H_4(CO.NHMe)_2$. [175°]. Plates (Wallach a. Kamenski, *B.* 14, 170).

Dimethylamide $C_2H_4(CO.NMe_2)_2$. [81°]. Formed from succinyl chloride and $NHMe_2$ in ether (Franchimont, *R. T. C.* 4, 202). Crystals (from ether), v. sol. water.

Benzyl-di-amide $C_2H_4(CONH_2)(CONHCH_2Ph)$. [189°]. Formed from the benzylimide and ammonia at 100° (Werner, *C. J.* 55, 633). Minute prisms, sl. sol. ether and hot benzene. Yields the benzylimide when heated.

Di-benzyl-diamide $C_2H_4(CO.NHCH_2Ph)_2$. [206°]. Formed from succinic ether and benzylamine in alcohol. Thin plates, not decomposed by boiling NaOHAq.

Anilide $C_2H_4(CO.NHPh)_2$. [227°]. Formed by boiling succinic acid with aniline (Laurent a. Gerhardt, *A. Ch.* [3] 24, 179; *A.* 68, 27; Menschutkin, *A.* 162, 187). Needles (from alcohol), insol. water. Not affected by boiling alcoholic potash or by nitrous acid. Gives the phenylimide on distillation. Cold fuming HNO_3 converts it into $C_2H_4(CO.NHC_6H_4(NO_2)[1:4])_2$ [260°] (Hübner, *A.* 209, 377). Benzoic aldehyde at 180° forms succinic phenylimide and benzylidene-aniline (Schiff, *A.* 148, 338).

Amide-anilide $CO(NH_2).C_2H_4.CONHPh$. [181°]. Formed by heating the phenylimide with alcoholic NH_3 at 100° (Menschutkin, *A.* 162, 182). Broad needles (from water), sl. sol. hot alcohol. Alkaline KOBr followed by heating with HOAc forms $C_2H_4{:}C_2O_2{:}(NHBr)(NHPh)$ crystallising in minute needles, converted by boiling alcohol into $C_2H_4{:}C_2O_2(NH_2)(NHC_6H_4Br)$ [215°], whence potash forms the compound $CO_2H.C_2H_4.CO.NHC_6H_4Br[1:4]$ [187°] (Hoogewerff a. Van Dorp, *R. T. C.* 9, 41).

Di-(α)-naphthyl-di-amide $C_2H_4(CO.NHC_{10}H_7)_2$. [285°]. Needles (from HOAc). Converted by fuming nitric acid into $C_2H_4(CO.NH.C_{10}H_5(NO_2)_2)_2$, [225°], and $C_2H_4(CO.NH.C_{10}H_3(NO_2)_4)_2$ [256°].

Tetra-phenyl-di-amide $C_2H_4(CO.NPh_2)_2$. [234°] (Piutti, *G.* 14, 467). Needles (from alcohol).

o-Tolyl-diamide $C_2H_4(CONH_2).CO.NHC_7H_7$. [160°]. Formed by heating the *o*-tolylimide with alcoholic NH_3 at 100°. Plates.

Di-o-tolyl-diamide $C_2H_4(CO.NHC_7H_7)_2$. [100°]. White needles (Bechi, *B.* 12, 25, 321). V. sl. sol. water, m. sol. alcohol.

p-Tolyl-di-amide $C_2H_4(CONH_2).CONHC_7H_7$. [148°]. Formed by heating the *p*-tolylimide with alcoholic NH_3.

Di-p-tolyl-diamide $C_2H_4(CO.NHC_7H_7)_2$. [256°]. Plates (from alcohol), sl. sol. hot water (Bechi, *B.* 12, 323; Hübner, *A.* 209, 380). Yields on nitration $C_2H_4(CO.NHC_7H_6.NO_2)_2$ [217°] and $C_2H_4(CO.NH.C_7H_5(NO_2)_2)_2$.

(β)-Naphthalide $C_2H_4(CO.NHC_{10}H_7)_2$. [266°] (Bischoff a. Reebe, *B.* 25, 3267). Got by heating succinic acid (10 g.) with (β)-naphthylamine (24 g.). Insol. ordinary solvents, sol. H_2SO_4.

Amic acid $CO_2H.C_2H_4.CO.NH_2$. *Succinamic acid.* [157°]. Formed by warming succinimide with an equivalent quantity of baryta water (Teuchert, *A.* 134, 136) or milk of lime (Menschutkin, *A.* 162, 175). Formed also from nitrosoglutaric acid by heating alone or with Ac_2O (Serda a. Wiedemann, *B.* 23, 3284; Wolff, *A.* 260, 114). Needles, m. sol. water, insol. alcohol. Decomposed at 200° into water and succinimide. Boiling water forms acid ammonium succinate.

Salts.—KA': very hygroscopic mass (Landsberg, *A.* 215, 201).—BaA'_2: needles, v. sol. water.—CaA'_2.—MgA'_2 3aq: trimetric crystals.—MgA'_2 6aq.—CdA'_2 aq: prisms.—CuA'_2.—PbA'_2. Concentric needles, v. sol. water.—MnA'_2 5aq.—ZnA'_2.—AgA': monoclinic crystals, v. sol. NH_3Aq.

Ethyl-amic acid $CO_2H.C_2H_4.CONHEt$. Formed by warming the ethylimide with baryta water (Menschutkin, *A.* 182, 92).—BaA'_2: crystals, v. sol. water.

Ethylene-di-amic acid $C_{10}H_{16}N_2O_6$ *i.e.* $C_2H_4(NH.CO.C_2H_4.CO_2H)_2$. *Ethylene-disuccinamic acid.* [185°]. Formed by boiling the di-imide with baryta (Mason, *C. J.* 55, 13). Large plates, v. sol. hot water. Does not yield an oxim or a phenyl-hydrazide.—CaA″ 3aq: prisms.—Ag_2A'': white amorphous powder.

Benzylamic acid $CO_2H.C_2H_4.CO.NHC_7H_7$. [139°]. Formed by boiling the benzyl-imide (2 mols.) with aqueous barium hydroxide (1 mol.) (Werner, *C. J.* 55, 631). Flat prisms, m. sol. hot water, v. sl. sol. ether.

Phenylamic acid $CO_2H.C_2H_4.CO.NHPh$. *Succinanilic acid.* [149°]. Formed by boiling the phenylimide with NH_3Aq (Laurent a. Gerhardt, *A. Ch.* [3] 24, 179) or baryta (Menschutkin, *A.* 162, 176). Flat needles, v. sl. sol. cold water. Decomposed by heat into water and the phenylimide. Boiling alcoholic HCl forms succinic acid. — $CaA'_2$4aq. — $BaA'_2$3aq. — AgA′: crystalline pp.

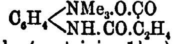
o-Tolyl-amic acid $CO_2H.C_2H_4.CO.NHC_7H_7$. [97°]. Got by boiling the *o*-tolylimide with baryta water (Bechi, *B.* 12, 322). White needles.—BaA'_2aq.

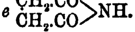
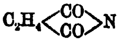
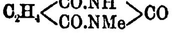
p-Tolyl-amic acid [157°].—BaA'_2aq.

(*α*)-*Naphthyl-amic acid* $CO_2H.C_2H_4.CO.NHC_{10}H_7$. [171°]. Formed by heating the (*α*)-naphthylimide with KOHAq (Pellizzari, *A.* 248, 158; *G.* 18, 323). Needles or plates (from alcohol), v. e. sol. HOAc and benzene.

(*β*)-*Naphthyl-amic acid* [192°]. Crystals.

Di-phenyl-amic acid $CO_2H.C_2H_4.CONPh_2$. [119°]. Plates (Piutti, *G.* 14, 468).—AgA′: pp.

Phenylene-di-amic acid $C_6H_4(NH.CO.C_2H_4.CO_2H)_2$. Formed by heating phenylene-diamine with succinic acid at 200° (Biedermann, *B.* 9, 1668). Small crystals (from HOAc). Melts above 360°. Converted by KOHAq and MeI into  $C_6H_4<{NMe_3.O.CO \atop NH.CO.C_2H_4}$ crystallising in plates or tables (containing $1\frac{1}{2}$aq) (Griess, *B.* 18, 2410).

Imide  ${CH_2.CO \atop CH_2.CO}>NH$. [126°] (Erlenmeyer, *Z.* [2] 5, 175). (288°). H.C. 439,000. H.F. 110,500 (Berthelot a. André, *Bl.* [3] 4, 229). Formed from succinic anhydride and dry NH_3 (D'Arcet, *A. Ch.* [2] 58, 294), and also by heating succinamide or ammonium succinate (Fehling, *A.* 49, 198; Laurent a. Gerhardt, *Compt. Chim.* 1849, 108; Menschutkin, *A.* 162, 165, 187; 182, 93). Large efflorescent crystals (containing aq) or octahedra (from acetone) (Bunge, *A. Suppl.* 7, 118), v. sol. water and alcohol, m. sol. ether. Not attacked by pure HNO_3 (S.G. 1·53) (Franchimont, *R. T. C.* 6, 228). Converted by hot baryta water into succinamic acid, and finally into succinic acid. Alcoholic NH_3 at 100° forms succinamide. Yields pyrrole on distillation with zinc-dust. KOH (6 mols.) and KBrO (1 mol.), acting for two hours at 60°, form (*β*)-amido-propionic acid [196°] (Hoogewerff a. Van Dorp, *R. T. C.* 10, 4). Bromine forms bromo-succinimide [225°] and bromo-maleïmide [152°] (Kisielinski, *Sitz. W.* [2] 74, 561; *cf.* Kusseroff, *A.* 252, 158). Chlorine at 160° forms chloro- and di-chloro-maleïc imide. PCl_5 forms a compound melting at 145°-148° (Bernthsen, *B.* 18, 1047). A solution of bleaching-powder added to a solution of succinimide containing excess of HOAc forms  $C_2H_4<{CO \atop CO}>NCl$ [148°], which separates from benzene in large crystals, and is reconverted by acids and alkalis into succinimide (Bender, *B.* 19, 2273). Hydroxylamine at 65° forms $NH(CO.C_2H_4.CO.NH.OH)_2$ [171°], crystallising in needles, v. e. sol. water, and yielding a picrate $B'C_6H_3N_3O_7$ [266°] (Garny, *B.* 24, 3434). Methyl cyanate forms  $C_2H_4<{CO.NH \atop CO.NMe}>CO$ [149°], while EtNCO forms corresponding $C_7H_{10}N_2O_3$ [95°] (Menschutkin, *A.* 178, 204).

Salts.—$KC_4H_4NO_2\frac{1}{2}$aq. Ppd. by adding alcoholic potash and ether to an alcoholic solution of succinimide (Landsberg, *A.* 215, 200).—KA′: needles. V. sol. water and alcohol.—$BaA'_2$2aq. — $BaA'_2$$2\frac{1}{2}$aq. — $MgA'_2$3aq. — HgA'_2. — $NH_2.HgA'$. — ClHgA′. — CyHgA′. — $Cu_4A'_6(OH)_2$9aq. — $Cu_2A'_2(OH)_2$2aq.—AgA′ $\frac{1}{2}$aq. Needles. Converted by iodine into $IC_4H_4NO_2$, crystallising in dimetric prisms; $a:c = 1:·873$, melting, with evolution of I, at 135°. Silver succinimide is converted by succinyl chloride in ethereal solution into 'trisuccinamide' $(C_4H_4O_2)_3N_2$ [83°], crystallising from ether (Gerhardt a. Chiozza, *A.* 90, 108).—$AgA'NH_3$: crystalline.

Methylimide $C_2H_4:C_2O_2:NMe$. [66·5°]. (234°). Formed by distilling methylamine succinate. Plates. Got also by the action of conc. H_2SO_4 on the oxim of *β*-acetyl-propionic acid (Rischbieth; Bredt a. Boeddinghous, *A.* 251, 316).

Ethylimide $C_2H_4:C_2O_2:NEt$. [26°]. (234°). Formed by distilling acid ethylamine succinate (M.), and by adding alcoholic EtI to sodium succinimide (Landsberg, *A.* 215, 212). Long lancet-shaped crystals, v. sol. water, alcohol, and ether. Yields ethyl-pyrrole on distillation over zinc-dust.

Allylimide $C_2H_4:C_2O_2:NC_3H_5$. (245°). S.G. $\frac{0}{4}$ 1·1543; $\frac{12}{4}$ 1·1432. Formed by heating succinic acid with allyl thiocarbimide. Liquid, v. sol. water and alcohol.

Ethylene-imide $(C_2H_4:C_2O_2:N)_2C_2H_4$. [251°]. (395°). Formed by heating succinic acid with the hydrate of ethylene-diamine at 180° (Mason, *C. J.* 55, 10). Prisms, sol. hot water, v. sl. sol. hot alcohol, insol. ether.

Propylene-imide $(C_2H_4:C_2O_2:N)_2C_3H_6$. [100°]. Formed from the anhydride and propylene-diamine (Strache, *B.* 21, 2360). Crystals (from benzene).

Phenylimide $C_2H_4:C_2O_2:NPh$. *Succinanil.* [156°] (L. a. G.; Kauder, *J. pr.* [2] 31, 17). [150°] (Hübner, *A.* 209, 373; Bischoff a. Nastvogel, *B.* 22, 1807) (above 300°). Formed by heating succinic acid with aniline, and crystallising the product from water and alcohol successively (Laurent a. Gerhardt, *A. Ch.* [3] 34, 179). Formed also by the action of PCl_5 on $C_2H_4(CO.NHPh).CO_2H$ in chloroform (Anschütz, *B.* 21, 957). Needles, sl. sol. hot water. PCl_5 in presence of boiling $POCl_3$ forms the phenylimide of di-chloro-maleïc acid $C_2Cl_2:C_2O_2:NPh$. Alcoholic NH_3 forms $C_2H_4(CONH_2).CONHPh$. Boiling lime-water forms $C_2H_4(CO_2H).CONHPh$. Fuming HNO_3 forms an *o*-nitro- derivative [156°]

and the *p*-nitro- derivative [205°–208°]. The salt $C_2H_4{:}C_2O_2{:}NC_6H_4.SO_3Na$ is got by heating succinic acid with sodium amido-benzene *p*-sulphonate (Pellizzari, *G.* 18, 317).

Benzylimide $C_2H_4{:}C_2O_2{:}NCH_2Ph$. [99°]. Formed from benzyl chloride, succinimide, and alcoholic NaOH (Werner, *C. J.* 55, 629). Six-sided prisms, sol. alcohol.

o-Tolylimide $C_2H_4{:}C_2O_2{:}NC_6H_4Me$. [75°]. (345° uncor.). Formed by heating *o*-toluidine with succinic acid (Michael, *B.* 10, 579; Bechi, *B.* 12, 25, 321). Needles, v. sol. water.

p-Tolylimide. [150°]. (345°). Needles (from water), sl. sol. cold water. Yields on nitration $C_2H_4{:}C_2O_2{:}NC_6H_3Me(NO_2)$[1:4:2] [140°] (Hübner, *A.* 209, 378).

Tri-methyl-phenyl-imide $C_2H_4{:}C_2O_2{:}NC_6H_2Me_3$. *Succinmesidil.* [137°]. Formed by heating succinic acid with mesidine (Eisenberg, *B.* 15, 1018). Pearly plates, sol. alcohol and ether, sl. sol. water.

(*a*)-*Naphthylimide* $C_2H_4{:}C_2O_2{:}NC_{10}H_7$. [153°]. Formed by heating succinic acid with (*a*)-naphthylamine (Hahnemann, *B.* 10, 1713; Hübner, *A.* 209, 381; Pellizzari, *A.* 248, 158). Needles, m. sol. alcohol. Yields a di-nitro-derivative [250°]. The sulphonic acid $C_2H_4{:}C_2O_2{:}NC_{10}H_6SO_3H$, prepared from (*a*)-naphthylamine *p*-sulphonic acid, yields KA′2aq (Pellizzari, *G.* 18, 321).

(*β*)-*Naphthylimide.* [180°]. Colourless needles, v. sol. alcohol. Converted by KOHAq into $CO_2H.C_2H_4.CO.NHC_{10}H_7$ [192°] (Pellizzari, *A.* 248, 159).

Benzimidide $C_2H_4{:}C_2O_2{:}NCPh{:}NH$. [212°]. Formed from acetyl-succinic ether $C_{10}H_{16}O_5$, benzamidine hydrochloride, and NaOHAq (Pinner, *B.* 22, 2620). Needles, sl. sol. cold acetone and ether, sol. alcohol.

References.—Amido-, Bromo-, Bromo-amido-, Chloro-, Nitro-, and Oxy-succinic acid and Di-iodo-succinamic acid.

Isosuccinic acid *v.* Methyl-malonic acid.

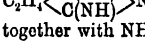
SUCCINIC ALDEHYDE. Reduction of succinic anhydride, which might be expected to yield the aldehyde, forms instead the isomeric *γ*-oxy-butyric lactone.

Oxim $C_2H_4(CH{:}NOH)_2$. [173°]. Formed by heating pyrrole with hydroxylamine hydrochloride at 100° and, together with ethylamine, by the action of hydroxylamine on *ν*-ethyl-pyrrole (Ciamician, *B.* 17, 533; 22, 1968; 23, 1788). Small white crystals (from alcohol). May be reduced to tetramethylene-diamine $C_2H_4(CH_2.NH_2)_2$ [28°].

Phenyl hydrazide $C_2H_4(CH{:}N_2HPh)_2$. [125°]. Formed by heating a solution of the oxim (1 pt.) in water (50 pts.) with phenyl hydrazine (5 pts.) dissolved in dilute HOAc (Ciamician, *B.* 22, 1974; 23, 1784). Small silky plates, v. sol. alcohol. Converted by cold conc. HClAq into a base $C_{20}H_{20}N_4$ [185°], which crystallises from EtOAc in needles, v. sl. sol. alcohol, and gives a deep-blue colour with $K_2Cr_2O_7$ and H_2SO_4.

Succinic semi-aldehyde. *Nitrile* $CN.CH_2.CH_2.CHO$. *β-Cyanopropionic aldehyde* (77°). S.G. $\frac{15}{15}$ ·89. Formed by heating $CH_2I.CH_2.CHO$ (92 g.) with alcohol (180 g.) and AgCy (67 g) for ten hours (Chautard, *A. Ch.* [6] 16, 182). Oil, not solid at −20°, miscible with alcohol and ether. Reduces Fehling's solution. Does not combine with $NaHSO_3$ or phenyl-hydrazine. Decomposed by hot alkalis and acids. Aniline at 350° forms the compound $CH_2Cy.CH(NHPh)_2$.

Succinimidine $C_4H_7N_3$ *i.e.*

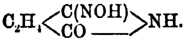


$C_2H_4{<}\begin{array}{l}C(NH)\\ C(NH)\end{array}{>}NH$. Formed, as hydrochloride, together with NH_4Cl, by the action of water on succinamidine (Pinner, *B.* 16, 362, 1657; 18, 2845).—B″HCl: long plates, v. sol. water, sl. sol. alcohol. Converted by acetoacetic ether into crystalline $C_8H_{11}N_3O_2$.—B″$(HNO_3)_2$ ½aq: leaflets (Grabowski, *A.* 265, 168).—$AgC_4H_6N_3$: ppd. by adding ammoniacal $AgNO_3$ to a solution of the hydrochloride.

SUCCINIMIDO-ACETIC ETHER $C_8H_{11}NO_4$ *i.e.* $C_2H_4{:}C_2O_2{:}N.CH_2.CO_2Et$. [67°]. Formed by heating succinimide with alcohol, NaOEt, and $CH_2Cl.CO_2Et$ (Haller a. Arth, *C. R.* 105, 280). Needles, v. sol. water, alcohol, and ether. Alcoholic NaOEt forms gelatinous $C_8H_{10}NaNO_4$.

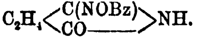
SUCCINIMIDO-ETHYL ETHER $C_8H_{16}N_2O_2$ *i.e.* $C_2H_4(C(NH).OEt)_2$. The hydrochloride B″2HCl is prepared by passing gaseous HCl into an ethereal solution of ethylene cyanide (Pinner, *B.* 16, 359). It is v. sl. sol. alcohol and ether, and decomposed by water into succinic ether and NH_4Cl. With ammonia it gives $C_2H_4(C(NH).NH_2)_2$.

SUCCINIMIDOXIM



$C_2H_4{<}\begin{array}{l}C(NOH)\\ CO\end{array}{>}NH$. [197°]. Formed by heating ethylene cyanide with alcoholic hydroxylamine at 65° (Garny, *B.* 24, 3427). White crystals, sol. water.—B′HCl. [98°]. Needles.—$B'C_6H_3N_3O_7$. [212°].

Benzoyl derivative



$C_2H_4{<}\begin{array}{l}C(NOBz)\\ CO\end{array}{>}NH$. [184°]. Formed from the oxim, NaOH, and BzCl. White powder, sol. alcohol, sl. sol. ether.

SUCCINOPHENONE *v.* Di-phenyl ethylene diketone.

SUCCINOXYL-AMIDO-BENZOIC ACID *v.* Carboxy-phenyl-succinamic acid.

SUCCINYL-AMIDO-BENZOIC ACID *v.* Amido-benzoic acid.

SUCCINYL-SUCCINIC ACID *v.* Di-oxy-terephthalic acid dihydride, vol. iii. p. 777.

SUCCISTERENE $C_{15}H_{10}$. [160°]. (above 300°). Occurs in the product of distillation of amber (Pelletier a. Walter, *A. Ch.* [3] 9, 96). Flat needles, nearly insol. cold alcohol, v. sl. sol. ether.

SUGAR, a term applied to the members of a group of carbohydrates in consequence of the property they possess of being sweet to the taste and of their relationship to the substance to which the term was originally given. The known natural members of this group are not very numerous. They are all easily soluble in water crystallisable, and diffusible. When solutions of them are heated with alkaline solutions of the more easily reducible metals, reduction takes place with precipitation of the lower oxides in some cases, and of the metals in others; some sugars, before exhibiting this property, require to be digested with dilute mineral acids. Enzymes also convert some of the non-reducing members into reducing ones. With phenyl hydrazine they yield *phenylhydrazides* and *phenylosazones*. Oxidising agents easily convert them into acids, and reducing agents into alcohols. Some of them undergo fermentation when submitted to the action of beer yeast, *i.e.* they are decomposed into alcohol, CO_2, &c. They yield solutions which are optically active, those of some rotating the plane of polarisation to the right, of others to the left. They give colour reactions with aromatic acids and phenols.

The group may be divided into two classes: (1) those which, when digested with dilute acids, do not yield any other sugar or sugars—the sugars of this class are distinguished by the termination *-ose*; (2) those which, when digested with dilute acids, do yield some other sugar or sugars—these sugars are distinguished by the termination *-on*. They are designated according to the number of carbon atoms they contain: thus, pentose containing C_5, hexose containing C_6, &c., and di-penton containing C_{10}, di-hexon containing C_{12}, &c.

The members of the *-ose* class are:

Triose $C_3H_6O_3$, glycerose
Tetroses $C_4H_8O_4$, erythrose
$C_4H_7(C_6H_5)O_4$, phenyltetrose
Pentoses $C_5H_{10}O_5$, arabinose
,, ribose
,, xylose
$C_5H_9(CH_3)O_5$, rhamnose (methyl pentose)
,, fucose (ditto)
Hexoses $C_6H_{12}O_6$, *d*- *l*- and *i*-[1] glucose (*d*-glucose = dextrose)
,, *d*- *l*- and *i*-mannose
,, *d*- *l*- and *i*-gulose
,, *d*- *l*- and *i*-fructose (*d*-fructose = lævulose)
,, *d*- *l*- and *i*-galactose
,, sorbose (sorbinose)
,, formose
,, lokaose
,, *β*-acrose
$C_6H_{11}(CH_3)O_6$, rhamnohexose (methyl hexose).
Heptoses $C_7H_{14}O_7$, mannoheptose
,, *α*- and *β*-glucoheptose
,, galaheptose
,, fructoheptose
,, digitalose
$C_7H_{13}(CH_3)O_6$, rhamnoheptose (methyl heptose).
Octoses $C_8H_{16}O_8$, mannoctose
,, *α*- and *β*-glucooctose
Nonoses $C_9H_{18}O_9$, mannononose
,, glucononose

The members of the *-on* group are:

Di-penton $C_{10}H_{18}O_9$, arabinon
Di-hexon $C_{12}H_{22}O_{11}$, cane-sugar (saccharon)
,, milk-sugar, lactose (lacton)
,, maltose (di-glucon, amylon)
,, iso-maltose
,, melibiose
,, trehalose
,, cyclamose
,, para- saccharose
,, tewfikose (tewfikon)
Tri-hexon $C_{18}H_{32}O_{16}$, raffinose
,, melezitose
Hex-hexon $C_{36}H_{62}O_{31}$, gentianose
,, stachyose

Occurrence.—Some of these sugars have been obtained by synthesis, others are products of the action of dilute acids or ferments on more complicated bodies, and others occur naturally. The most important source of the latter is the vegetable kingdom. Little, if anything, is known concerning the formation of the sugars in nature; it is very probable that they are intermediate products of assimilation between CO_2 and H_2O, and starch, inulin, cellulose, and such bodies. For an account of the various theories, see text-books of vegetable and animal physiology. The sugars found in animals are most probably of vegetable origin.

Determination.—Owing to the fact that the sugars possess many properties in common, the presence of a particular sugar can only be definitely proved by its isolation in the pure state, and a determination of its optical activity, reducing power, and other definite distinguishing properties (*v.* end of art.).

Molecular Weight.—Until quite recently none of the accepted methods for determining molecular weights were applicable to the sugars. At the present time there are several, chief among which are the physical methods of Raoult (*A. Ch.* [5] 28, 133; [6] 2, 66-124; [6] 4, 401; [6] 8, 289 a. 317), and De Vries, which are of general application, and the various chemical ones which are of special application. By Raoult's method Brown and Morris (*C. J.* 1888. 610; 1889. 462), Tollens and Mayer (*B.* 21, 1566), and Tollens, Mayer, and Wheeler (*B.* 21, 3508), Ekstrand and Mauzelius (*Vetensk. Akad. für Handl.* 1889. 157), and O'Sullivan (*C. J.* 1890. 62) have determined the molecular weight of xylose and arabinose to be 150, corresponding to a formula $C_5H_{10}O_5$; of dextrose, lævulose, galactose to be 180, corresponding to a formula $C_6H_{12}O_6$; of arabinon to be 282, corresponding to a formula $C_{10}H_{18}O_9$; of cane sugar, maltose, lactose to be 342, corresponding to a formula $C_{12}H_{22}O_{11}$; and of raffinose to be 504, corresponding to a formula $C_{18}H_{32}O_{16}$. These numbers have been confirmed in the case of the simpler sugars by various chemical methods (see succeeding paragraphs). In the case of arabinose it was first shown to be $C_5H_{10}O_5$ by Kiliani (*B.* 20, 339) by the analysis of some of its compounds, its formula previously having been considered to be $C_6H_{12}O_6$.

Synthesis.—The first step towards the synthesis of the sugars was made by Butlerow (*A.* 120, 295; *C. R.* 53, 145). He obtained a sweet syrup, having the common characteristics of the sugars, by adding lime-water to a hot solution of di-oxymethylene; the product he called *methylenitan*, and considered its formula to be $C_7H_{14}O_6$. The next step was made by Loew (*J. pr.* 33, 321), who, having discovered a method for the preparation of formaldehyde (CH_2O) in quantity, investigated its condensation by lime-water. He obtained a sweet syrup, which he called *formose*, and considered it to have a formula $C_6H_{12}O_6$. Neither methylenitan nor formose fermented with yeast (see also Tollens, *B.* 19, 2133). Fischer (*B.* 21, 989) finds these products to be a mixture of various saccharine bodies, the chief which is a sugar, formose $C_6H_{12}O_6$, yielding an osazone $C_{18}H_{22}N_4O_4$, m.p. 144°. Another sugar is present in smaller quantities in the condensation products of formaldehyde. It yields an osazone greatly resembling glucosazone, which has been identified with α-acrosazone. Later, Loew (*B.* 22, 475), by the condensation of formaldehyde with lead oxide and magnesia, obtained a sugar which is fermentable. Loew called this *methose*, but Fischer has shown it to be identical with α-acrose.

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[1] *d*, *l*, and *i*. Fischer's notation, see p. 532.

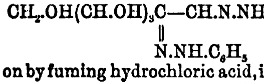
Acrose was obtained by Fischer (*B.* 20, 1093 and 2566) by acting on acrolein bromide with bases $2C_3H_4OBr_2 + 2Ba(OH)_2 = C_6H_{12}O_6 + 2BaBr_2$. Two isomeric sugars, α-acrose and β-acrose, are thus produced.

Glycerose yields these two sugars by the action of alkalis. (Glycerose is a sugar $C_3H_6O_3$, obtained by the action of bromine and soda on glycerol and other methods by Van Deen, *J.* 1863. 501; Grimaux, *C. R.* 104, 1276; and Fischer a. Tafel, *B.* 20, 1088 and 3385; 22, 106. It is probably a mixture of the aldehyde and ketone of glycerol.) The formation of α-acrose from glycerose may be represented

$$CH_2(OH).CH(OH).COH + CH_2.OH.CO.CH_2OH = CH_2OH.CH(OH).CH(OH).CH(OH).CO.CH_2OH.$$

The sugars can only be separated from the products thus obtained as osazones; α-acrosazone is identical with glucosazone in every way except in its action on polarised light.

α-acrosazone



$$\begin{array}{l}CH_2.OH(CH.OH)_3C—CH.N.NHC_6H_5\\ \qquad\qquad\qquad\quad\ \| \\ \qquad\qquad\qquad\ N.NH.C_6H_5\end{array}$$

acted on by fuming hydrochloric acid, is converted into α-acrosone $CH_2.OH.(CH.OH)_3CO.COH$, which, when reduced by zinc and acetic acid, yields a sugar $CH_2.OH(CH.OH)_3.CO.CH_2OH$, in the form of a sweet syrup; it ferments with yeast, yields lævulinic acid when heated with hydrochloric acid, and is reduced by sodium-amalgam to a hexahydric alcohol α-acritol, which resembles mannitol in every way except that it is optically inactive. By these various reactions so much is lost that from 1 kilo. glycerol only 0·2 g. acritol is obtained. Further, all the bodies obtained in the processes were optically inactive. More knowledge was necessary before the natural sugars could be synthesised. At this stage a new light was thrown on the subject by an observation of Fischer (*B.* 23, 870) that arabinose carboxylic acid and mannonic acid were identical in every way except that their optical activities, although equal, were opposite in sign, and that they combined to form an optically inactive acid. These three acids were reduced by sodium-amalgam to three sugars resembling one another in all respects except that one of them had a right-handed optical activity, the other an equal but left-handed one, while the third was optically inactive. They are named *l-mannose*, *i-mannose*, and *d-mannose*;[1] by further reduction they yielded the corresponding hexahydric alcohols *l-mannitol*, *i-mannitol*, and *d-mannitol*.

The sugar obtained from α-acrosazone as above described is identical with lævulose except that it is inactive. If, then, we can decompose this lævulose into *d*-lævulose and *l*-lævulose, the synthesis of the natural sugar will be accomplished. This Fischer has done (*B.* 23, 870). If *i*-lævulose be submitted to the action of yeast, the lævo- constituent ferments and the residue is dextrorotatory. This is *l*-lævulose; it is not the natural sugar: that belongs to the *d*- group, and was destroyed by the ferment.

To obtain the natural sugar from the inactive synthetic one, Fischer proceeded as follows:—*i*-mannitol, *i.e.* α-acritol, is oxidised by nitric acid to *i*-mannose, and this further by bromine-water to *i*-mannonic acid. By fractional crystallisation of the strychnine or morphine salts it can be mesotomised, the result being *d*- and *l*- mannonic salts, which, on being freed from the base, yield by reduction the corresponding mannoses and mannitols. These, by means of the osazones, can be converted into the corresponding lævuloses (see *Dextrosazone*).

Dextrose and mannose both yield the same osazone; the difference in their constitution must therefore be caused by the position of the group marked with a * in the formula

$$CH_2(OH).CH(OH).CH(OH).CH(OH).{}^*CH(OH).COH.$$

Fischer (*B.* 23, 799 a. 2611) found that by heating gluconic acid with quinoline, part was converted into mannonic acid and part unaltered; and also that mannonic acid, treated in the same way, yielded some gluconic acid. Dextrose may then be obtained by reducing the gluconic acid thus obtained. The corresponding reaction with *l*-mannonic acid does not take place easily, if at all, but *l*-gluconic acid is produced simultaneously with arabinose carboxylic acid (*l*-mannonic acid) by Kiliani's mode of preparation (see *Arabinose*). From *l*-gluconic acid, by reduction, *l*-glucose, the optical isomer of dextrose, is obtained. The table on next page gives a concise view of the synthesis of dextrose, lævulose, and mannose.

Another sugar, *gulose*, stereoisomeric with glucose, has been obtained by Fischer (*B.* 23, 93; 24, 521) by the reduction of saccharic acid, the *d*-, *l*- and *i*- modifications being obtained by the reduction of *d*-, *l*- and *i*- saccharic acids. As these are the products of the oxidation of *d*- *l*- and *i*- glucose, the synthesis of gulose is complete.

Galactose has not been synthesised up to the present (June 1893), but by the reduction of mucic acid Fischer and Hertz (*B.* 25, 1247) have obtained *i*-galactonic acid and *i*-galactose; *i*-galactonic acid, by the fractional crystallisation of its strychnine salt, may be mesotomised into *d*- and *l*- galactonic acids from which *d*- and *l*-galactose are obtained; *d*-galactose is identical with ordinary galactose.

Arabinose has not been directly synthesised, but its relationship to the synthetical sugars is shown by the fact that the two acids obtained from arabinose by the nitrile reaction are *l*-mannonic acid and *l*-gluconic acid (Fischer, *B.* 23, 2611; 24, 539).

Of xylose the same must be said; but by the nitrile reaction it yields *l*-gulonic acid (Fischer a. Stahel, *B.* 24, 528).

Arabonic acid, when heated with quinoline, is partly changed into its stereoisomeride ribonic

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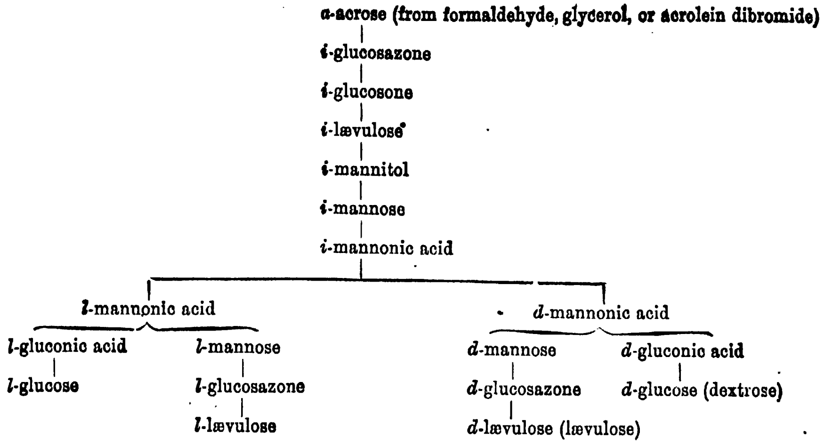
[1] *l*, *i*, and *d* are very unsatisfactory, and somewhat misleading; but as Fischer has introduced them we must let them stand. A little study will make their meaning clear.



acid, just as gluconic acid yields gulonic acid; ribonic acid, by reduction, yields the stereoisomeride of arabinose, which it is proposed to call *ribose*.

The synthetical passage from an *-ose* sugar to an *-on* one is said to be accomplished for lactose (lacton) and cane sugar (saccharon) as well as for maltose (amylon).

Lacton. A mixture of dextrose and galactose, is acted on by acetic anhydride, and the resulting products, carefully saponified with alkali, yield lacton (Demole, *C. R.* 89, 481). This has been contradicted by Berthelot (*Bl.* [2] 34, 82) and by Herzfeld (*A.* 220, 219).

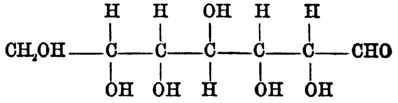
Sucron. A body having a dextrorotatory power, and by inversion becoming lævorotatory, was obtained by acting on aceto-chlorhydrose (a derivative of dextrose) with an alcoholic solution of lævulose in the presence of barium carbonate. Another body which was lævorotatory, and became less lævorotatory on inversion, was obtained by acting on aceto-chlorhydrose by sodium lævulosate (Colley a. Vakovitch, *Bl.* [2] 34, 326).

Isomaltose has been prepared by Fischer (*B.* 23, 3687) by the action of HCl on dextrose. Dilute acids again hydrolyse it to dextrose, the same product as is yielded by maltose.

Phenyl-tetrose has been prepared synthetically from cinnamaldehyde cyanhydrin; this, by the action of bromine, yielding phenyl-dibromo-oxy-butyronitrile CH.Ph.Br.CH.Br.CH.OH.CN, which, when heated with hydrochloric acid, yields phenyl-bromo-di-oxy-butyrolactone, from which the corresponding acid OH.CH.Ph.CHBr.CH.OH.COOH is easily obtained, and which on reduction yields the sugar OH.CH.Ph.CH(OH).CH(OH).COH.

It will not be out of place here to indicate what has been done in the way of converting a sugar into one containing a carbon atom more. To do this, Fischer (*B.* 22, 2204; 23, 370, 799, 930, 2226, and 3102; *Ann.* 270, 64) made use of the well-known reaction for proceeding from one alcohol to its next higher homologue by means of the nitrile. Now, in this reaction, where an asymmetric carbon atom is added to the molecule, Van't Hoff has predicted that two isomeric bodies will be formed which will differ by the arrangement of the groups round the new carbon atoms. Fischer (*Ann.* 270, 64) has shown that this is so in the case of the glucose homologues, the two acids obtained from glucose being α- and *β-glucoheptonic acids*; α-glucoheptonic acid is always the principal product of the reaction, and is identical with the dextrose carboxylic acid described by Kiliani (see *Dextrose*). When the reaction takes place at 20°–25° hardly a trace of the β- acid is formed; but at 40° about 13 p.c. of the latter is obtained. By oxidation these acids yield two penta-oxy-pimelic acids, the α- acid being optically inactive, and by reduction the two sugars α- and *β-glucoheptose* are obtained.

α-Glucoheptose

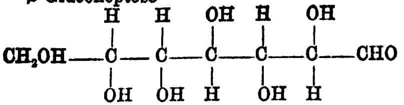


$$CH_2OH - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - \overset{OH}{\underset{H}{C}} - \overset{H}{\underset{OH}{C}} - \overset{H}{\underset{OH}{C}} - CHO$$

separates from its aqueous solution in rhombic prisms, m.p. 180°–190°; they have a faintly sweet taste, dissolve in 10·5 pts. of water at 14°, and are easily soluble in hot water and sparingly in hot alcohol. Its solution is optically active. Freshly-prepared solutions show a slight bi-rotation; for a 10 p.c. solution, $[\alpha]_{D20^\circ} = -19{\cdot}7^\circ$. It does not ferment with yeast, but reduces Fehling slightly less than dextrose. It is oxidised by bromine to α-glucoheptonic acid. It yields a hydrazone $C_7H_{14}O_6N_2HC_6H_5$, very soluble in water, m.p. 170°, and also an osazone $C_7H_{12}O_5(N_2HC_5H_5)_2$, forming yellow needles, m.p. 195°, almost insoluble in water and difficultly in hot alcohol. Treated with acetic anhydride and zinc chloride it yields a hexacetate, m.p. 156°, and with sodium acetate and acetic anhydride it yields *dec-acetyl-diglucoheptose* $C_{14}H_{16}(C_2H_3O)_7O_{13}$, m.p. 131°–132°.

By reduction with sodium-amalgam, α-glucoheptose yields α-glucoheptitol, which crystallises in delicate prisms, m.p. 127°–128°, is optically inactive, easily soluble in water and sparingly in alcohol. It yields a heptacetyl derivative $C_7H_9(C_2H_3O)_7O_7$.

β-Glucoheptose



$$\begin{array}{ccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \mathrm{OH} & & \\ & & | & & | & & | & & | & & | & & \\ \mathrm{CH_2OH} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{C} & — & \mathrm{CHO} \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{OH} & & \mathrm{OH} & & \mathrm{H} & & \mathrm{OH} & & \mathrm{H} & & \end{array}$$

is obtained by the reduction of β-glucoheptonic acid, it has not yet been obtained in a crystalline state, it forms a phenyl-hydrazide $C_7H_{11}O_6N_2H.C_6H_5$, crystallising from alcohol in slender needles, m.p. 192°; the osazone is identical with α-glucoheptosazone.

Just as dextrose yields two isomeric glucoheptonic acids, so α-glucoheptose yields two isomeric glucoctonic acids. The α- acid is the chief product, and the amount of β- acid formed varies with the temperature. α-Glucoctonic acid yields a lactone $C_8H_{14}O_8$, sparingly soluble in alcohol and readily in water, m.p. 145°–147° $[\alpha]_{D20^\circ} = -45{\cdot}9$; by reduction with sodium-amalgam it yields *α-glucoctose* $C_8H_{16}O_8.2H_2O$, which crystallises in colourless needles, m.p. 93°. Its aqueous solutions are optically active and show bi-rotation, $[\alpha]_{D20^\circ}$ $= -50{\cdot}5^\circ$ for the anhydrous sugar. It yields a phenyl hydrazone $C_8H_{16}O_7.(N_2HC_6H_5)$, m.p. 190°, and an osazone $C_8H_{14}O_6(N_2HC_6H_5)_2$, m.p. 210°–212°, almost insoluble in water. By reduction with sodium-amalgam it yields α-glucoctitol $C_8H_{18}O_8$, which is easily soluble in water; it forms slender white needles, m.p. 141°. From α-glucoctose two gluconononic acids may be prepared. Only one has been examined; this when reduced yields gluconononose $C_9H_{18}O_9$, its phenylhydrazide $C_9H_{18}O_8N_2HC_6H_5$ is sparingly soluble in cold water and alcohol, m.p. 195°–200°, its phenyl osazone $C_9H_{18}O_7(N_2HC_6H_5)_2$ is sparingly soluble in hot water and alcohol, m.p. 220°–223°. Unlike mannononose, gluconononose does not ferment with yeast. By reduction gluconononitol is obtained.

Mannoheptose $C_7H_{14}O_7$ is obtained by the reduction of mannoheptonic acid. It crystallises from alcohol in fine needles, it has a sweet taste, m.p. 134°–135°. It is easily soluble in water, and does not ferment with yeast; its solution is dextrorotatory and exhibits bi-rotation, the constant value is $[\alpha]_D = +68{\cdot}6^\circ$. It yields a difficultly soluble hydrazide $C_7H_{11}O_6.N_2H.C_6H_5$, m.p. 197°–200°, and an osazone $C_7H_{12}O_5(N_2H.C_6H_5)_2$, m.p. 200°. By reduction with sodium-amalgam it yields a heptahydric alcohol which is identical with the naturally produced body, perseit (Maquenne, *A. Ch.* [6] 19, 1; *C. R.* 107, 583). It combines with hydrocyanic acid, and the compound decomposed by hydrochloric acid yields mannoctonic acid.

Mannoctose $C_8H_{16}O_8$ is obtained by the reduction of mannoctonic acid. It is easily soluble in water, has a sweet taste, and does not ferment with yeast. Its aqueous solutions are lævorotatory, $[\alpha]_D = -3{\cdot}3^\circ$. It yields a hydrazone $C_8H_{16}O_7.N_2H.C_6H_5$, difficultly soluble in water, m.p. 212°; and an osazone $C_8H_{14}O_6(N_2H.C_6H_5)_2$, m.p. 223°. By reduction it yields the octohydric alcohol mannoctitol. It combines with hydrocyanic acid, and the compound decomposed by hydrochloric acid yields mannonononic acid.

Mannononose $C_9H_{18}O_9$ is obtained by the reduction of mannonononic acid. It is easily soluble in water and crystallises from alcohol, m.p. about 130°, its solution is dextrorotatory, $[\alpha]_D$ $= +50^\circ$ approx. It ferments readily and completely with yeast, and resembles dextrose in many ways. It yields a difficultly soluble hydrazide $C_9H_{18}O_8.N_2H.C_6H_5$, m.p. 223°, and an osazone, m.p. 217°.

Galactoheptose $C_7H_{14}O_7$ is obtained by the reduction of galacto-heptoic acid. Its hydrazide (m.p. 199°) is sparingly soluble; so is its osazone (m.p. 220°).

Fructoheptose is obtained from lævulose by the same set of reactions.

Rhamnohexose $CH_3.(CH.OH)_5COH$ is obtained by the reduction of rhamnohexolactone (Fischer a. Piloty, *B.* 23, 3102); it does not ferment with yeast, but exhibits all the characters of a sugar; the osazone is obtained in stellate groups of needles, m.p. 200°. On reduction the sugar yields *rhamnohexitol* $CH_3(CH.OH)_5CH_2OH$; by the action of hydrocyanic acid on rhamnohexose, the lactone of rhamnoheptonic acid is obtained, which on reduction yields *rhamnoheptose.* The osazone forms yellow needles, m.p. 200°; by the action of hydrocyanic acid, *rhamnooctonic* acid is obtained. These compounds have the following optical activities:—

Rhamnose, $[\alpha]_D = +8^\circ$.
Rhamnohexose, $[\alpha]_D = -61{\cdot}1^\circ$.
Rhamnoheptose, $[\alpha]_D = +8{\cdot}4^\circ$.
Rhamnitol, $[\alpha]_D = +10{\cdot}7^\circ$.
Rhamnohexitol, $[\alpha]_D = +11{\cdot}6^\circ$.
Rhamnohexonolactone, $[\alpha]_D = +83{\cdot}8^\circ$.
Rhamnoheptolactone, $[\alpha]_D = +55{\cdot}6^\circ$.
Rhamnoctonolactone, $[\alpha]_D = -51{\cdot}2^\circ$.

The reverse of the method of proceeding from one sugar to its next higher homologue—*i.e.* the production of a sugar containing one less carbon atom than the original one—has been effected by Wohl (*B.* 26, 730). When dextrose oxim (*vide* below) is treated with acetyl chloride it yields an acetyl compound from which hydrocyanic acid can be eliminated, and on hydrolysis of the resulting compound a pentose is obtained, which is *d-arabinose*; *l*-arabinose (ordinary arabinose) treated in the same way as dextrose yields a tetrose.

As is well known, mucic and saccharic acids are products of the oxidation of the sugars with nitric acid. The action of reducing agents on these bodies indicates their relationship to the sugars and helps to a clearer idea of the synthetical process.

Reduction of mucic acid. Sulphuric acid and zinc-dust reduce mucic acid to *i*-galactonic acid (Fischer a. Hertz, *B.* 25, 1247). The lactone crystallises in delicate prisms, m.p. 122°–125°. It is optically inactive. By further reduction with sodium-amalgam *i*-galactose is obtained. This can be prepared as a crystalline mass, m.p. 140°–142°; it yields a hydrazide, m.p. 158°–160° and an osazone, m.p. 195°, which is identical with that obtained from the oxidation product of dulcitol (Fischer a. Tafel, *B.* 20, 3384).

i-Galactonic acid may be separated into the *d*- and *l*- acids by fractional crystallisation of the strychnine salts. The two acids yield respectively *d*- and *l*-galactose; *d*-galactose is identical with ordinary galactose. *l*-Galactose may also be obtained by the fermentation of *i*-galactose syrup. The sugar crystallises from alcohol, m.p. 162°–163°, its specific rotatory power is $[\alpha]_D = -73{\cdot}6^\circ$, the phenyl-hydrazide

melts at 158°–160° and the osazone at 192°–195°. From this, as well as from other matters connected with the synthetical portion of the work, it will be seen that *d*-, *i*-, and *l*- were intended to mean dextro-, inactive, and lævo-, as indicating the optical activity of the substances to which they are prefixed ; but it is obvious the *d*- body is not always dextro-, nor the *l*- body lævo-. Hence the unsatisfactoriness already indicated.

Reduction of saccharic acid. Fischer (*B.* 23, 930 ; 24, 521) found that the lactone of saccharic acid was easily reduced by sodium-amalgam with formation of glycuronic acid. Thierfelder (*H.* 15, 71) has shown that this latter is further reduced to an acid $C_6H_{12}O_7$, which reaction Fischer has confirmed, and calls the acid *gulonic acid* and the corresponding sugar *gulose.* The relationship of these bodies to the others of the sugar group is shown here:

Dextrose .	. $OH.CH_2.(CH.OH)_4.COH$.
Gluconic acid	. $OH.CH_2.(CH.OH)_4.COOH$.
Saccharic acid	. $COOH.(CH.OH)_4.COOH$.
Glycuronic acid	. $COOH.(CH.OH)_4.COH$.
Gulonic acid	. $COOH.(CH.OH)_4.CH_2OH$.
Gulose .	. $COH.(CH.OH)_4.CH_2OH$.

Glycuronic acid obtained by the reduction of *d*-saccharic acid has $[\alpha]_D = +19{\cdot}1°$, m.p. 175°–178° ; *d-gulonic acid* obtained by the reduction of glycuronic acid yields a lactone, m.p. 180°–181°, $[\alpha]_D = +55°$; its phenyl-hydrazide is easily soluble in hot water and hot alcohol, m.p. 147°–149° ; *d-gulose* obtained by the reduction of *d*-gulonic lactone is a colourless syrup, easily soluble in water and sparingly in absolute alcohol, it is oxidised by nitric acid to saccharic acid, it does not ferment with yeast.

CONSTITUTION. Dextrose and galactose are represented by the formula

$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).COH$

and lævulose by

$CH_2(OH).CH(OH).CH(OH).CH(OH).CO.CH_2OH$

and for the following reasons.

By oxidation dextrose and galactose yield acids containing the same number of carbon atoms as themselves, whilst lævulose yields acids containing less carbon atoms than itself ; dextrose and galactose yielding gluconic and galactonic acids $CH_2(OH)\{CH(OH)\}_4.COOH$ and by further oxidation saccharic and mucic acids $COOH\{CH(OH)\}_4COOH$ respectively ; whilst lævulose gives rise to trioxybutyric $CH_2(OH)\{CH(OH)\}_2COOH$, formic $H.COOH$, and glycollic $CH_2OH.COOH$ acids.

By reduction dextrose and galactose yield respectively mannitol and dulcitol ; lævulose also yields mannitol. These yield hexacetyl derivatives, and are reduced by hydriodic acid to secondary hexyl iodide $CH_3.(CH_2)_3CHI.CH_3$ (Wanklyn a. Erlenmeyer, *J.* 1861. 731 ; 1862. 480) ; they are evidently hexahydric alcohols of normal hexane.

All three sugars combine with hydrocyanic acid to form nitriles which when boiled with hydrochloric acid yield different acids $C_7H_{14}O_8$, which are reduced by hydriodic acid to heptoic acids ; dextrose and galactose yielding normal heptoic acid $CH_3(CH_2)_5.COOH$ and lævulose yielding methyl-butyl-acetic acid $\left.\begin{matrix}CH_3\\C_4H_9\end{matrix}\right\}CH.COOH$ (Kiliani, *B.* 18, 3066 ; 19, 221, 767 a. 1128). **Galactose, dextrose, and lævulose form oxims or iso-nitroso- compounds by combination** with hydroxylamine (Rischbieth, *B.* 20, 2673 ; Jacobi, *B.* 24, 696 ; Wohl, *B.* 24, 993). With phenyl-hydrazine, dextrose and galactose yield hydrazides

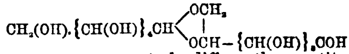
$CH_2(OH)\{CH(OH)\}_4CH.N_2H.C_6H_5$;

lævulose does not ; but all three yield osazones $CH_2(OH)\{CH(OH)\}_3C.N_2H.C_6H_5.CH.N_2H.C_6H_5$. All three yield pentacetyl derivatives (Erwig a. Koenigs, *B.* 22, 2207). Previous to Fischer's synthetic work, other formulæ had been suggested (Tollens, *Kurzes Handbuch d. Kohlenhydrate* ; *B.* 16, 921 ; Sorokin, *J. pr.* [2] 37, 312), but there is no doubt now that the above are correct.

From the synthetic work above described, it is evident that the aldehyde formula belongs also to mannose, gulose, arabinose, xylose, and ribose, and also their synthetic homologues. Rhamnose, as is evident from its reactions, has also an aldehyde constitution ; it appears to be methyl-arabinose.

Sorbose appears to be isomeric with lævulose. By oxidation it yields tri-oxyglutaric acid $COOH.\{CH(OH)\}_3COOH$ and other acids, and by reduction it yields mannitol. It combines with hydrocyanic acid. By reduction with hydriodic acid and phosphorus it yields hexyl iodide (Kiliani a. Scheibler, *B.* 21, 3276).

Little is known concerning the *-on* sugars. Maltose and lactose are probably anhydrides of equal molecules of dextrose and dextrose, and dextrose and galactose respectively ; they yield acids (maltobionic and lactobionic) which on boiling with dilute mineral acids are decomposed into dextrose and gluconic acid and galactose and gluconic acid respectively. Both sugars thus appear to contain the dextrose-aldehyde group unaltered. Fischer (*B.* 21, 2633) has represented lactose as

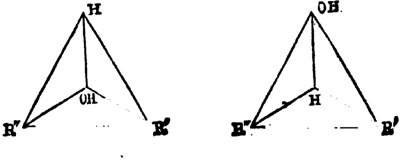


$$CH_2(OH).\{CH(OH)\}_3CH\left\langle\begin{matrix}OCH_2\\|\\OCH-\{CH(OH)\}_3COH.\end{matrix}\right.$$

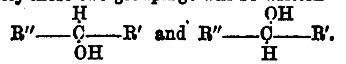
Cane sugar appears to be differently constituted from either maltose or lactose.

It thus appears that the formula $CH_2(OH).\{CH(OH)\}_4COH$ must be assigned to eight known sugars—*i.e.* *d*- and *l*- glucose ; *d*- and *l*- gulose, *d*- and *l*- mannose, *d*- and *l*- galactose (the *i*- modifications being analogous to racemic acid, *i.e.* compounds of the *d*- and *l*- modifications).

Now, as this formula contains four asymmetric carbon atoms, according to Van't Hoff's theory there will be possible $2^4 = 16$ isomers, which in the case of the symmetrical derivatives, as the hexahydric alcohols and dibasic acids, will be reduced to 10, of which $\frac{1}{2}2^4 = 8$ compounds are grouped in pairs (*d*- and *l*-) and $\frac{1}{2}2^2 = 2$ inactive, amesotomic (Fischer, *B.* 24, 1836 a. 2683 ; Van't Hoff, *La Chimie dans l'Espace* and *Dix Années dans l'Histoire d'une Théorie*). Each of the groups R″——C.H.OH——R′ may be grouped in two positions represented thus

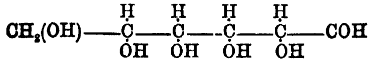


(the carbon atom being considered to be at the centre of the tetrahedron). For the sake of brevity these two groupings will be written

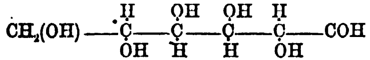


$$R''—\underset{OH}{\overset{H}{C}}—R' \text{ and } R''—\underset{H}{\overset{OH}{C}}—R'.$$

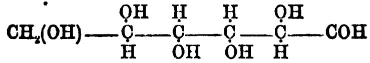
The sixteen possible modifications of the glucose formula may then be expressed by the following symbols; in the case of the symmetrical derivatives (hexahydric alcohols and dibasic acids) Nos. 11–16 are identical with Nos. 5 to 10:—

1.


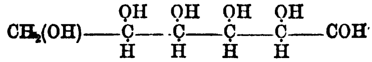
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

2.


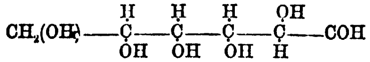
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

3.


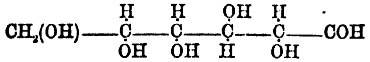
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

4.


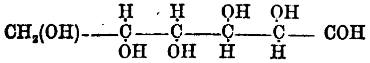
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

5.


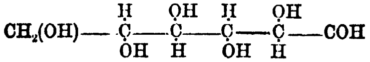
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

6.


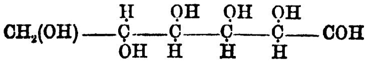
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

7.


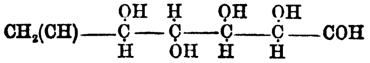
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

8.


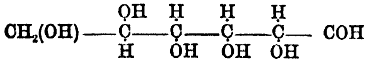
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

9.


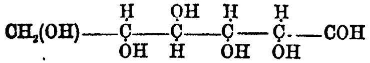
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

10.


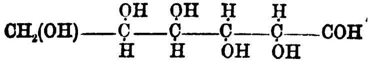
$$CH_2(CH)—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

11.


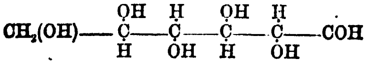
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

12.


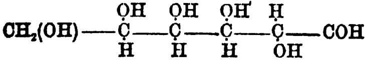
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

13.


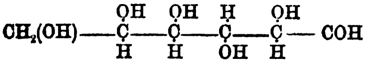
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

14.


$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

15.


$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

16.


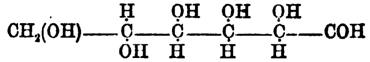
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

Since saccharic acid may be obtained either from glucose or its stereoisomeride gulose, then the *d*- and *l*- saccharic acids must be represented by formulæ corresponding to two of those numbered 5 to 10. Now, 7 and 8 may be eliminated, as they are optically inactive from internal compensation. Nos. 6 and 10 may be excluded for the following reasons: Glucose and mannose yield the same osazone, and consequently differ only in the arrangement of the groups round the asymmetric carbon atom next to the COH group. Other facts which confirm these formulæ are (1) *l*-gluconic and *l*-mannonic acids are both produced by the nitrile reaction from arabinose; (2) fructose reduced by sodium-amalgam yields mannitol and sorbitol; (3) mannonic and gluconic acids can be converted, one into the other, by heating with quinoline; (4) all attempts to resolve gluconic and mannonic acids into two components have been unsuccessful.

If saccharic acid has the configuration 6 or 10, then manno-saccharic acid must have the configuration 7 or 8; but the latter are optically inactive, and therefore cannot be the configuration of manno-saccharic acid. Hence *d*- and *l*-saccharic acid must have a configuration corresponding to 5 and 9; for convenience we may assign 5 to the *d*- and 9 to the *l*- bodies.

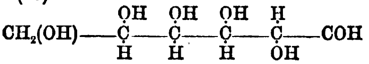
Now the two sugars corresponding to *d*-saccharic acid—*i.e.* *d*-glucose and *d*-gulose—must consequently have the configuration 5 and 11; but in order to determine which to assign to one and which to the other, we must consider xylose and arabinose.

Arabinose by the nitrile reaction yields *l*-glucose and xylose yields *l*-gulose; now since *l*-glucose and *l*-gulose are

(9)


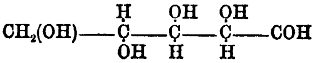
$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

and (15)

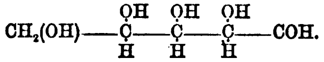


$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

then xylose and arabinose must be

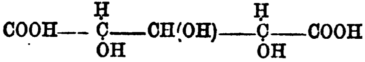
(*a*)


$$CH_2(OH)—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH$$

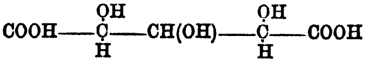
and (*b*)


$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—\underset{H}{\overset{OH}{C}}—COH.$$

According to theory, there will be $2^3 = 8$ isomeric pentoses, but when the formula becomes symmetrical, the asymmetry of the centre carbon is destroyed, and there will be only three isomeric pentahydric alcohols and three isomeric tri-oxy-glutaric acids, of which two are optically active, *i.e.*:

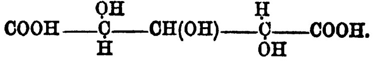


$$COOH—\underset{OH}{\overset{H}{C}}—CH(OH)—\underset{OH}{\overset{H}{C}}—COOH$$



$$COOH—\underset{H}{\overset{OH}{C}}—CH(OH)—\underset{H}{\overset{OH}{C}}—COOH$$

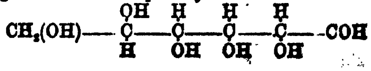
and one is optically inactive, *i.e.*



$$COOH—\underset{H}{\overset{OH}{C}}—CH(OH)—\underset{OH}{\overset{H}{C}}—COOH.$$

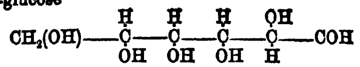
The same applies to the pentahydric alcohols. As arabitol and the tri-oxy-glutaric acid from arabinose are both lævorotatory, whilst the corresponding compounds from xylose are optically inactive, the formula marked (*a*) is the formula for xylose, and (*b*) is the formula for arabinose, (9) and (15) being the formulæ for *l*-gulose and *l*-glucose respectively.

d-gulose will consequently be



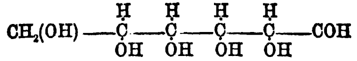
$$CH_2(OH)—\underset{H}{\overset{OH}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COH$$

d-glucose



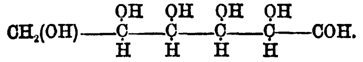
$$\mathrm{CH_2(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{COH}$$

d-mannose



$$\mathrm{CH_2(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COH}$$

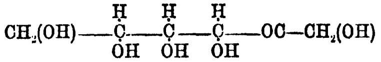
l-mannose



$$\mathrm{CH_2(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{COH}.$$

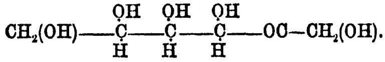
As lævulose yields the same osazone as mannose and glucose,

d-fructose



$$\mathrm{CH_2(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OC}-\mathrm{CH_2(OH)}$$

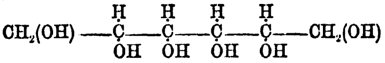
and *l*-fructose



$$\mathrm{CH_2(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{OC}-\mathrm{CH_2(OH)}.$$

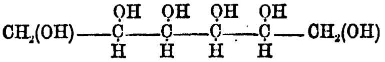
The alcohols will be represented as follows:

d-mannitol



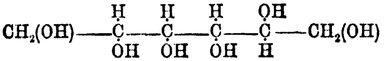
$$\mathrm{CH_2(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2(OH)}$$

l-mannitol



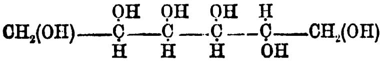
$$\mathrm{CH_2(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2(OH)}$$

d-sorbitol



$$\mathrm{CH_2(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{CH_2(OH)}$$

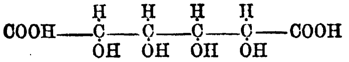
l-sorbitol



$$\mathrm{CH_2(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2(OH)}$$

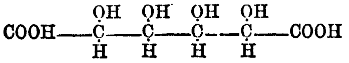
and the dibasic acids:

d-monosaccharic



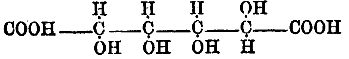
$$\mathrm{COOH}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH}$$

l-mannosaccharic



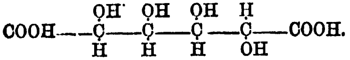
$$\mathrm{COOH}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{COOH}$$

d-saccharic



$$\mathrm{COOH}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\mathrm{COOH}$$

l-saccharic



$$\mathrm{COOH}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{COOH}.$$

The other di-basic acids known are mucic acid, which is optically inactive; allomucic acid, formed by the action of pyridine on mucic acid, which is also optically inactive; another isomeride of mucic acid, which is optically active, obtained by treating galactonic acid with quinoline and oxidising the product; and iso-saccharic acid. We have as yet not sufficient data to write the constitution of these with certainty.

So far we have considered the sugars in general; we must now turn to a description of the individual members of the group.

Class I. **-*Ose* sugars.**

Arabinose $C_5H_{10}O_5$. It does not occur in nature.

Formation.—By the action of dilute acids on metapectic acid, a constituent of beetroot, gum arabic, cherry-tree gum, gedda gum, gum tragacanth, and many other gums (Scheibler, *B.* 1, 58, 108; 6, 612; Claësson, *B.* 14, 1271; Martin, Sachsse's *Phytochem. Unter.* p. 69; Bauer, *J. pr.* [2] 34, 47; Kiliani, *B.* 19, 3030; v. Sandersleben, Sachsse, *l.c.*, p. 90; O'Sullivan, *C. J.* 1884. 41, 1891, 1029; Stone a. Tollens, *A.* 249, 257; Stone, *Am.* 12, 435); wheat and rye bran (*B.* 23, 3110). Owing to the fact that most of the above gums yield galactose besides arabinose, the two were for some time confused (H. Kiliani, *B.* 13, 2304; 15, 34; Claësson, *B.* 14, 1270; *B. C.* 205; Scheibler, *B.* 17, 1729; E. O. v. Lippmann, *B.* 17, 2238). Arabinon yields on hydrolysis arabinose alone (O'Sullivan, *C. J.* 1890. 59).

Preparation.—A dextrorotatory gum, or one yielding little mucic acid when oxidised by nitric acid, is selected. A solution containing 30–40 g. per 100 c.c. is heated to 100° in a water bath and digested at that temperature with 2 p.c. sulphuric acid for 10–15 minutes. The solution is then cooled, neutralised with milk of lime, baryta water, or calcium or barium carbonate, and hot alcohol, S.G. 0·83, added as long as a precipitate is formed. The clear alcoholic solution is poured off the pp. which in a short time collects at the bottom, and evaporated in a vacuum to a syrup. After standing a few hours arabinose crystallises out in well-formed rhombic prisms with monoclinic terminations, and is purified by recrystallisation from water.

Formula and synthesis. See general part.

Properties.—Arabinose crystallises in fine rhombic prisms out of aqueous solution. The termination and habitat of the crystals vary with the source. From alcoholic solutions it separates in sphenoids. The crystals melt at 160°. Its specific rotatory power is $[\alpha]_D = +104{\cdot}5°$ for 10 p.c. solution at 20°C.; in more concentrated solutions it is higher, $[\alpha]_D = +110°$ being observed for nearly saturated solutions. Freshly-prepared solutions possess bi-rotation, an angle of $[\alpha]_D = 156{\cdot}7°$ having been observed (Scheibler, *l.c.*; O'Sullivan, *l.c.*; E. O. v. Lippmann, *l.c.*; Bauer, *L. V.* 36, 304; Tollens, *A.* 257, 160; Groth, *B.* 6, 615; Griess a. Harrow, *B.* 20, 3111). The specific gravity of aqueous solutions does not increase regularly with the strength, being less in proportion for high concentrations than for low ones. The S.G. of a solution containing 10 g. in 100 c.c. at 15·5° is 1·0385–1·0384.

Action of acids. The action of boiling dilute mineral acids destroys much of the opticity and K. of arabinose in a short time (O'Sullivan, 1884, 55). The first products of the change have not been studied. When, however, the action is continued for a considerable time, no lævulinic acid is produced, but furfural is present in large quantities (Ganz, Stone, a. Tollens, *B.* 21, 2148; 23, 3791). Chalmont a. Tollens (*B.* 24, 694) obtained 52·7 p.c. furfural by precipitating the distillate from the products of action of acids with phenylhydrazine acetate. Formic and aceto-propionic acids and humus substances are also present (Conrad a. Guthzeit, *B.* 18, 2905).

Reduction.—Treated with sodium-amalgam in acid solutions, arabinose yields *arabitol*, a body resembling sorbitol, m.p. 102°. This body does not reduce Fehling's solution, and is optically inactive (Kiliani, *B.* 20, 1233).

Oxidation.—By oxidation with nitric acid arabinose yields *arabonic acid* (lævorotatory trioxyglutaric acid), and by violent oxidation at an elevated temperature oxalic acid (Kiliani, *B.* 21, 3006). Bromine also oxidises it to arabonic acid $C_5H_{10}O_6$, m.p. 89° (Bauer, *J. pr.* [2] 34, 47; *C. C.* 1877. 732; Kiliani, *B.* 19, 3031; 20, 345). It is oxidised by alkaline solutions of metallic oxides, 100 c.c. of Fehling's solution being reduced by 0·4303 g. arabinose, and 100 c.c. of Sachsse's solution being reduced by 0·4375 g. arabinose (Bauer, *L. V.* 36, 304). Its K = 108 110 (O'S., *l.c.*), *i.e.* 100 pts. of it reduce as much CuO as 108–110 pts. dextrose.

Fermentation.—Arabinose does not seem to be capable of fermentation with yeast (Stone a. Tollens, *l.c.*; Scheibler, *l.c.*; v. Lippmann, *B.* 17, 2238); with *Bacillus ethaceticus* it ferments with the production of ethyl alcohol, acetic, formic, and carbonic acids, and hydrogen (Frankland a. MacGregor, *C. J.* 1892. 737).

Compounds with cyanogen. By the nitrile reaction arabinose yields a mixture of *l*-gluconic and *l*-mannonic acids (Kiliani, *B.* 19, 3029; 20, 282, 339, 2710; Fischer, *B.* 23, 2611; 24, 539). The first product of the action of HCy on arabinose seems to be a compound of both bodies. HCl converts this into a crystalline amide $C_6H_{13}NO_6$, which on treatment with baryta yields the acids just mentioned.

Hydrazine compounds. Arabinose yields with phenylhydrazine, just as dextrose (*q.v.*) does, an osazone, m.p. 157°–158° (Scheibler, *B.* 17, 1729; Kiliani, *B.* 20, 345).

Compounds with diamines. With *o*-diamidobenzene, arabinose yields arabinose-*o*-diamidobenzene $C_6H_4.(NH)_2C_5H_8O_4$. It is a neutral body, not reducing Fehling's solution, and is dextrorotatory, m.p. 235° with decomposition; it withstands boiling with dilute hydrochloric acid or potash, and yields a hydrochloride and hydrobromide. Arabinose-*m-p*-diamido-toluene $C_6H_3(CH_3)(NH)_2{:}C_5H_8O_4$, m.p. 238°, and arabino-γ-diamido-benzoic acid $COOH.C_6N_2{:}(NH)_2{:}C_5H_8O_4 + 2H_2O$, m.p. 235°, have also been obtained (Griess a. Harrow, *B.* 20, 3111). Arabinose gives colour reactions with orcinol and phloroglucinol (Wheeler a. Tollens, *A.* 254, 314; 260, 304).

Ribose. Fischer a. Piloty, *B.* 24, 4214.

When certain carboxylic acids of the sugar group are heated with quinoline or pyridine, they are converted with stereo-isomeric acids.

When arabonic acid $OH.CH_2(CH.OH)_3.COOH$ is treated in this manner it yields a new acid $COOH.(CH.OH)_3.CH_2OH$, which the authors name *ribonic acid*; ribonic lactone crystallises from solution in ethyl acetate in long prisms, m.p. 72°–76°, does not reduce Fehling's solution, and is easily soluble in water, alcohol, and acetone. Its specific rotatory power is $[\alpha]_{D20^\circ} = -18$. Its phenylhydrazide forms colourless needles, m.p. 162°–164°. Ribonic acid may be converted into arabonic acid by heating with quinoline.

By reducing ribonic lactone with sodium-amalgam, it yields the new sugar *ribose*, which forms a phenylhydrazide crystallising from alcohol in colourless crystals, m.p. 154°–155°; ribose-osazone is identical with arabinose-osazone. By oxidation ribonic acid yields tri-oxy-glutaric acid, which differs from the tri-oxy-glutaric acid obtained by the oxidation of xylose, but which is also optically inactive. By the further reduction of ribonic lactone, a penta-hydric alcohol was obtained which has been found to be identical with the naturally occurring adonitol, obtained from *Adonis vernalis* (Fischer, *B.* 26, 636).

Xylose. $C_5H_{10}O_5$. It does not occur free in nature.

Formation.—It is obtained by the action of dilute boiling acids on xylan or wood gum (Koch, *B.* 20, ref. 145; Wheeler a. Tollens, *B.* 22, 1046; *A.* 260, 289; Winterstein, *H.* 17, 381; Stone a. Test, *Am.* 15, 195), on the carbohydrate from the epidermis of *Psyllium gallicum* (Bauer, *A.* 248, 140), on vegetable amyloid (Winterstein, *Z. P. C.* 17, 353), on brewer's grain (Stone a. Tollens, *A.* 249, 227; 271, 55), on jute (Wheeler a. Tollens, *l.c.*), and other vegetable bodies (Voswinkel, *C. C.* 1891, 2, 655; Hebert, *Ann. Ag.* 16, 358; 18, 261; Stone a. Lotz, *B.* 24, 1657; Allen a. Tollens, *B.* 23, 137; Bertrand, *Bl.* [3] 5, 554).

Preparation.—Xylose may be prepared by extracting straw or any other of the above-mentioned materials by 5 p.c. soda, precipitating the wood gum from the solution by alcohol, and hydrolysing this by boiling with dilute sulphuric acid. The digested solution is treated in the same way as described in the case of arabinose, and the xylose may be easily purified by crystallisation from water.

The formula and synthesis have already been discussed in the general part.

Properties.—Xylose is easily soluble in water; 100 pts. of water at 20·3° dissolve 117 pts. of xylose; it is insoluble in absolute alcohol, 90 p.c. alcohol will dissolve in 10 c.c. 0·4 g. sugar at 19° (Bertrand, *Bl.* [3] 7, 499). Its solutions are optically active, freshly-prepared solutions having about four times the constant optical activity (Parcus a. Tollens, *A.* 207, 160). For a 10 p.c. solution at 20° $[\alpha]_D = +19{\cdot}3^\circ$ (Parcus a. Tollens, *l.c.*; Bertrand, *l.c.*). Schulze a. Tollens (*A.* 271, 40) give the formula $[\alpha]_D = +18{\cdot}095 + 0{\cdot}06986p$ at 15°–20°, where p = percentage of xylose in solution. Xylose frequently crystallises in prisms belonging to the ortho-rhombic system. Its solutions are not fermentable by yeast. It reduces Fehling's solution, K = 109·6, agreeing in this respect very closely with arabinose (Bertrand, *l.c.*). Boiled with acids it yields about 50 p.c. furfural (Günther a. Tollens, *B.* 23, 1751; Chalmont a. Tollens, *B.* 24, 694; Bertrand, *l.c.*).

It is reduced by sodium-amalgam to a penta-hydric alcohol xylitol (Bertrand, *Bl.* [3] 5, 554; Fischer a. Stahel, *B.* 24, 528). It is oxidised by bromine to xylonic acid (Bertrand, *l.c.*; Allen a. Tollens, *A.* 260, 306); it is oxidised by nitric acid to inactive tri-oxy-glutaric acid $C_5H_8O_7$ (Fischer, *B.* 24, 1836). By the nitrile reaction xylose yields *l*-gulonic acid, the stereo-isomeride of *l*-gluconic acid (Fischer a. Stahel, *B.* 24, 528; Fischer, *B.* 23, 2625; Fischer a. Curtis, *B.* 25, 1025).

With phenyl hydrazine it yields an osazone, m.p. 160°. Warmed with phloroglucinol and hydrochloric acid, it gives a cherry-red coloration, just as arabinose does under the same conditions (Tollens a. Mayer, *B.* 21, 3508; Wheeler a. Tollens, *B.* 22, 1046).

Rhamnose. *Isodulcite, rhamnodulcite* $C_6H_{12}O_5.H_2O$.

Preparation.—Rhamnose is obtained, together with other bodies, by the action of hot dilute acids on quercitrin, hesperidin, xanthorhamnin, naringin, and frangulin (Rayman a. Kruis, *Bl.* [2] 48, 632; *C. C.* 1888, 6; Hlasiwetz a. Pfaundler, *A.* 127, 362; Liebermann a. Hörmann, *A.* 196, 323; Kruis, *A.* 196, 333; Berend, *A.* 196, 328; Rigaund, *A.* 90, 292; Will, *B.* 18, 1316; 20, 297 and 1186; Dehn, *Zeit. d. Ver.* 15, 562; Rayman, *Bl.* [2] 47, 668; Tanret, *Bl.* 49, 20; Thorpe a. Miller, *C. J.* 1892. 8).

Properties.—Rhamnose forms fine crystals, which have a sweet taste, and a composition corresponding to the formula $C_6H_{12}O_5.H_2O$; by careful drying it loses water and then melts at 90°-110° (Websky, *B.* 18, 1318; Hirschwald, *A.* 196, 330). It is easily soluble water, and its solutions are dextrorotatory, $[\alpha]_D = +9°$. Freshly-prepared solutions show bi-rotation (Schnelle a. Tollens, *A.* 271, 61). In alcoholic solutions the optical activity decreases as the proportion of alcohol to water increases, until the solution becomes lævorotatory (Rayman a. Kruis, *C. C.* 1888. 6). It reduces Fehling's solution, 1 c.c. being reduced by 0·0052–0·0055 g. rhamnose (K = 91–96) (Rayman a. Kruis, *l.c.*). Its solution does not ferment with yeast.

Action of acids. Boiled with moderately strong acids furfural is evolved (Maquenne, *C. R.* 109, 603). Concentrated nitric acid converts it into a nitrate.

Oxidation.—Nitric acid oxidises rhamnose to tri-oxy-glutaric acid (Will a. Peters, *B.* 22, 1697). Malin (*A.* 145, 197) obtained an acid $C_6H_{10}O_9$. Bromine water oxidises it to rhamnonic acid $C_6H_{12}O_6$, which is obtained in the form of the lactone $C_6H_{10}O_5$, m.p. 148° (Will a. Peters, *B.* 21, 1813; Rayman, *B.* 21, 2046). With bromine and silver oxide it is oxidised to acetaldehyde and acetic acid (Herrig, *Chem. Zeit.* 1887, Rep. 145; *M.* 8, 227).

Reduction.—Sodium-amalgam reduces rhamnose to rhamnitol $CH_3(CH.OH)_4.CH_2OH$, which crystallises from alcohol or acetone in triclinic prisms, m.p. 121°, and has a sweet taste (Fischer a. Piloty, *B.* 23, 3102).

Compounds.—With phenylhydrazine rhamnose yields a hydrazide $C_6H_{12}O_4{:}N_2HC_6H_5$, m.p. 159°, and an osazone $C_{18}H_{22}N_4O_3$, m.p. 180° (Will, *B.* 20, 1186; Fischer a. Tafel, *B.* 20, 1089, 1091 a. 2566). With aniline it forms a compound $C_6H_{12}O_4NC_6H_5$, m.p. 118° (Rayman a. Kruis, *l.c.*). With ammonia and ethylaceto-acetate it forms rhamnodiasine $C_{18}H_{32}O_8N_2$, m.p. 186° (Rayman a. Chodoünský, *B.* 22, 304 and 3247).

Rhamnose combines with hydrocyanic acid to produce rhamnonamide. The lactone $C_7H_{12}O_6$ crystallises in needles, melting-point 168°; this is reduced by hydriodic acid and phosphorus to normal heptoic acid (Fischer a. Tafel, *B.* 21, 1657 a. 2178). Rhamnose hexoic acid lactone is reduced by sodium-amalgam to a sugar (Fischer, *B.* 22, 2204; Fischer a. Tafel, *B.* 23, 3102). Sodium rhamnose $C_6H_{12}O_6Na_2$ is precipitated by adding sodium ethylate to an alcoholic solution of rhamnose (Liebermann a. Hamburger, *B.* 12, 1186). With benzoyl chloride tri- and tetra- rhamno-benzoates are formed; with acetic anhydride rhamno-tetracetate (Rayman, *B.* [2] 47, 668). From thermo-chemical considerations rhamnose appears to be methyl-xylose (Stohmann a. Langbein, *J. pr.* [2] 45, 305).

Fucose $C_6H_{12}O_5$ is obtained by the hydrolysis of *fucus*. The sugar forms microscopic needles. Its solution has a sweet taste and is lævorotatory, $[\alpha]_D = -77°$. With phenyl-hydrazine it forms a hydrazide, melting-point 170°, and an osazone, melting-point 159° (Bieler a. Tollens, *A.* 258, 110; Günther a. Tollens, *B.* 23, 2585). Fucose appears to be methyl-arabinose (Stohmann a. Langbein, *l.c.*).

Dextrose. *d-glucose, glucose, starch-, corn-, grape-, honey-, diabetic-sugar.* (Ger. *Krümmelzucker, Traubenzucker*; Fr. *Sucre de raisin.*) $C_6H_{12}O_6$ and $C_6H_{12}O_6 + H_2O$.

Occurrence.—Dextrose is widely distributed throughout the vegetable kingdom, being usually accompanied by lævulose and cane sugar. The most important sources are honey, most fruits, the sap of plants, seeds. It occurs in the animal kingdom in the liver, blood, and other parts of the body, and in diabetic urine (S. Sachsse, *Die Ch. und Phys. der Farbst. Kohlenhydrate u. Protein subst.*, Leipzig, 1877; F. Mack, *J.* 1869, 892; Girard, *B.* 17, 17*c*; Neubauer, *Fr.* 12, 39; Gorup-Besancz, *B.* 4, 906; Petit, *B.* 6, 1313; v. Schneider, *A.* 162, 235; *Report on Sorghum and Cornstalks*, Dep. of Agr., Report No. 35, Washington, 1881; Hermann a. Tollens, *A.* 230, 50; Vogel, *B.* 15, 2271; Fischer a. Bödecke, *A.* 117, 111; De Bary, *Hoppe-Seyler's Medic. Ch. Unt.* p. 72; Hoppe-Seyler, *Handb. d. phys. Ch. Ana.*, 1883, 301; Klason, *B.* 19, 2541; Wehmer, *Inaug. Diss.*, Göttingen, 1886, 40; O'Sullivan, *C. J.* 1886, 58; Wehmer a. Tollens, *B.* 19, 707; Seegen a. Kratzschmer, *Pf.* 22, 206; Kütz, *Pf.* 24, 52; Boussingault, *C. R.* 91, 639; J. Sieben, *B. C.* 1885. 134; Hermann a. Tollens, *A.* 230, 50; Müller, *Ann. Agronom.* 13, 88; Seegen, *Pf.* 37, 348; 39, 121; 40, 48; Cuisinier, *C. C.* 1886, 614; H. Thoms, *B.* 21, 1916*a*; Reali, *G.* 17, 325; Maquenne, *A. Ch.* [6] 17, 495).

Formation.—By the action of acids and ferments on the following glucosides: amygdalin (Schmidt, *A.* 119, 92; Hesse, *l.c.*, 176, 112); populin (*v.* Lippmann, *B.* 12, 1648 *b*); ruberythric acid (Liebermann a. Bergami, *B.* 20, 2247); salicin (Schmidt, *A.* 119, 97; Hesse, *l.c.*, 176, 112); lupinin (*B.* 11, 2200 *b*); hesperidin (Tanret, *Bl.* 49, 20); phlorizin (Rennie, *C. J.* 1887, 636). Other glucosides yield dextrorotatory, reducing, fermentable, and crystallisable sugars, but there is not sufficient evidence to prove with certainty that they are dextrose. These are: æsculin (Rochleder a. Schwarz, *A.* 87, 186; Zwenger, *l.c.*, 90, 76); arbutin (Hlasiwetz a. Grabowski, *Ar. Ph.* 141, 329); coniferin (Tiemann a. Harmann, *B.* 7, 608).

By the action of dilute acids the following carbohydrates yield dextrose, alone or with other glucoses. Some of them are also hydrolysed to dextrose by ferments:

α- and β- amylan yield dextrose.

Cellulose yields dextrose (Flechsig, *H.* 7, 523; Lindsay a. Tollens, *A.* 267, 370).

Glycogen yields dextrose.

Lichenin yields dextrose.
Tunicin „
Starch „
Dextrin „
Maltose „
Lactose yields dextrose and galactose.
Cane sugar yields dextrose and lævulose.
Raffinose yields dextrose, lævulose, and galactose.

Preparation.—Dextrose can be prepared from any of the substances above mentioned, but it is in many cases difficult to obtain it in any quantity in the pure state. Starch and sucrose are the bodies usually employed, and we find that lactose can also be used with advantage.

(*a*) A white saccharum (the commercial glucose obtained by the action of acids on starch) with an optical activity approaching that of dextrose is selected. This is scraped as fine as possible, and treated with boiling ethyl alcohol S.G. ·820. On cooling, the clear saturated solution is separated from the undissolved syrup and a little previously prepared dextrose added to it. Crystallisation soon begins and continues for some time; a crop of fairly pure dextrose is thus obtained. Further purification can be effected by melting the crystals in 8–10 p.c. boiling water and adding dry boiling methyl alcohol until a slight cloud is produced. Anhydrous dextrose in a state of great purity separates abundantly from this solution. Or the saccharum is melted in 5 or 6 p.c. water, allowed to crystallise, the crystals pressed and further purified by treatment with methyl alcohol as described.

(*b*) A 25 p.c. aqueous solution of crystallised sucrose is taken and heated to 50°–55° and 2–3 p.c. pressed brewers' yeast stirred in (Tompson, *E. P.* 8686, 1884), the temperature is maintained for 2–3 hours, when the sucrose is completely inverted—that is, converted into dextrose and lævulose. The solution is then evaporated in a vacuum to a syrup, S.G. 1·5 or thereabouts. On standing for a short time this solidifies to a crystalline mass; it is washed with cold alcohol, S.G. ·830, and the residue dissolved to saturation in alcohol of the same strength. Dextrose soon begins to crystallise out; the crystals can be further purified by dissolving in methyl alcohol and recrystallisation.

Sucrose may also be inverted by digestion with sulphuric acid, the acid separated by baryta water, and the filtrate from the barium sulphate evaporated to a syrup and treated in the way mentioned. Inversion by yeast yields the best result. Soxhlet (*J. pr.* [2] 21, 242) recommends that inversion be effected by alcoholic hydrochloric acid. 480 c.c. of strong hydrochloric acid are mixed with 12 litres of alcohol, S.G. ·810, in a glass vessel, the mixture heated 45°–50°, 4 kilos. powdered sucrose stirred in, and the whole maintained at that temperature for two hours. When cool a little previously prepared anhydrous dextrose is added, and in a few days there is an abundant crystallisation of dextrose. This can be purified by crystallisation from methyl alcohol. Should any colour be developed, the aqueous solution is treated with animal charcoal and again concentrated in a vacuum. Under such circumstances it is better to begin again, for if proper care be taken no colour need be produced.

An aqueous solution containing 25 p.c. lactose and 3 p.c. sulphuric acid is digested in a water-bath for three hours, care being taken by continued agitation that no colour is developed, the sulphuric acid is separated by baryta water, and the filtrate concentrated to a syrup containing 76–80 p.c. solid matter. On standing this solidifies, and after a few days is treated with boiling methyl alcohol; this dissolves out the dextrose, leaving the galactose undissolved; the former soon crystallises from the saturated methyl alcohol. A recrystallisation yields the pure body in moderately large, well-defined crystals.

Hydrous dextrose $C_6H_{12}O_6.H_2O$ can be obtained from any of the above preparations by dissolving in 12 to 20 p.c. water, and allowing to crystallise. If honey is used as a source of dextrose, any sucrose it may contain should be inverted by yeast or acids, and the residue obtained by evaporation crystallised from methyl alcohol as in the case of inverted sucrose. A pure product may be obtained in a few crystallisations.

Formula and synthesis. See first part on the sugars generally.

Properties.—Dextrose crystallises out of 93–95 p.c. ethyl or methyl alcohol in the anhydrous state. Anhydrous crystals may also be obtained by special treatment from concentrated aqueous solutions at 30°–35°. As a rule aqueous solutions deposit crystals containing one molecule of water of crystallisation. Anhydrous dextrose crystallises in rhombic, hemihedric forms; the axial relationship is $a:b:c = 0·704:1:·335$. Hydrated dextrose forms hemimorphous crystals; the elements are $a:b:c = 1·7350:1:1·9080$, $\beta = 97° 59'$ (F. Becke, *M.* 10, 231). Well-defined crystals of both varieties are difficult to obtain; usually the first separates as a powder and the second in cauliflower-like masses; both dissolve easily in water, the first with evolution of heat. Hydrated dextrose dissolves easily in strong ethyl and methyl alcohol, but the anhydrous sugar is almost insoluble in them. It is insoluble in ether and hydrocarbons, slightly soluble in aniline, acetic acid, and acetic ether. Hydrated dextrose easily loses its molecule of water of crystallisation when exposed in a vacuum over sulphuric acid, or when heated gently. The anhydrous sugar melts at 144°–146° (Hesse, *A. Ch.* 176, 106); its specific gravity is, according to Guérin-Varry a. Heintz, 1·386; according to Bödecker, 1·5384 (v. Lippmann, *Zuckerarten*, p. 12). Dextrose is not so sweet as cane sugar. Behr (*B.* 15, 1106) finds it $\frac{3}{5}$ as sweet, and T. Schmidt (*B. C.* 1887, 405) that 1·53 pts. of dextrose are as sweet as 1 part of cane sugar. An aqueous solution of 10 g. dry dextrose in 100 c.c. of solution at 17·5° has a specific gravity of 1·0381 (water at 17·5 = 1) (Salomon, *B.* 14, 2710). This is fairly accurate. K = 100. Its solutions rotate the plane of polarisation of a ray of polarised light to the right. According to Hesse a. Tollens (*B.* 17, 2234), the amount of rotation for the D line is expressed by the formula $[\alpha]_D = 52·5 + ·018796P + ·00051683P^2$ for anhydrous dextrose, and
$[\alpha]_D = 47·73 + ·015534P + ·0003883P^2$ for hydrated dextrose, in which P is the percentage of the two varieties respectively in solution. In solutions containing 10 p.c. dry sugar and thereabouts, the

factors $[\alpha]_D = 52{\cdot}7$ and $[\alpha]_j = 58{\cdot}3$ are sufficiently accurate, but probably a shade too low. These values are not materially affected by the temperature. The presence of some inactive bodies in the solution appears to have some effect (Pribram, *M.* 9, 395); bodies such as potash, soda, lime, &c., which act on dextrose reduce its optical activity; other bodies, such as urea, do not alter it (N. Wender, *B.* 24, 2200). Freshly-prepared solutions have a greater optical activity than those which have stood a few hours. F. Urech (*B.* 17, 1547) has observed a rotation 2·19 times greater than the constant value. Parcus a. Tollens (*A.* 257, 160) observed an angle of $[\alpha]_D = 105{\cdot}16$ in a 10 p.c. solution 5½ min. after commencing solution. This phenomenon is called *bi-rotation*; the optical activity quickly falls, and the constant value is reached in about six hours in the cold and immediately on boiling. The bi-rotation is also immediately destroyed by potash (O'Sullivan a. Tompson, *C. J.* 1890, 920), or ammonia (Schulze a. Tollens, *A.* 271, 49). Dextrose when produced by the inversion of cane sugar at a low temperature is set free in the bi-rotatory state (O'Sullivan a. Tompson, *l.c.*). Only crystallised dextrose exhibits this phenomenon; fused dextrose does not show it (Hesse, *A.* 176, 113). A solution of dextrose in strong alcohol retains its bi-rotation (?) The dispersive power of dextrose solution is practically the same as that of quartz (Hoppe-Seyler, *Fr.* 3, 1866, 412). The ratio between the specific rotatory power for the C and D lines respectively is 1:1·258 (Grimbert, *J. Ph.* [5] 16, 295 and 345). The heat of combustion of dextrose is +677·2 cal., and the heat of formation +300·8 cal. (Berthelot a. Recoura, *C. R.* 104, 1571).

Action of heat. When the dry sugar is heated to 170°, a molecule of water is eliminated and dextrosan $C_6H_{10}O_5$ is produced, which may be reconverted into dextrose by the action of water and dilute acids. If the temperature is raised to 200°, gas, water, and volatile acids are given off, and if the heating be continued without raising the temperature, a brownish black mass is finally left. This substance is soluble in water and constitutes the colouring matter (caramel) used in beer, wine, cooking, &c. Should the temperature be raised, carbon monoxide, dioxide, and methane are evolved, and aldehyde, furfural, acetone, metacetone, propionic, acetic, and formic acids distil over, and a black carbonaceous mass is left. If the hydrate be heated for a considerable time in a closed tube a fluid is obtained which absorbs oxygen and nitrogen (?) from the air (Thénard, *C. R.* 52, 795).

Action of acids. Dextrose is dissolved by strong sulphuric acid without blackening, dextrose-sulphuric acid being formed (Péligot, *A. Ch.* [2] 67, 170); from this solution alcohol precipitates a compound of diglucose with alcohol (Musculus a. Meyer, *B.* 14, 850). Similar compounds are produced by the action of chlorosulphonic acid (Claësson, *J. pr.* [2] 20, 1). A mixture of sulphuric and nitric acids converts dextrose into a nitro-compound (Carey Lea, *Bl.* [2] 10, 415). Dextrose phosphoric acid is said to exist (Amato, *B.* 4, 418). Several acetyl derivatives have been described. Dextrose diacetate $C_6H_{10}O_4(C_2H_3O_2)_2$ and dextrose triacetate $C_6H_9O_3(C_2H_3O_2)_3$ are amorphous, soluble in water, alcohol and ether (Schützenberger a. Naudin, *Bl.* [2] 12, 107, 204; Liebermann a. Hörmann, *B.* 11, 1619; Herzfeld, *B.* 13, 265). Dextrose pentacetate $C_6H_7O(C_2H_3O_2)_5$ is prepared by the action of acetic anhydride and zinc chloride on dextrose, m.p. 111–112 (Erwig a. Koenigs, *B.* 22, 1464, 2207). Didextrose octoacetate $C_{12}H_{14}O_3(C_2H_3O_2)_8$ is prepared by the action of acetic anhydride and sodium acetate on dextrose, m.p. 134 (Herzfeld a. Erwig a. Koenigs, *l.c.*). Dextrose-monochlorhydrin-tetracetate is formed by the action of acetyl chloride on dextrose (Culley, *C. R.* 70, 401). Tri-, tetra-, and penta-benzyl $(C_6H_7(C_7H_5O)_5O_6)$ dextroses are obtained by the action of benzoic chloride and potash on dextrose (Skraup, *M.* 10, 389; Kueny, *H.* 14, 330; Panormoff, *J. R.* 23, 375). Compounds of dextrose with other organic acids have been prepared (Berthelot, *A. Ch.* [3] 54, 74; *Gm.-K.* 7, 764; v. Lippmann, *Zuckerarten*, p. 40; Baumann, *B.* 19, 3218; Colley, *C. R.* 76, 436). If dextrose is boiled with dilute sulphuric acid the specific gravity of the solution gradually increases for some time, apparently from the fixation of the elements of water. On continued boiling the solutions become coloured, brown humus substances, acetopropionic and formic acids, are produced (Malaguti, *A. Ch.* [2] 59, 407; Tollens a. Grote, *A.* 175, 181; 206, 207; Wohl, *B.* 23, 2084). Dilute hydrochloric acid produces similar results, but more rapidly. Gummy bodies are also produced (Grimaux a. Lefèvre, *C. R.* 103, 146). See also Conrad a. Guthzeit (*B.* 18, 439; 19, 2569) and Wehmer a. Tollens (*B.* 19, 707).

Action of alkalis. Alkalis give a brownish colour with dextrose solution, quickly on heating, slower in the cold, with production of acetal, acetone, and lactic, acetic, and formic acids. Other bodies of unknown composition are also formed, such as glucinic, saccharumic and japonic acids. When potash is used oxygen is absorbed. With calcium hydroxide, saccharin or calcium saccharinate is also produced; this is not one of the products of the action of potash (Emmerling a. Loge, *B.* 14, 1005; 16, 838; Henry, *B.* 14, 2272; Breuer a. Zincke, *B.* 13, 638; Rochleder a. Kawalier, *J. pr.* 94, 403; Hoppe-Seyler, *B.* 4, 346; Kiliani, *B.* 15, 700; Nencki a. Sieber, *J. pr.* [2] 24, 498; Péligot, *A. Ch.* 30, 75; Mulder, *A. Ch.* 36, 260; Reichardt, *Z.* 1870. 404; v. Lippmann, *Zuckerarten*, p. 22; Péligot, *B.* 13, 196; Scheibler, *B.* 13, 212; Kiliani, *B.* 15, 701; Cuisinier, v. Lippmann, *Zuckerarten*, p. 25; Scheibler, *B.* 16, 2434). Thénard (*C. R.* 52, 444) obtained bitter bodies containing 10–19 p.c. nitrogen, by acting on dextrose with ammonia; they absorb oxygen from the air, and resemble certain nitrogenous humic acids. Tanret (*Bl.* [2] 44, 102) obtained two volatile bases: α-glucosine $C_6H_8N_2$ b.p. 136° and β-glucosine $C_7H_{10}O_2$ b.p. 160°, by heating dextrose with strong ammonia. Heated with aniline, dextrose anilide is produced (Schiff, *A.* 140, 123; Sorokin, *B.* 19, 298).

Reduction.—Nascent hydrogen reduces dextrose in alkaline solutions to mannitol, but not in neutral or acid solutions (Linnemann, *A.* 128, 136; Dewar, *Z.* 1870. 413; Bouchardat, *Bl.* [2] 16, 88; Krusemann, *B.* 9, 1465). Under the most favourable conditions the yield does not exceed 10 p.c. If the reduction be carried on at a high temperature other fatty alcohols are formed. Meunier (*C. R.* 111, 49) obtained sorbitol by reducing dextrose with sodium-amalgam.

Oxidation.—Gluconic acid $C_6H_{12}O_7$ is produced by oxidising dextrose with mercuric oxide (Heffter, *B.* 22, 1049; Herzfeld, *A.* 245, 27) or with chlorine or bromine and subsequent treatment with silver oxide (Hlasiwetz a. Habermann, *A.* 155, 122; 156, 253; Kiliani, *A.* 205, 182; Kiliani a. Kleeman, *B.* 17, 1298; Herzfeld, *A.* 220, 335, 358), or by the action of *Bacterium aceti* (Brown, *C. J.* 1886. 179; Boutroux, *C. R.* 1880. 236). Oxygen has no action on dextrose in neutral or acid solutions, but it is absorbed by alkaline solutions. Ozone oxidises dextrose to saccharic and formic acids (Renard, *A. C.* 5, 17, 289). Platinum black acts similarly (Loew, *B.* 23, 865). Nitric acid oxidises dextrose to saccharic acid $C_6H_{10}O_8$, and finally to oxalic, formic, and carbonic acids (Liebig, *A.* 113, 1; Heintz, *P.* 51, 183; Hornemann, *J. pr.* 89, 304; Kiliani, *A.* 205, 172; Guérin-Varry, *A.* 8, 31; Sohst a. Tollens, *Z.* 11, 99). Iodine when acting on alkaline solutions of dextrose yields a little iodoform (Lieben, *A. Suppl.* 7, 228; Hermann a. Tollens, *B.* 18, 1335; Millon, *C. R.* 21, 828). Alkaline solutions of many metallic oxides oxidise dextrose, in some cases being reduced to the metal, in others to lower oxides. Potassium ferrocyanide, potassium permanganate, indigo, picric acid, litmus, &c., oxidise dextrose also. The chief products are formic, oxalic, glycollic, and carbonic acids. Some of these reactions are employed for the quantitative estimation of dextrose (Tollens, *B.* 16, 921; Herzfeld, *Zeitschr. d. Ver. d. Rübenzucker-Ind.* 37, 337; Habermann a. Hönig, *B.* 15, 2624; Worm-Müller a. Hagen, *Pf.* 22, 325; *B.* 13, 2096 a. 2442; Herzfeld a. Bruhns, *Zeitschr. d. Ver. d. Rübenzucker-Ind.* 36, 110; Reichardt, *A.* 127, 297; Felsko, *A.* 149, 356; Beyer, *A.* 131, 353; Claus, *A.* 147, 115; Smolka, *B.* 20, 167; *M.* 8, 1).

Fermentation.—Under the influence of various species of saccharomyces and other organisms, dextrose ferments, yielding alcohol and carbon dioxide as the chief products, glycerol, succinic acid, and small quantities of other bodies are formed at the same time. Bacteria decompose dextrose in other ways, one yielding chiefly lactic acid, another butyric, another cellulose, &c. (*v.* FERMENTATION).

Compounds with acids (*v. Action of acids*).

Compounds with bases. Potassium and sodium dextrose $C_6H_{11}KO_6$ and $C_6H_{11}NaO_6$ are prepared by adding potassium or sodium ethylate to a solution of dextrose in strong alcohol. A white, bulky precipitate is obtained, which is very hygroscopic, and decomposed by water (Hönig a. Rosenfeld, *B.* 10, 871; Franchimont, *B.* 10, 994). The compounds with the alkaline earths are differently constituted, being apparently a combination of the sugar and base. They are formed by mixing alcoholic solutions of the base and sugar, or by precipitating their mixed aqueous solutions with alcohol. Lime forms $C_6H_{12}O_6.CaO.H_2O$, $C_6H_{12}O_6.CaO$, $2C_6H_{12}O_6.3CaO.H_2O$, $2C_6H_{12}O_6.3CaO.2H_2O$, $4C_6H_{12}O_6.3CaO$, and similar compounds are formed with baryta, strontia, and magnesia. Neither lead acetate nor subacetate precipitate aqueous dextrose solutions, but lead oxide yields compounds similar to those with lime &c. (Brendecke, *Ar. Ph.* [2] 29, 84; v. Lippmann, *Zuckerarten*, p. 45; Péligot, *J. pr.* 15, 105; Franchimont, *B.* 12, 1939). Alkaline dextrose solutions dissolve copper hydroxide, and from these solutions soda or potash in proper proportions precipitates compounds of copper oxide and dextrose of varying composition (Guignet, *C. R.* 109, 528; Worm-Müller a. Hagen, *Pf.* 22, 325; Fileti, *B.* 8, 441; Salkowski, *B.* 12, 704). The compound $C_6H_{12}O_6.2ZnO.3H_2O$ is formed by adding an alcoholic solution of dextrose to an ammoniacal solution of zinc oxide (A. C. Chapman, *C. J.* 1889. 576). Dextrose forms amorphous compounds with nickel, chromium, and iron oxides (Chapman, *C. J.* 1891. 323).

Compounds with metallic salts. Dextrose forms well-defined crystalline compounds with sodium chloride and bromide; their formulæ are $2C_6H_{12}O_6.NaCl.H_2O$, which crystallises from diabetic urine, $C_6H_{12}O_6.NaCl$, $C_6H_{12}O_6.2NaCl$, $2C_6H_{12}O_6.NaBr$ (Pasteur, *A. Ch.* [3] 31, 92; Erdmann a. Lehmann, *J. pr.* 13, 111; v. Lippmann, *Zuckerarten*, p. 45; Städeler, *C. C.* 1854. 930; Hönig a. Rosenfeld, *B.* 10, 872; Stenhouse, *A.* 129, 286).

Compounds with cyanogen. By digesting an aqueous solution of dextrose with hydrocyanic acid solution, the following reaction takes place: $C_6H_{12}O_6 + HCN + 2H_2O = C_7H_{13}O_8NH_4$ (Kiliani, *B.* 19, 767). To prepare this compound Kiliani gives the following directions: 100 g. crystalline dextrose are dissolved in 30 g. water, and an equivalent quantity of 60 p.c. hydrocyanic acid is added and digested for six days at the ordinary temperature; after twenty-four hours' further digestion at 35°C. all smell of hydrocyanic acid had disappeared, and the liquid smelt of ammonia. The ammonium salt thus obtained is converted into a barium one by boiling with baryta, and the free acid obtained by removal of the barium by sulphuric acid. Fischer (*A.* 270, 64) dissolves 5 kilos. dextrose in 25 litres 3 p.c. hydrogen cyanide solution, adds 10 c.c. ammonia solution, and digests the solution at 25°C. for six days, boils with baryta (6·7 kilos.) dissolved in water (20 litres) until all the ammonia is expelled, the hot liquid acidified with sulphuric acid, and boiled to expel hydrogen cyanide, neutralised with baryta, and filtered. The filtrate is concentrated. This syrup contains the lactones of α-heptonic acid and β-heptonic acid. After standing some weeks nearly the whole of the α-lactone will have crystallised out; the mass is triturated with alcohol of 80 p.c.; the filtrate yields a further crop of α-lactone, and the mother-liquor contains the β-lactone. This may be obtained by neutralising with brucine; the brucine β-heptonate crystallises out, and is purified by recrystallisation; the brucine may be separated by precipitation with baryta, and the barium salt decomposed by sulphuric acid.

α-Glucohepto-lactone forms rhombic crystals readily soluble in water, and has $[\alpha]_D = -55{\cdot}3$; boiled with concentrated hydriodic acid it yields a heptolactone, b.p. 216°-230° at 717 mm., with partial decomposition. About an equal quantity of normal heptoic acid is also produced (Kiliani, *B*. 19, 1128). By digestion with nitric acid S.G. 1·2 at 40° for 24 hours, α-glucoheptoic acid is oxidised to normal penta-oxy-pimelic acid (Kiliani, *B*. 19, 1916); this melts at 143°, is easily soluble in water, difficultly in alcohol, and soluble in ether. α-Gluco-heptonic acid yields a hydrazide $C_7H_{13}O_7N_2H_2C_6H_5$ m.p. 171°–179° (Fischer, *B*. 22, 2732).

β-Gluco-heptonic lactone crystallises in delicate needles, m.p. 151°–152°, reduces Fehling's solution, and is very soluble in water; its sp. rot. power is $[\alpha]_{D20°} = -67·7°$. Its phenylhydrazide $C_7H_{13}O_7N_2H_2Ph$ crystallises from alcohol in yellowish leaflets, and melts at 150°–152°. Heated with pyridine (4 lactone, 4 pyridine, and 20 water) in a sealed tube for three hours it is converted into the α- acid.

Hydrazine compounds. A concentrated solution of dextrose yields, with phenylhydrazine, dextrose phenylhydrazine $C_{12}H_{18}N_2O_5$; this forms fine crystals, melting at 144°–145°. When heated with an aqueous solution of phenylhydrazine, hydrochloride, and sodium acetate on the water-bath, yellow crystals of phenylglucosazone $C_{18}H_{22}N_4O_4$ are formed (Fischer, *B*. 20, 824). Phenylglucosazone can be prepared by heating on the water-bath 1 pt. dextrose, 2 pts. phenylhydrazine hydrochloride, 3 pts. sodium acetate, and 20 pts. water; after 10–15 minutes' heating the separation of osazone commences, and after 1½ hours the precipitate amounts to about 85–90 p.c. of the weight of dextrose taken. It is purified by recrystallisation from alcohol. Another method which gives satisfactory results is to heat a mixture containing 1 g. sugar in 100 c.c. water and 5 c.c. of a solution containing in 1 litre 400 g. phenylhydrazine and 400 g. glacial acetic acid. According to Maquenne's (*C. R.* 112, 799) numbers, the yield is low, but by increasing the strength of the sugar solution and keeping up the quantity of the phenylhydrazine acetate solution in proportion, it is materially increased. It is insoluble in water; not very soluble in cold, but fairly easily in boiling alcohol. It melts at 204°–205° with decomposition, and so in m.p. determinations it is important that the heating be done as quickly as possible. It reduces Fehling's solution, and is lævorotatory (Fischer, *B*. 17, 579). It dissolves in cold fuming hydrochloric acid, with a dark-red colouration, the osazone group $C_6H_5.HN_2:C:C:N_2HC_6H_5$ being thereby converted into the group .CO.CO. This reaction is common to all the osazones of the sugars, and Fischer (*B*. 21, 2631) has called the compounds thus obtained *-osones*. Dextrosone reduces Fehling's solution on boiling, and does not ferment with yeast; with phenylhydrazine acetate it again yields phenylglucosazone. The osazone is reduced by zinc and acetic acid to iso-glucosamine, which yields lævulose by treatment with nitrous acid (Fischer, *B*. 19, 1920; 20, 2569). The osone yields compounds with methyl phenylhydrazine and ortho-diamines (Fischer, *B*. 22, 87). By proceeding in the same way *o*-tolyldextrosazone $C_{20}H_{26}N_4O_4$ m.p. 201° and *p*-tolyldextrosazone $C_{20}H_{26}N_4O_4$ have been prepared (Raschen, *A*. 239, 229). Diphenyl-hydrazine combines with the sugars in alcohol solution; sparingly soluble crystalline hydrazones are formed, which are resolved into their constituents by concentrated hydrochloric acid. The dextrose compound $C_6H_{12}O_5N_2(C_6H_5)_2$ melts at 161° (Stahel, *A*. 258, 242). Roder (*A*. 236, 229) has prepared phenyldextrosazone carboxylic acid.

Compounds with aromatic amines. Dextrose-*o*-diamido-benzene $C_6H_4(NH)_2.C_6H_{10}O_5$ and anhydro-dextrose-*o*-diamido-benzene $C_6H_4.N_2.C_6H_{10}O_4 + 2H_2O$ are formed by the interaction of dextrose and *o*-phenylene-diamine in acid solution. Di-dextrose-*o*-diamido-benzene is obtained when the reaction takes place in neutral solution. They are all crystalline bodies, soluble in water, and having a bitter taste. The first one does not reduce Fehling's solution, the last two do (Griess a. Harrow, *B*. 20, 281 and 2205); *o*-tolylene-diamine gives a similar compound (Hinsberg, *B*. 20, 495). Dextrose-γ-diamido-benzoic acid is obtained by mixing boiling aqueous solutions of dextrose and γ-diamido-benzoic acid (Griess a. Harrow, *l.c.*). With aniline dextrose forms a crystalline anilide m.p. 147° (Schiff, *A*. 154, 30; Sorokin, *B*. 19, 513; *J. R.* 1887, 377). Dextrose forms compounds with aldehyde, acetone, benzaldehyde, chloral, &c. (Schiff, *A*. 244, 19; Heffter, *B*. 22, 1050).

Dextrose-oxim $C_6H_{13}O_6N$ is formed by the combination of dextrose and hydroxylamine. It forms colourless, microscopic crystals, m.p. 136°–137°; very soluble in water, sparingly soluble in alcohol, and insoluble in ether. It reduces Fehling, and is lævorotatory, having $[\alpha]_{D20°} = -2·2°$ (Jacobi, *B*. 24, 696).

On warming an alkaline solution of dextrose with picric acid a blood-red colour is produced (Braun, *Fr*. 4, 185). If to crystallised diazobenzene sulphonic acid be added soda, dextrose solution, and a little sodium-amalgam, a red colouration is produced in a short time (Penzold a. Fischer, *B*. 16, 657).

Many aromatic alcohols give a colouration with dextrose and other carbohydrates in the presence of sulphuric acid. If two drops of a 15–20 p.c. alcoholic solution of (α)-naphthol be added to a dextrose solution, and one part of concentrated sulphuric acid, a violet colouration will be produced, changing to bluish violet.

Optical isomerides of glucose, gluconic acid and saccharic acid (E. Fischer, *B*. 23, 2611).

l-Gluconic acid. *l*-Mannonic acid can be converted into *l*-gluconic acid by heating with quinoline, but it is most conveniently prepared from arabinose by treatment with hydrogen cyanide and baryta (Kiliani, *B*. 19, 3029); *l*-mannonic and *l*-gluconic acids are formed simultaneously. The greater portion of the *l*-mannonic acid may be separated as lactone, and the remainder may be separated from the *l*-gluconic acid by crystallising out the calcium *l*-gluconate.

i-Gluconic acid is obtained by mixing the *l*- and *d*- acids, or from *i*-mannonic acid by quinoline.

l-Glucose is formed by reducing *l*-gluconic lactone with sodium-amalgam; it resembles dextrose closely, but does not ferment with yeast; $[\alpha]_D = -51·4°$; its derivatives also resemble the corresponding ones of dextrose very closely.

i-Glucose is prepared by mixing *l*- and *d*- glucose or reducing *i*-gluconic acid.

***l*-Saccharic acid** is prepared by oxidising *l*-gluconic acid with nitric acid.

***i*-Saccharic acid** is prepared by oxidising *i*-gluconic acid or by mixing *l*- and *d*- saccharic acid.

Lævulose. *d-Fructose*, lævoglucose, fruit sugar; $C_6H_{12}O_6$.

Occurrence.—Lævulose is widely distributed in the vegetable kingdom, being found, together with dextrose, in many parts of plants, in honey, &c. (*v. Dextrose*).

Formation.—The following carbohydrates yield lævulose, either alone or accompanied by other sugars, when acted on by dilute acids:

Cane sugar yields dextrose and lævulose.

Raffinose yields lævulose, galactose, and dextrose.

Inulin yields lævulose.

Irisin (O. Wallach, *A.* 234, 364), lævulan (v. Lippmann, *B.* 14, 1509), triticin (Reidemeister, *C. C.* 1880. 808), scillin (Riche a. Remont, *J. Ph.* [5] 2, 291), sinistrin (Schmiedeberg, *B.* 12, 704), lævulin or synanthrose (Dieck a. Tollens, *A.* 198, 228; Ville a. Joulie, *Bl.* [2] 7, 262; Popp, *A.* 156, 185; Müntz, *C. R.* 287, 679), and inuloid (Pópp, *A.* 156, 190) also yield lævulose. Lævulose is formed by the oxidation of mannitol (Cotton, *Bl.* [2] 33, 546; Gorup-Besanez, *A.* 118, 273; Bodenbender, *Zeit. d. Ver.* 14, 812; Renard, *A. Ch.* [5] 17, 316), by the fermentation of mannitol by *B. aceti* and *B. xylinum* (A. J. Brown, *C. J.* 1886, 184; 1887, 641); from phenylglucosazone by reduction to isoglucosamine, and thence by the action of sodium nitrite; from glucosone by reduction with zinc and acetic acid (Fischer, *B.* 22, 87, 2566).

Preparation.—Inulin is heated with very weak sulphuric acid for some hours, after which the sulphuric acid is carefully precipitated by baryta water and the filtrate decolourised by charcoal and evaporated on the water-bath to a syrup. This is treated several times with absolute alcohol, which removes the water, and the syrup which remains put on one side for some time in a closed flask, when fine needles make their appearance, and in time the whole solidifies (Jungfleisch a. Lefranc, *C. R.* 93, 547; also Crookewitt, *A.* 45, 184; Krusemann, *A.* 282, 26; Wohl, *B.* 23, 2084). A 10 p.c. solution of cane sugar is carefully inverted with hydrochloric acid (20 c.c. to a litre of solution) at 60°. The solution is cooled to $-5°$, 6 g. of slaked lime added for each 10 g. sugar, the temperature allowed to rise to 2°, and the lime lævulose carefully pressed from the rest of the solution and washed repeatedly with water. It is finally suspended in water, decomposed by oxalic acid, and the filtered solution evaporated *in vacuo* to a syrup which, when treated with absolute alcohol as above described, yields crystals of lævulose (Girard, *Bl.* [2] 33, 154; Dubrunfaut, *C. R.* 42, 901; 69, 438).

Formula and synthesis. See general part.

Properties.—Lævulose forms colourless, fine, shining needles, belonging to the rhombic system, the axial ratio is $a:b:c = 0{\cdot}80067:1:0{\cdot}90674$; they are slightly biaxial as regards their action on polarised light; they have a composition corresponding to the formula $C_6H_{12}O_6$, melt at 95°, and lose water at 100°. According to Hönig a. Jesser (*M.* 9, 562), the crystals contain water of crystallisation and have a formula $2C_6H_{12}O_6.H_2O$. If free from alcohol they are not deliquescent in the air (Hönig a. Schubert, *M.* 8, 529; Jungfleisch a. Lefranc, *l.c.*). The sugar is almost insoluble in cold absolute alcohol, and soluble in a boiling mixture of alcohol and ether (Dieck a. Tollens, *A.* 198, 228). With regard to the specific rotatory power of lævulose there are many and varied statements; all those based on the factors of unpurified solutions obtained by the inversion of inulin or cane sugar are worthless, as lævulose is extremely easily decomposed by acids (Jungfleisch a. Grimbert, *C. R.* 108, 144), and many apparent discrepancies may be explained by the fact that the optical activity varies very much with the temperature. Jungfleisch a. Grimbert (*C. R.* 107, 390) found for crystallised lævulose $[\alpha]_D = -101{\cdot}38° - 0{\cdot}56t + 0{\cdot}108\,(p-10)$, where t is the temperature and p the weight of lævulose in 100 c.c. solution. This formula holds for temperature 0°–40° and for concentrations below 40 p.c. The $[\alpha]_j = -108°$ ($c = 10$ g. sugar in 100 c.c.), calculated from $[\alpha]_j = -24{\cdot}5$ for invert sugars, and $[\alpha]_j = +58{\cdot}5$ for dextrose agree very well with the numbers of Jungfleisch a. Grimbert. Hönig a. Jesser (*M.* 9, 562) give $[\alpha]_j = -111{\cdot}38, c\,10, t = 20°$ for a carefully crystallised preparation. Herzfeld a. Winter (*B.* 19, 390) give for 20 p.c. solution at 20° $[\alpha]_D = -71{\cdot}4°$; but these determinations cannot be for the pure body. Freshly-prepared solutions of crystallised lævulose have a greater sp. rot. power than after standing a short time; Parcus a. Tollens (*A.* 257, 160) found for a 10 p.c. solution at 20° observed in a 200 mm. tube, $[\alpha]_D = -104{\cdot}02°$ six minutes after commencing solution, which sank to a constant value $[\alpha]_D = -92{\cdot}25°$ in 35 minutes. This cannot have been pure lævulose. $K = 100$; but Soxhlet makes it 92–93 (J. O'Sullivan, *C. J.* 1892, 408).

Action of heat and acids. Lævulose is exceedingly easily decomposed by heat and acids. Its aqueous solutions colour exceedingly quickly if heated for any length of time. Wohl (*B.* 23, 2084) found that by the action of minute quantities of acid on a hot concentrated solution of lævulose, a dextrin-like body was produced which was reconverted into lævulose by boiling with dilute acids. This instability accounts for the many different numbers which have been given for the sp. rot. power and for the fact that the opt. act. of invert sugar does not in all cases correspond with that of a mixture of pure lævulose and dextrose in equal quantities. On boiling with dilute sulphuric or hydrochloric acids, acetopropionic, formic, and other acids are produced (Jungfleisch a. Grimbert, *C. R.* 108, 144; Grote a. Tollens, *A.* 175, 181; Sieben, *Zeitschr. d. Ver.* 34, 237; Conrad a. Guthzeit, *B.* 19, 2569).

Action of alkalis. Alkalis quickly decompose lævulose, especially on warming; caustic soda and baryta yield lactic acid among other products (Sorokin, *J. R.* 1885, 368). Sodium lævulose $C_6H_{11}NaO_6$ is produced by acting on an alcoholic solution of lævulose with sodium ethylate (Hönig a. Rosenfeld, *B.* 12, 45). Lime yields a compound $C_6H_{12}O_6.CaO.H_2O$, which is soluble in 137 parts cold water (E. Péligot, *C. R.* 90, 153; Herzfeld a. Winter, *B.* 19, 390); and $2(C_6H_{12}O_6)3CaO$, which forms needles soluble in 333 parts cold water (Dubrunfaut, *A. Ch.* [3] 21, 169). Similar compounds are formed with potash, baryta, lead oxide, and bismuth oxide (Herzfeld a. Winter, *B.* 9, 390, and v. Lippmann, *Zuckerarten*, p. 68). If a solution of lævulose be boiled with lime, saccharin is formed (Scheibler, *B.* 13, 2212).

Reduction.—Lævulose in alkaline solution is reduced by nascent hydrogen to mannitol, and more easily than dextrose (Scheibler, *B.* 16, 3010; H. Krusemann, *B.* 9, 1465; Herzfeld, *A.* 244, 274). Fischer (*B.* 23, 3684) finds that equal parts of mannitol and sorbitol are produced.

Oxidation.—Mercuric oxide and baryta boiled with an aqueous solution of lævulose yield formic, glycollic and normal trioxybutyric acid (Börnstein a. Herzfeld, *B.* 18, 3353). Bromine water in the same way yields normal trioxybutyric acid (Hönig, *B.* 19, 171; Herzfeld a. Winter, *B.* 19, 390; *C. C.* 1886, 271). Lævulose by oxidation always yields an acid containing less carbon atoms than itself (Herzfeld a. Börnstein, *C. C.* 1886, 187; Herzfeld a. Winter, *C. C.* 1886, 271; *B.* 19, 390). Chlorine and bromine with silver oxide oxidise lævulose to glycollic acid (Hlasiwetz a. Habermann, *A.* 155, 130; Kiliani, *A.* 205, 175). Nitric acid yields oxalic acid, tartaric acid, glycollic acid, formic acid, a little saccharic acid, malic acid, acetic acid, and racemic acid (Dragendorf, *Materialien zu einer Monographie des Inulins*; Kiliani, *A.* 205, 162; Hornemann, *J. pr.* 89, 283).

Fermentation.—Lævulose ferments easily with yeast, with formation of alcohol and carbonic acid &c., but rather slower than dextrose, so that towards the end of a fermentation of invert sugar the solution is always lævorotatory (Bourquelot, *A. Ch.* [6] 9, 245; *C. R.* 101, 958; *C. R.* 100, 1404 and 1466; Maumené, *C. R.* 100, 1505; 101, 695; Leplay, *C. R.* 101, 479; Gourgon a. Dubourg, *C. R.* 110, 865).

Compounds with acids. Chlorosulphonic acid gives a tetra-sulphate (Claësson, *J. pr.* [2] 20, 1 a. 18). Acetyl chloride yields an acetochlorhydrin (Colley a. Wachowitsch, *B.* 13, 2390; *Bl.* [2] 34, 326). With acetic anhydride, acetic acid, and zinc chloride lævulose yields pentacetyl lævulose (Erwig a. Koenigs, *B.* 23, 672). Benzoyl chloride yields pentabenzoyl lævulose, m.p. 85° (Skraup, *M.* 10, 389).

Compounds with bases. See *Action of alkalis* above.

Compounds with metallic salts. Compounds with potassium or sodium chloride have not been described. A compound with lead chloride is known (Herzfeld a. Winter, *B.* 19, 390).

Compounds with cyanogen. By treatment with strong hydrocyanic acid, lævulose yields a cyanhydrin $C_7H_{13}O_8N$, this crystallises from water in tabular monoclinic crystals, m.p. 110°–115°, and has a slight dextrorotatory power; fuming hydrochloric acid converts it into the lactone of fructoheptonic acid $C_7H_{12}O_7$, and this, heated with hydriodic acid and phosphorus, yields a heptolactone $C_7H_{12}O_2$, b.p. 220°, which does not solidify in a freezing mixture. When the lactone is further treated with hydriodic acid and phosphorus an acid is obtained boiling at 210°, which is identical with methyl-butyl-acetic acid as synthetically prepared (Kiliani, *B.* 18, 3066; 19, 221 and 1914; Kiliani a. Düll, *B.* 23, 449). Tetra-oxy-butane-tri-carboxylic acid $COOH.(CH.OH)_3.C(OH)(COOH)_2$ is obtained by oxidising fructoheptonic acid by nitric acid (Düll, *B.* 24, 348).

Hydrazine compounds. Lævulose yields an osazone which appears to be identical with, and is prepared in the same manner as, dextrose osazone (*q.v.*).

Anilides. By heating an aqueous solution of lævulose with aniline, an anilide is formed $C_{12}H_{17}NO_5$; it is easily obtained in crystals which melt at 147° with partial decomposition (Sorokin, *B.* 19, 513; *J. R.* 1886, 129; 1887, 377). With hydroxylamine lævulose combines to form lævulosoxim (Wohl, *B.* 24, 993). It strongly resembles dextrosoxim in appearance, m.p. 118°, it is lævorotatory, and reduces ammoniacal silver solutions on warming, whilst dextrosoxim does so in the cold.

Galactose. Lactose. $C_6H_{12}O_6$. Galactose does not occur in nature.

Formation.—By the action of dilute acids on many carbohydrates and similar substances of vegetable and animal origin. Lactose yields dextrose and galactose (Pasteur, *C. R.* 42, 347; Fudakowski, *B.* 9, 42; *C. C.* 1877, 6). Raffinose yields lævulose, galactose, and dextrose. α-Galactin, β-galactin, paragalactin, lactosin, agar-agar, carragheen moss, plum gum, peach gum, gum arabic, gedda gum, and many other similar vegetable substances, yield galactose amongst other products of their hydrolysis (Müntz, *Bl.* [2] 37, 409; *A. Ch.* [6] 10, 566; *C. R.* 94, 453; 102, 624, 681; A. Meyer, *B.* 17, 690; Bauer, *J. pr.* [2] 30, 375; *L. V.* 1888, 33 a. 214; Hädicke, Bauer a. Tollens, *A.* 238, 302; Kiliani, *B.* 13, 2304; 15, 36; v. Lippmann, *B.* 17, 2238; Scheibler, *B.* 1, 58; 6, 612; 17, 1729; O'Sullivan, *C. J.* 1884, 41; 1391, 1029; Hädicke a. Tollens, *A.* 238, 308; Schulze a. Steiger, *B.* 19, 827; 20, 290; *L. V.* 36, 391; Schulze, *B.* 25, 2213; Maxwell, *Am. C. J.* 12, 51 a. 265; v. Lippmann, *Deutsche Zuckerind.*, 1887, 455; *B.* 20, 1001; Stone, *Am.* 12, 435). Galactose is also produced by the long-continued action of dilute sulphuric acid on certain nitrogenised constituents of the brain (Thudichum, *Ann. of Chem. Med.* [2] 209; Thierfelder, *Z. P. C.* 14, 209; Brown a. Morris, *C. J.* 1890, 57). This sugar was called by the discoverer *cerebrose*; B. a. M. proved it to be galactose.

Preparation.—A solution of lactose (milk-sugar) containing in every 100 c.c. 25 g. dry lactose; 2 to 3 grams H_2SO_4 is digested in a flask on the water-bath for 2½ to 3 hours, the water being kept boiling all the time and care being taken by continual shaking of the flask to avoid colouring. The acid is, on cooling the solution, carefully neutralised with baryta water and the $BaSO_4$ separated by filtration. On evaporating the filtrate to a strong syrup in a vacuum solidification takes place in a short time. The solid crystallised mass is digested several times with dry methyl alcohol; this dissolves out the dextrose and other products of the action of the acid on lactose and the hydrolysed sugars, and leaves galactose as a white crystalline powder. This is dissolved in the least possible quantity of boiling water, again allowed to solidify, and again treated with boiling methyl alcohol. If the whole of the lactose hydrolysed, and it generally is under the conditions indicated, the residue is white, nearly pure, galactose. It can be rendered pure by recrystallisation from water. If the crystals are allowed to form slowly from solutions not too concentrated they are distinct and well-defined (Rendell, *N. Z.* 4, 163; Soxhlet, *J. pr.* 2, 21, 269). The sugar can also be prepared from certain gums of the arabin group. For this purpose the most suitable are those having a lævorotatory power and yielding the larger percentage of mucic acid on oxidation with nitric acid. The dextro- gums also yield the sugar, but in less quantity (O'Sullivan, *C. J.* 1884, 41; 1891, 1029). A solution of the gum selected—gum arabic, Turkey, Levantine or East India gum—is made containing about equal weights of water and gum; this is heated in a flask in a water-bath as high as the boiling bath will take it, and 5 grams H_2SO_4 diluted to 15 c.c. added for every 100 c.c. of the gum solution employed. The mixture is digested for 30 to 35 minutes, then rapidly cooled, and alcohol, S. G. 0·83, added as long as a pp. is produced. This pp. is again dissolved in water, and again ppd. One or two repetitions of this process frees the pp. from arabinose. A solution of the same strength as that above described for the original gum is then made of the pp. and heated as high as the boiling water of a water-bath will take it, and then for every 100 c.c. of the solution 5 grams H_2SO_4 diluted to 15 c.c. added. At the end of about 8 hours' digestion the solution is cooled, carefully neutralised with baryta water, and alcohol, 0·82, added as long as a pp. is thrown out. The alcoholic solution becomes clear on standing; it contains galactose, and on concentration in a vacuum yields crystals of the body in a fairly pure state. They may be completely purified by washing with methyl alcohol, recrystallising the residue from ethyl alcohol, and finally from water.

Formula and synthesis. See general part.

Properties.—Galactose crystallises in hexagonal plates, m.p. 163°–164° (after drying at 100°) (E. Bourquelot, *J. Ph.* [5] 13, 51), or, according to v. Lippmann (*B.* 18, 3335), in microscopic six-cornered prisms and needles, m.p. 168°. Galactose is easily soluble in water, almost insoluble in methyl alcohol. Solutions of galactose rotate a ray of polarised light to the right, the specific rotatory power for the D line being given by the formula $[\alpha]_D = 83{\cdot}883 + 0{\cdot}0785P - 0{\cdot}209t$ (Meissl, *J. pr.* [2] 22, 97); this formula agrees well with numbers found by other observers. Freshly-prepared solutions exhibit the phenomenon of bi-rotation (Pasteur, *J. pr.* 68, 428). Parcus a. Tollens (*A.* 257, 160) observed an angle of $[\alpha]_D = 117{\cdot}48°$ in a 10 p.c. solution at 20°, 7 minutes after commencing solution. K = 100, and varies slightly with the conditions of determination.

Action of acids. By prolonged heating with dilute acids, galactose yields aceto-propionic and formic acids (Kent a. Tollens, *A.* 227, 228; *B.* 17, 668; Conrad a. Guthzeit, *B.* 18, 2905); sulphuric acid and chloro-sulphuric acid yield galactose-sulphuric acids (Hönig a. Schubert, *M.* 7, 455; Claësson, *J. pr.* [2] 20 a. 18).

Action of alkalis. Alkalis colour galactose yellow; the action of milk of lime produces saccharin (Cuisinier, v. Lippmann, *Zuckerarten*). Fusion with KHO gives rise to acetic and oxalic acids.

Reduction. — By reduction with sodium-amalgam, galactose yields dulcitol and other alcohols (Bouchardat, *A. Ch.* [4] 27, 79).

Oxidation.—Bromine oxidises galactose to galactonic acid (lactonic acid) $C_6H_{12}O_7$, isomeric with gluconic acid (Hlasiwetz a. Habermann, *A.* 122, 96; Kiliani, *B.* 13, 2307; 18, 1551; Bauer, *J. pr.* [2] 30, 379); which when heated loses 1 mol. water, and is converted into the lactone; it yields with phenylhydrazine a hydrazide which melts at 200°–205° with decomposition (Fischer a. Passmore, *B.* 22, 2731). Nitric acid oxidises galactose to mucic acid, isomeric with saccharic acid. As mucic acid is only slightly soluble in water, the yield of mucic acid, which is normally 75 to 78 p.c., is sometimes made use of for the estimation of galactose; but the yield varies considerably with the condition of experiment (Pasteur, *C. R.* 42, 349; Kent a. Tollens, *A. Ch.* 227, 228). Neutral or alkaline solutions of cupric hydroxide are reduced by galactose; carbonic, formic, glycollic, and lactic acids are produced (Habermann a. Hönig, *M.* 5, 208).

Fermentation.—According to Kiliani (*B.* 13, 2305) and Koch (*B.* 20, Ref. 145), galactose does not ferment with yeast, whilst v. Lippmann (*B.* 17, 2238; 20, 1001), Bourquelot (*C. R.* 106, 283), and Pasteur find that it does ferment. Stone a. Tollens (*A.* 249, 257; *B.* 21, 1572) find that it ferments with beer yeast as well as with *Mucor racemosus*, but slower than dextrose. Certain bacteria yield lactic acid (Pranzmovaski a. v. Tieghem, *B.* 12, 2087).

Compounds.—Galactose yields a crystalline compound with sodium chloride (Fudakowsky, *Bl.* [2] 30, 433). With a solution of baryta in methyl alcohol, galactose yields the compound $(C_6H_{11}O_6)_4Ba_2.BaO$ (Fudakowsky, *l.c.*). With acetic anhydride, a pentacetate is produced $C_6H_7O(C_2H_3O_2)_5$, m.p. 62°–66° (Fudakowsky). According to Erwig a. Koenigs (*B.* 22, 2207) this body melts at 142°, crystallises in rhombic prisms, reduces Fehling's solution, is dextrorotatory, and differs in all its properties from Fudakowsky's galactose pentacetate. With aniline, galactose forms an anilide, crystallising in long triclinic prisms, and lævorotatory (Sorokin, *J. R.* 1887, 377; *B.* 19, 298). With hydroxylamine, galactose yields the oxim $C_6H_{13}NO_6$, the crystals melt at 175°–176°, and are easily soluble in water and weak alcohol (Rischbieth, *B.* 20, 2673). With ortho-diamido-benzene, galactose yields galactose-*o*-diamido-benzene $C_6H_4(NH)_2.C_6H_{10}O_5$, melting at 246° with decomposition. Galactose-γ-diamido-benzoic acid $COOH.C_6H_3(NH)_2.C_6H_{10}O_5 + H_2O$ crystallises in needles (Griess a. Harrow, *B.* 20, 3111). With hydrocyanic acid, galactose yields galactoheptonamide $C_7H_{15}NO_7$, m.p. 194°; it is converted into the barium salt of galactoheptonic acid $C_7H_{14}O_8$ by digesting with baryta. The free acid melts at 145° and crystallises in slender needles; it is reduced by hydriodic acid and phosphorus to the lactone of normal γ-oxyheptoic acid (b.p. 231°) and a very small quantity of normal heptoic acid (Maquenne, *C. R.* 106, 286; Kiliani, *B.* 21, 915; 22, 521 a. 1885). With phenylhydrazine, galactose forms galactose-phenylhydrazide, crystallising in colourless needles, m.p. 158°, and *galactose*-osazone, m.p. 193°–194° (Fischer, *B.* 20, 821). Fischer's first determination of the melting-point (*B.* 17, 579) was 182°, Scheibler (*B.* 17, 1731) gave 171°, and other observers have given lower numbers; this may be accounted for by the fact that unless the osazone be heated up very quickly it decomposes before it fuses. By the action of hydrochloric acid it yields galactose-osone (Fischer, *B.* 22, 87). Galactose also yields a diphenylhydrazide, m.p. 157° (Stahel, *A.* 258, 242). Galactose forms a penta-benzoate $C_6H_7O(C_7H_5O_2)_5$, m.p. 165° (Skraup, *M.* 10, 389).

Sorbose. Sorbinose $C_6H_{12}O_6$. Sorbose is obtained from the juice of the mountain ash after allowing it to stand for some time. It is doubtful if it exists in the fresh juice as a free sugar, but it is probably formed by the decomposition of a glucoside (Pelouze, *A. Ch.* [3] 35, 222; Boussingault, *C. R.* 74, 939; Delffs, *B.* 4, 799; Byschl, *J. pr.* 62, 504; Freund, *M.* 11, 560). The expressed juice of the unripe berries of the mountain ash is allowed to ferment for eight or ten months, the clear solution is filtered from the organisms by which the fermentation was effected, and evaporated to a syrup, when the sorbose crystallises out on standing. It forms colourless rhombic crystals easily soluble in water. Its solutions are lævorotatory: for 10 p.c. solution, $[\alpha]_D = -43{\cdot}4°$ (Wehmer a. Tollens, *B.* 19, 708). It is oxidised by chlorine and silver oxide to glycollic acid; it behaves with bromine water like lævulose, being practically unaltered (Kiliani a. Scheibler, *B.* 21, 3276); nitric acid oxidises it to oxalic, aposorbic and tartaric acids. By more careful oxidation with HNO_3 Kiliani a. Scheibler (*l.c.*) obtained trioxyglutaric acid. Copper hydrate oxidises it to carbonic and formic acids and other bodies, amongst which is possibly glyceric acid (Dessaignes, *J. pr.* 89, 313; Hlasiwetz a. Habermann, *A.* 155, 129; Habermann a. Hönig, *M.* 5, 208). Hydriodic acid reduces it to hexyl iodide (Kiliani a. Scheibler, *l.c.*). It reduces Fehling's solution, and is coloured yellow by alkalis. Sorbose ferments slowly with beer yeast (Stone a. Tollens, *A.* 249, 257). By prolonged heating with dilute acids it is decomposed, yielding, amongst other bodies, lævulinic acid (Wehmer a. Tollens, *l.c.*). With phenyl-hydrazine it yields an osazone $C_{18}H_{22}N_4O_4$, m.p. 164°, which is almost insol. in water, but fairly easily soluble in alcohol, from which it crystallises in fine microscopic needles (Fischer a. Tafel, *B.* 19, 1920; 20, 217 and 2566; Fischer, *B.* 20, 828).

Mannose. *Seminose* $C_6H_{12}O_6$. This sugar does not occur free in nature.

Formation.—It is obtained by the action of dilute sulphuric acid on the so-called reserve cellulose (Reiss, *B.* 22, 609, 3218) and on salep juice (Tollens a. Gans, *A.* 249, 256), and by the oxidation of mannitol (Fischer a. Hirschberger, *B.* 21, 1805; 22, 1155 a. 3218; Carlet, *J.* 1860. 250; Gorup-Besanez, *A.* 118, 257; Dafert, *B.* 17, 227).

Preparation. — **Sifted ivory nut shavings (1 pt.) are digested with 6 p.c. hydrochloric acid (2 pts.) for six hours on the water-bath, filtered hot, and the residue pressed and extracted with water. The brown solution contains the sugar. It may be obtained as hydrazide by adding phenyl-hydrazine acetate, and this is decomposed by hydrochloric acid with reproduction of the sugar (Fischer a. Hirschberger, *B.* 22, 365 a. 3218).**

Properties.—Mannose is precipitated from its alcoholic solution by ether; the syrup, on keeping under absolute alcohol, solidifies to a hard colourless mass which shows no sign of crystalline structure. Its solutions are dextrorotatory, $[\alpha]_D = 13{\cdot}0°$ approx.; they are reduced by Fehling's solution, 1 c.c. of this solution being reduced by 4·307 mgm. mannose, *i.e.* K = 110°–112°. It is fermented by yeast.

Reduction.—Mannose is reduced by sodium-amalgam to mannitol.

Oxidation.—Mannose is oxidised by bromine to mannonic acid, the lactone of which ($C_6H_{10}O_6$) crystallises in colourless needles, readily soluble in water and less in alcohol; it is dextrorotatory in aqueous solutions, $[\alpha]_D = 53{\cdot}8°$, and forms a phenylhydrazide $C_{12}H_{18}N_2O_6$, m.p. 214°–216°. Its optical isomeride, *l*-mannonic acid, is obtained by the nitrile reaction from arabinose. Oxidised with nitric acid, manno-saccharic acid is obtained (Easterfield, *C. J.* 1891, 306; Fischer, *B.* 24, 539). It crystallises in colourless needles, m.p. 180°–190°, and $[\alpha]_D = 201{\cdot}8°$. With ammonia it yields a monamide, and with phenylhydrazine a mono- and di-phenylhydrazide. Kiliani's metasaccharic acid is its optical isomeride (*l*-mannosaccharic acid) (Fischer, *l.c.*).

Action of acids. Hot hydrochloric acid has little action on mannose, but if the heating be continued for some time, humus substances are formed.

Action of alkalis. Alcoholic potash precipitates a flocculent hygroscopic substance from solutions of the sugar.

Compounds.—Lead acetate and ammonia produce a precipitate which becomes yellow on keeping. With phenylhydrazine it yields a sparingly soluble hydrazide, $C_{12}H_{18}N_2O_5$, crystallising in yellow slender prisms, m.p. 195°–200°, lævorotatory in dilute hydrochloric acid solution. By heating the hydrazide with excess of phenylhydrazine hydrochloride, sodium acetate, and water, it yields an osazone $C_{18}H_{22}N_4O_4$ crystallising in yellow needles, which is identical with phenylglucosazone. With di-phenyl-hydrazine it yields a di-phenyl hydrazide, m.p. 155°. With hydrocyanic acid it yields a compound which is easily decomposed, yielding mannose-heptonic acid; its lactone $C_7H_{12}O_7$ crystallises in needles, m.p. 148°–150°; by reduction with hydriodic acid normal heptoic acid is obtained. With hydroxylamine mannose yields an oxim $C_6H_{13}O_6N$, m.p. 184° (Reiss, *l.c.*; Fischer a. Hirschberger, *B.* 22, 1155). Aceto-chloro-mannose is obtained by the action of acetyl chloride (Fischer, *l.c.*).

Phlorose $C_6H_{12}O_6$. This has been shown to be identical with dextrose (Rennie, ***C. J.* 887,** 636; Fischer, *B.* 21, 988).

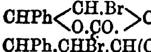
Crocose $C_6H_{12}O_6$. Kayser (*B.* 17, 2232) a. Rochleder a. Mayer (*J. pr.* 74, 1) obtained a dextrorotatory sugar by heating saffron (from *Crocus electus* or yellow shoots of *Gardenia grandiflora*) with dilute sulphuric acid. It forms rhombic crystals, which only reduce half as much copper oxide as dextrose. According to Fischer (*B.* 21, 988), it yields, with phenylhydrazine, an osazone identical with phenyl glucosazone.

Lokaose $C_6H_{12}O_6$ is obtained from lokao or Chinese green by boiling with dilute sulphuric acid, lokaonic acid yielding lokanic acid and lokaose $C_{42}H_{48}O_{27} = C_{36}H_{36}O_{21} + C_6H_{12}O_6$. Lokaose forms minute acicular crystals, and is distinguished from dextrose by being optically inactive and having a lower reducing power (K = 50) (R. Kayser, *B.* 18, 3417).

Tabakose is said to exist in tobacco (Attfield, *Ph.* 541).

Digitalose $C_7H_{14}O_7$ is obtained, together with dextrin, by the action of strong hydrochloric acid on digitalin; oxidised with bromine it yields digitalonic lactone $C_7H_{12}O_5$; hence the formula of the sugar (Kiliani, *Ar. Ph.* 230, 250; *B.* 25, 2116).

Aromatic sugar. *Phenyltetrose* (Fischer a. Stewart, *B.* 25, 2555). Cinnamaldehyde cyanhydrin, when dissolved in chloroform and bromine added, yields phenyl-dibromo-oxybutyronitril CHPhBr.CHBr.CH(OH)CN; this when heated with hydrochloric acid yields phenylbromodioxybutyrolactone



$\mathrm{CHPh}{<}\begin{matrix}\mathrm{CH.Br}\\ \mathrm{O.CO.}\end{matrix}{>}\mathrm{CH.OH}$, from which the acid CHPh.CHBr.CH(OH).COOH is easily obtained; on reduction this yields phenyltetrose OH.CHPh.CH(OH).CH(OH).COH. It yields a phenylhydrazide, m.p. 154°.

For *Acrose*, *Formose*, *Glycerose*, see *Synthesis of the Sugars.*

Class II. The '*-on*' sugars.

(*a*) *Dipentose.*

Arabinon, diarabinose, or arabinbiose $C_{10}H_{18}O_9$. A product of the partial hydrolysis of a series of gum acids. A 25 p.c. solution of any of the strongly rotating gum acids is heated to boiling, and 2 g. sulphuric acid for every 100 c.c. solution, previously diluted with 4 to 5 volumes water, added. At the end of 10 to 15 minutes' digestion the solution is quickly cooled and alcohol, sp.gr. ·830, added as long as a precipitate forms. The clear alcoholic solution contains *arabinon* and arabinose, and some arabinon is taken down with the precipitate; and on again dissolving it in a little water and reprecipitating with alcohol, the arabinon often appears on the surface of the syrup in spherocrystals, and the alcoholic supernatant liquid contains it in quantity. It is easily soluble in water and methyl alcohol. Dilute ethyl alcohol also dissolves it, but absolute alcohol precipitates it as a syrup from a strong methyl alcohol solution. Ether also precipitates it. Its solutions are dextrorotatory, $[\alpha]_D = +202°$ (c. 6·466), there appears to be an increase with the concentration; it reduces Fehling's solution; K = 58 (K = 57·5 if 2 mols. sugar reduce 9 mols. CuO). D = 3·95. It tastes sweet, and is easily diffusible. Dilute acids hydrolyse it, the sole product being arabinose,

$$\underset{\text{Arabinon}}{C_{10}H_{18}O_9} + H_2O = 2\underset{\text{Arabinose}}{C_5H_{10}O_5}$$

(O'Sullivan, *C. J.* 1890, 59).

(*b*) *Dihexoses.*

Cane sugar. *Saccharon*, *sucrose* $C_{12}H_{22}O_{11}$.

Occurrence.—Cane sugar is widely distributed throughout the vegetable kingdom, and is frequently accompanied by dextrose and lævulose. The most important sources are the sugar-cane (*Saccharum officinarum*); the sugar-beet (*Beta vulgaris*); the sugar-maple (*Acer saccharinum*) and *Sorghum saccharatum* (Girard, *C. R.* 102, 108; *Centrbl. f. Agric. Ch.* 1886. 683; Berthelot, *C. R.* 53, 583; *A. Ch.* [3] 55, 289; Buignet, *A Ch.* [3] 61, 233; Maxwell, *L. V.* 36, 15, *Am.* 12, 265; *Reports of the Department of Agriculture, Washington*, No. 6; *The Sugar Industry of the United States*, by Wiley, 1885; *The Literature of the Sugars*, H. L. Roth, London, 1890; Gössmann, *A.* 104, 335; Hermbstädt, *Gehlen's J. f. Ch. Ph. Min.*, 8, 589 (1809); Boier, *Jahresb. f. Zuckerfabr.* 5, 139; Balland, *J. Ph.* [4] 25, 97; Corenwinder, *C. R.* 83, 1238; A. v. Wachtel, *B. C.* 1880, 344; Stone, *B.* 23, 1406; Wiley, *C. N.* 51, 88; *Ann. Agronom.* 11, 392; Schulze a. Seliwanoff, *L. V.* 1887. 403; Washburn a. Tollens, *B.* 22, 1047; Stingl a. Morawski, *M.* 7, 176; 8, 82; Déon, *Bl.* [2] 32, 125; Reali, *G.* 17, 325; Schulze, *L. V.* 1887, 403, 408; *v.* also the references under the heading *Dextrose*, *Occurrence*, and many others throughout the range of chemical literature).

Formation.—Icery (*A. Ch.* [4] 5, 350) and Jackson (*C. R.* 46, 55) found that in the early period of vegetation of many plants, invert sugar only occurs, and that cane sugar is formed later. Leplay (*C. R.* 46, 444) confirms this observation in the case of sugar-cane. Barley contains from 0·8 to 1·6 p.c. cane sugar, whereas germinated barley (malt) contains from 2·8 to 6·0 p.c. cane sugar; the starch of the endosperm being converted into cane sugar for the use of the growing plant (Kuhnemann, *B.* 8, 202, 387; Kjeldahl, *Rés. du C. R. des Travaux du Lab. de Carlsberg*, 1881, 189; O'Sullivan, *C. J.* 1886, 58). Brown a. Morris (*C. J.* 1890, 516) found that the cane sugar of germinated barley was chiefly localised in the embryo, whilst maltose appears in the endosperm; they consider that starch is first converted by diastase into maltose in the endosperm, and then, being transferred to the embryo, is converted into cane sugar for the purpose of growth. Colley a. Vakovitch (*Bl.* [2] 34, 326) may have obtained cane sugar by acting on barium lævulosate with acetochlorhydrose, but the evidence is not satisfactory. Aubert a. Giraud (*D. P. J.* 257, 298) state that by passing an electric current through acidified starch-paste at 100°C. cane sugar may be manufactured (?).

Preparation.—(For the commercial preparation of cane sugar see Thorpe's Dictionary of Applied Chemistry.) The best samples of commercial cane sugar consist of almost the pure sugar. Dry, clean, glassy sugar-candy is sufficiently pure for most purposes. Absolutely pure saccharon may be obtained by careful crystallisation from warm aqueous solutions; or a cold, clear saturated solution made with carefully-purified distilled water is mixed with an equal volume of purified ethyl alcohol, S.G. ·820, with continual stirring. On standing, saccharon crystallises out in pure glassy crystals.

Properties.—Cane sugar forms fine large monoclinic hemihedral crystals, S.G. $\frac{17·5}{17·5}$ 1·58047 (Schröder, *B.* 12, 562; Gerlach, *D. P. J.* 172, 31 and 286; Joule a. Playfair, *C. J.* 1, 130), which do not contain water of crystallisation. It is easily soluble in water; 100 parts of a solution saturated at 0° contain 65·0 pts. saccharon, at 20° 67 pts., and at 40° 75·8 pts. (Scheibler, *Z. V.*[1] 22, 253). A large number of figures have been given to represent the relation between the quantity of sugar in solution and the specific gravity thereof (v. Lippmann's *Zuckerarten*; Brown a. Heron, *C. J.* 1879, 644; Périer, *C. R.* 108, 1202), and much apparent contradiction exists on the subject; but the bulk of this disappears when the processes by which the figures were obtained are inquired into. The general agreement is with the numbers of Balling, confirmed, within the limits of error, by Scheibler a. Mategczek (*Z. V.* 15, 586; 24, 827; 27, 32) and others. These are:—

Per cent. saccharon in sol.	Sp. gr. sol. $\frac{17\cdot5^\circ}{17\cdot5^\circ}$
5	1·01970
10	1·04014
20	1·08329
40	1·17943

The relation is sometimes more convenient when expressed as weights in measure. If a vessel be made to hold 100 g. H_2O at 15·5°, and such is the 100 c.c. vessel most generally in use, then a solution containing

20 g. saccharon in this 100 c.c. = sp. gr. 1·07686
10 ,, ,, ,, 1·03857
5 ,, ,, ,, 1·01931
1 ,, ,, ,, 1·00386

Hence, if the sp.gr. of a pure cane sugar is known the amount of sugar in the 100 c.c. can be arrived at broadly by dividing the S.G. – 1·000 by ·00385. This number multiplied by 1000 has been called the D of the sugar. D = 3·85 for saccharon. The use of the number gives too low an indication for the higher specific gravities and too high a one for the lower ones, being almost accurate for solutions containing between 10 and 20 g. sugar per 100 c.c. It is a useful, practical factor when its meaning and value are understood, being at most 3 per 1000 incorrect.

Concentrated sugar solutions possess a higher boiling-point than water, an 80 p.c. solution boils at 112°, a 90·8 p.c. solution at 130° (Gerlach, *D. P. J.* 172, 31 and 286).

Solutions of pure cane sugar crystallise quickly, but if foreign matters are present the crystallisation is very much slower, and the forms of the crystals vary with the character of the impurity; some impurities entirely prevent crystallisation. These facts play a most important part in the refinery (see art. in DICTIONARY OF APPLIED CHEMISTRY and v. Lippmann's *Zuckerarten*, p. 115). Solutions of cane sugar are highly diactinic (Hartley, *C. J.* 1887, 59). Cane sugar is soluble in methyl and ethyl alcohol, acetone, and glycerin in proportion to the amount of water they contain, being almost insoluble in them when they are anhydrous (Scheibler, *Z. V.* 22, 246; *B.* 5, 343). Solutions of cane sugar and the fused sugar are optically active, rotating the plane of polarisation to the right; crystallised sugar is not optically active. The oldest value given for specific rotatory power is $[\alpha]_j = +73\cdot8^\circ =$

$$[\alpha]_D = +66\cdot6^\circ\ (24:21\cdot67::73\cdot8^\circ:66\cdot6^\circ).$$

This is only an approximate average number, much of the same value as the D described above. It is the *apparent* specific rotatory power, and may be called the working value. Tollens (*B.* 17, 1757), Schmitz (*B.* 10, 1419), Girard a. de Luynes (*C. R.* 80, 1355), and Calderon (*C. R.* 83, 393), from numerous observations worked out an absolute value. Tollens gives $[\alpha]_D = 66\cdot386 + 0\cdot015035P - 0\cdot0003986P^2$, where P is the p.c. of sugar; Schmitz's numbers are $[\alpha]_D = 64\cdot156 + 0\cdot051596q - 0\cdot00028052q^2$, where q = p.c. of water. The optical activity diminishes with the concentration of the solution, so that for a 100 p.c. solution (*i.e.* for the dry sugar, if the curve follows the same course as the observations) the specific rotatory power is $[\alpha]_D = 64^\circ$ approximately, while very weak solutions, as 1 p.c. for example, it is $[\alpha]_D = 67^\circ$ (Pibram, *B.* 20, 1849; Nasini a. Villavecchia, *Gaz.* 22, 1, 97). The temperature of observation has but a very slight influence on the optical activity (Dubrunfaut, *A. Ch.* [3] 18, 99; Andrews, *M. S.* [4] 3, 1366). The specific rotatory powers of solutions of the sugar in mixtures of water and ethyl alcohol, methyl alcohol, and acetone respectively are slightly greater than that of aqueous solutions; if the latter be taken at $[\alpha]_D = 66\cdot67^\circ$ they are respectively $[\alpha]_D = 66\cdot83^\circ$, $68\cdot63^\circ$, and $67\cdot40^\circ$ (Tollens, *B. C.* 1881, 570). The optical activity of fused sugar is less than that of its solutions, and diminishes according to the length of time it has been kept fused. This is, no doubt, due to the presence of decomposition products. The specific rotatory power of aqueous solutions is altered by the presence of most foreign substances; alkalis and alkaline earths diminish it (Thomsen, *B.* 14, 1649; v. Lippmann, *Zuckerarten*, p. 157; Farnsteiner, *B.* 23, 3570). Lead acetate does not appear to have any influence, while ammonia increases the rotation (Ost, *N. Zeitsch. f. Rübenz.-Ind.* 9, 42). The dispersion of cane-sugar solutions is almost the same as that of quartz, so that the rotation of the plane of polarisation caused by a sugar solution may be almost completely neutralised by a plate of left-handed quartz of the correct thickness. Grimbert (*J. Ph.* [5] 16, 295) gives $[\alpha]_D = 66\cdot45^\circ$ and $[\alpha]_G = 52\cdot85^\circ$, so that the dispersive power for these two wave-lengths is 1·257. The refractive index for sugar solutions has been determined for seven lines of the spectrum (Obermeyer, Landolt-Börnstein, *Physikalisch-chem. Tabellen*, Berlin, 1883, p. 213; Kanonnikoff, *B.* 16, 3047). Gladstone (*C. J.* 1891, 589) finds the molecular refraction of cane-sugar solutions to be 118·7 for the A line, and the molecular dispersion between A and H lines 4·73.

Action of heat. Dry cane sugar melts at 160°, and solidifies on cooling, if care be taken and the temperature does not exceed 160°, to a colourless, glassy mass; but if the temperature be maintained the fused mass becomes slightly coloured, and on cooling yields the substance known as barley-sugar, this after a time becomes crystalline; but even with the greatest care it seems impossible to fuse the sugar without producing some decomposition. With the appearance of the colour dextrose and lævulosan are probably the chief products; but although much work has been done on the subject, the exact nature of the alteration is not settled. A little furfural is formed at times (Gélis, *A. Ch.* [3] 57, 234; *C. R.* 51, 331; Schiff, *B.* 20, 540). When the temperature is raised to 200° distinct decomposition sets in, caramel is formed, gases are evolved, and finally a residue of charcoal remains. Among the gases are carbon dioxide, carbon monoxide, marsh gas, ethylene, acetylene; among the volatile products are water, acetone, formic, acetic, and propionic acids, aldehyde, furfural, acrolein, benzoic aldehyde, and a bitter substance assamur (Völckel, *A.* 85, 59; 86, 63; 87, 303; Fremy, *A.* 15, 278; Schiff, *B.* 20, 540; *A.* 238, 380; Reichenbach, *A.* 49, 3). Caramel has the same composition as cane sugar, less one or more molecules of water. It is soluble in water and partly soluble in alcohol, and probably consists of a mixture of several bodies. Baryta and basic lead acetate give precipitates with it. It combines with aniline, reduces some metallic salts, and yields an acid with chlorine. It is largely used as a colouring matter in cookery, brewing, &c. (Gélis, *A. Ch.* [3] 52, 386; 65, 190 a. 496; Graham, *A. Ch.* 65, 190; Péligot, *A. Ch.* [2] 67, 172; Völckel, *A.* 75, 59; 85, 74; Pohl, *J. pr.* 82, 148; Schiff, *B.* 4, 908; Wachtel, *Org. d. Centr.-Ver.* 17, 930).

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[1] *Z. V.* = *Zeitschrift des Vereins für die Rübenzucker industrie des deutschen Reiches.*

It seems proved that when dry saccharon is heated at 100°, even for a long time, no change takes place, and, as has been said, the sugar can be heated to the melting-point, 160°, without producing any marked decomposition, but it would appear that rapid heating to this temperature can produce a mixture of dextrose and lævulosan, without any change in weight. If, however, a mixture of 100 pts. of the sugar and about 5 pts. water is heated at 150° for some time, a mixture is produced which contains little or no unaltered saccharon, but which consists, in part at least, of a sugar said to be optically inactive, and to be a compound of bi-rotating dextrose and lævulose. Other bodies must also be present, probably dextrose and lævulose. The compound sugar is, no doubt, present, but inasmuch as it has never been isolated it cannot be said with certainty that it is inactive (Morin, *C. R.* 86, 1033; Berzelius a. Mitscherlich, *J. Ph.* 3, 4, 216). The so-called inactive sugar is easily converted by boiling with water into dextrose and lævulose. Neutral aqueous solutions of saccharon are slowly inverted on boiling. They are, however, stable in the cold, if sterilised, and can be concentrated under diminished pressure at 50°-60° without undergoing much change (Kreuster, *Z. V.* 25, 521; Béchamp, *A. Ch.* [3] 54, 28; Morin, *C. R.* 86, 1,083; Horsin-Déon, *Bl.* [2] 32, 121; Gunning, *Z. V.* 27, 895). By heating to 150°-200° in a sealed tube, humus substances, formic acid, pyrocatechin, and other bodies are formed (Löw, *Z.* 1867, 510; Hoppe-Seyler, *B.* 4, 15).

Action of acids. All dilute acids, even carbonic acid, hydrolyse (invert) cane sugar, causing the assimilation of one molecule of water and the production of equal quantities of dextrose and lævulose,

$$\underset{\text{Saccharon}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Lævulose}}{C_6H_{12}O_6}$$

This mixture is called invert sugar. The experiments made on this phenomenon may be classified under two headings: (*a*) the action of *different* acids acting under the *same* conditions on the sugar solutions; (*b*) the action of the *same* acids under *varying* conditions. With regard to those coming under the first heading, Ostwald's experiments are the most complete (*J. pr.* [2] 29 385; 30, 93 a. 225; 31, 307; Koral, *J. pr.* [2] 34, 109). He examined the action of thirty-two acids, and finds that there is a close relation between the constants of inversion and the affinities of the acids. See also Fleury (*D. P. J.* 219, 436; *J. Ph.* [4] 22, 423). With regard to reactions coming under the second heading, it is found that inversion proceeds more rapidly in hot solutions than in cold ones (several formulæ have been given to express this relation, *v.* Arrhenius, *Zeit. phys. Ch.* 4, 226; Urech, *B.* 20, 1836); that increase in the percentage of acid increases the rapidity of inversion; that, the percentage of acid to water being constant, increase of volume decreases the time; and that the percentage of acid to sugar being constant, increase of volume (dilution) increases the time (Löwenthal a. Lenssen, *J. pr.* 85, 321 a. 401; Urech, *B.* 13, 1696; 15, 2130; *B. C.* 1881, 570; 1883. 501). The presence of neutral salts sometimes increases and sometimes diminishes the rapidity of inversion; for a detailed account see Spohr (*J. pr.* [2] 32, 32 and 33, 265). If the heating be long continued, or if too strong acids be used, most of the lævulose and part of the dextrose is destroyed, and humus substances, acetopropionic and formic acids are produced (Mulder, *J. pr.* 21, 219; Malaguti, *A.* 17, 52; Stein, *A.* 30, 82; Conrad, *B.* 11, 2178; Tollens, *B.* 14, 1951; Sestini, *L. V.* 26, 285; 27, 163; Conrad a. Guthzeit, *B.* 18, 439; 19, 2569 a. 2844; Tollens a. Grote, *A.* 175, 181, 206, 237 a. 233. The inversion of cane sugar cannot be carried out by heating with acids without destroying some lævulose (*q. v.*), unless the temperature and quantity of acid be kept within well-defined limits (Jungfleisch a. Grimbert, *C. R.* 108, 144; Wohl, *B.* 23, 2084). Nicol (*Fr.* 14, 180) and Clerget (*A. Ch.* [3] 26, 175) give instructions for the preparation of pure invert sugar. According to the latter, 5 c.c. of strong hydrochloric acid is added to 50 c.c. sugar solution, containing 8·175 g. saccharon, and heated for ten minutes at 68°. Under these conditions the sugar is completely inverted, and the products are unacted upon. They are identical in optical activity and cupric reducing power with the sugar obtained by the action of invertase (see *Action of ferments*) under the most favourable conditions. There is no doubt that invert sugar is a mixture of lævulose and dextrose in equal quantities (Jungfleisch a. Grimbert, *C. R.* 108, 144; 107, 390), as its properties agree in every particular with that of a mixture of these two sugars in molecular proportions. Concentrated sulphuric acid dissolves cane sugar at the freezing temperature, without the production of colour, but slight heating causes it to swell up to a black, frothy mass; a blue fluorescent body is formed (Simmler, *C. C.* 1862, 378). Other acids act in a similar way (Gmelin-Kraut, *Handbuch d. Ch.*; van Kerckhoff, *J. pr.* 69, 48).

Action of alkalis. Dilute alkalis do not act on cane sugar in the cold, and but slowly on heating (Michaelis, *J. pr.* 56, 430). By heating with potassium hydroxide and but little water, decomposition takes place, carbon dioxide, acetone, and formic, acetic, propionic, and oxalic acids are formed (Gottlieb, *A.* 52, 122). Potash

or baryta under certain conditions yield a large quantity of lactic acid (Schützenberger, *Bl.* [2] 25, 289). Milk of lime and strontia also decompose cane sugar by prolonged heating (Fremy, *A.* 15, 278; Benedict, *A.* 162, 303; Niedschlag, *Deutsche Zuckerind.* 1887. 159; Pinner, *B.* 16, 1728).

Oxidation. Cane sugar is easily oxidised by almost all the common oxidising agents. Free oxygen does not act on it, but in the presence of platinum black it does; ozone also oxidises it (Gorup-Besanez, *A.* 110, 103). Chlorine or bromine yields gluconic acid, glucose, and other substances (Reichardt, *B. C.* 1880, 559; Grieshammer, *A. Ph.* [3] 15, 193); the same reaction takes place in the presence of lead or silver oxide (Hlasiwetz a. Habermann, *A.* 155, 128; Herzfeld, *A.* 220, 353). Iodine and potassium carbonate yield a little iodoform (Millon, *C. R.* 21, 828). The more powerful oxidising reagents—such as strong chromic acid, chlorate of potash, strong sulphuric acid, &c.—act so violently as to cause explosions. Strong nitric acid acts very energetically; dilute nitric acid yields saccharic and oxalic acids; anhydrous nitric acid, or a mixture of strong nitric and sulphuric acids, yields a nitrate (Sobero, *C. R.* 24, 247; Schönbein, *P.* 70, 104; Carey-Lea, *Bl.* [2] 10, 415; Tollens, *B.* 15, 1828; Salkowski, *B.* 15, 1738; Heintz, *A.* 51, 185; *P.* 61, 315; Reinsch, *Jahrb. f. Pharm.* 18, 337; Hornemann, *J. pr.* 89, 304; Tollens, *Chem. Zeit.* 11, 1178). Fehling's solution is not reduced by cane-sugar solution, neither are alkaline solutions of other oxides, except ammoniacal silver solutions, which are reduced slowly in the cold and quicker on warming; but many neutral or acid metallic solutions are reduced (Tollens, *Z. V.* 32, 712; *B.* 15, 1828; Salkowski, *B.* 15, 1738). Dilute chromic acid oxidises cane sugar to oxalic, formic, and carbonic acids; potassium permanganate yields carbonic acid and water; by careful oxidation in the cold, oxalic and formic acids are also produced (Heyer, *Ar. Ph.* [3] 20, 336 a. 430; Brunner, *B.* 12, 549). Maumené (*Bl.* [2] 22, 2; 30, 99) says that three acids, di-, tri-, and hexa-pinic acids $C_2H_4O_4$, $C_3H_6O_5$, and $C_6H_{12}O_3$, are formed under certain conditions.

Action of ferments. Cane sugar is not directly fermentable by organised ferments, with the exception of *Monila candida*; it requires first to be hydrolysed (inverted), and for this purpose every organism which has the power of assimilating cane sugar produces an organised ferment or enzyme called *invertase*, which first inverts it (Bernard, *Leçons de Physiologie Expér.*, Paris, 1856; Hansen, *Meddelelser*, 1888, 2, 143; Brown, *C. J.* 1886. 173). The action of invertase was first studied by Kjeldahl (*Meddelelser*, 1881, 3, 186); O'Sullivan and Tompson (*C. J.* 1890, 834) have exhaustively investigated the subject. They find the change follows the same time curve as a catalytic reaction; the time necessary to perform a given percentage of hydrolysis varies directly with the amount of invertase; the most favourable concentration of the sugar solution is 20–25 p.c., and the most favourable temperature 55°. Hydrolysis proceeds slowly at the freezing-point; it ceases at about 65°; alkalis immediately stop the reaction, whereas very minute quantities of acid aid it. Invertase is uninjured by the reaction, and is capable of inverting about twenty-two times its weight of cane sugar per minute for an unlimited period. The dextrose formed is in the bi-rotatory state; on standing, the invert-sugar has the same optical activity as that obtained by the careful action of dilute acids. See also Barth (*B.* 11, 474), Mayer (*B. C.* 1881, 784; 1882, 850), Müller (*Ann. Agronom.* 12, 481), Tamman (*Zeit. phys. Ch.* 3, 25). Invertase acts at a temperature higher than is sufficient to kill the yeast whence it is derived. For production of alcohol, acids, &c., under the influence of organised ferments, see FERMENTATION.

Compounds with acids. Nitrosaccharon $C_{12}H_{18}(NO_2)_4O_{11}$ is prepared by treating the powdered sugar with a mixture of strong H_2SO_4 and fuming HNO_3 in the cold (Schönbein, *P.* 70, 167; Sobero, *C. R.* 24, 247). It is a white doughy mass, insoluble in water, soluble in alcohol and ether. Boiling water decomposes it; m.p. 20°. It is explosive.

With arsenious acid a compound $C_{12}H_{22}O_{11}.As_2O_3$ is said to be produced. The composition is improbable.

By the action of acetic anhydride and glacial acetic acid, or acetic anhydride and sodium acetate, a series of acetates have been obtained. In these the group C_2H_3O takes the place of H. We have the monoacetate $C_{12}H_{21}(C_2H_3O)O_{11}$ (Schützenberger a. Naudin, *Bl.* 12, 206); the tetracetate $C_{12}H_{18}(C_2H_3O)_4O_{11}$; the hexacetate (Herzfeld, *N. Z.* 3, 155); the heptacetate (Schützenberger, *Bl.* 12, 204; *C. R.* 61, 485); and the octacetate (Herzfeld, *B.* 13, 267; Démole, *C. R.* 89, 481), all more or less resinous substances. diminishing in solubility in water in proportion to the number of acetyl groups they contain, and increasing in solubility in alcohol and ether with the same change in composition. The octacetate is said to crystallise in needles, m.p. 67°. They are all decomposed by the action of acids and alkalis into acetic acid and the products of the inversion of saccharon. It is probable that by careful treatment with alkalis in equivalent quantities (sufficient to neutralise the acetic acid formed) saccharon is again produced. Benzoyl chloride yields with saccharon a hexabenzoate $C_{12}H_{16}(C_7H_5O)_6O_{11}$, m.p. 109° (Baumann, *B.* 19, 3220; Skraup, *M.* 10, 389).

Compounds with bases. By mixing sodium ethylate with a solution of cane sugar and precipitating with alcohol, a compound $C_{12}H_{21}NaO_{11}$ is obtained (Pfeiffer a. Tollens, *A.* 211, 285). A similar potassium compound has been prepared (Soubeyran, *A.* 43, 223; Brendeche, *An. Ph.* [2] 29, 73). Cane sugar combines with many bases, forming saccharates which are decomposed into the sugar and carbonate by carbon dioxide, and are but slightly soluble in water. The most important of these are barium saccharate $C_{12}H_{22}O_{11}.BaO$, strontium saccharate $C_{12}H_{22}O_{11}.SrO$, and $C_{12}H_{22}O_{11}.2SrO$, the former produced by mixing solutions of its constituents; it crystallises with $5H_2O$, the latter obtained by bringing together its constituents in boiling solution. Calcium saccharates: $C_{12}H_{22}O_{11}.3CaO$ 3aq is but slightly soluble in water; $C_{12}H_{22}O_{11}.2CaO$ 2aq and $C_{12}H_{22}O_{11}CaO$ are soluble in water and decomposed partly by boiling into the tri-saccharate and free sugar.

$C_{12}H_{22}O_{11}.CaO + 2H_2O$, $C_{12}H_{22}O_{11}.2CaO$, and $(C_{12}H_{22}O_{11})_2 3CaO$ have also been described. Lead acetate alone does not precipitate cane sugar; lead acetate and ammonia yield $C_{12}H_{16}Pb_3O_{11}$ and $C_{12}H_{18}Pb_2O_{11}$; iron and copper yield saccharates; it is doubtful if magnesia forms one (Soubeyran, *A.* 43, 223; Stromeyer, *Ar. Ph.* [3] 25, 229; Brendeche, *Ar. Ph.* [2] 29, 73; Péligot, *J. pr.* 13, 379; 15, 76; *A.* [3] 54, 377; Landolt a. Degener, *Z. V.* 32, 325; Scheibler, *B.* 15, 2945; 16, 985; v. Lippmann, *Organ d. Centr. Ver.* 18, 37; *B.* 16, 2764; Benedict, *B.* 6, 413; Harperath, *Chem. Zeit.* 1886. 323; Boivin a. Loiseau, *C. R.* 58, 60; also old editions of Watts' *Dict.*). Ammonia gas at 150° forms brown amorphous bodies; solutions of ammonia yield similar bodies (Thénard, *C. R.* 52, 444; Payen a. Schützenberger, *Jahresber. f. Zuckerfabr.* 1861-62, p. 191, 192; Laborde, *J.* 1874, 883).

Compounds with metallic salts. Several compounds of saccharon with sodium chloride, bromide, and iodide have been prepared (Péligot, *A.* 30, 71; Maumené, *Bl.* 15, 1; Gill, *C. J.* 1871, 269). Such compounds are $C_{12}H_{22}O_{11}.NaCl.2H_2O$; $2C_{12}H_{22}O_{11}.3NaCl.4H_2O$; $C_{12}H_{22}O_{11}.NaBr.1\frac{1}{2}H_2O$; and $2C_{12}H_{22}O_{11}.3NaI.3H_2O$; the latter is a very stable and definite compound, and is, like the others, easily prepared by boiling a mixture of the sodium salt and saccharon in equivalent quantities, and allowing the solution to stand in a quiet place over sulphuric acid. These bodies form distinct and definite crystals. No definite compounds of the halogen salts of potassium and ammonium with saccharon have been described, but there can be little doubt, from the work of Gill, that such are obtainable. Lithium salts seem to give lithium compounds. Compounds of saccharon with sodium-acetate, nitrate, iodate, and phosphate are not obtainable (Gill, *l.c.*). A double salt of copper sulphate and saccharon, $C_{12}H_{22}O_{11}.CuSO_4.2aq$ crystallises from a saturated solution of the constituents (Barreswil, *J. Ph.* [3] 7, 29). The sodium mercury chloride compound $2C_{12}H_{22}O_{11}.NaCl.HgCl_2$ crystallises in minute crystals on the slow evaporation of a solution of its constituents in weak alcohol (Boullay, *Bl.* 12, 292). A borax compound $3C_{12}H_{22}O_{11}.Na_2B_4O_7.4H_2O$ has also been described (Stürenberg, *Ar. Ph.* 18, 279). Many other compounds have been described, but they present no material interest.

Saccharon, like many other organic substances, prevents the precipitation of many metals from their solutions by ammonium, sodium, and potassium hydroxide; in some cases the prevention is complete, in others only a portion of the metal is retained in solution (Lussaigne, *C. R.* 14, 691; Groth, *J. pr.* [1] 92, 175; Pellet, *J. Fabr.*[1] 18, 22).

[illegible] the assimilation [illegible] saccharon yields only
With phenyl-hydrazi[illegible] production of equal [illegible] (*q. v.*).
lævulose and dextrose compounds [illegible], *milk sugar*

Lactose. *Lacton, lactobiose* [illegible] long known.
$C_{12}H_{22}O_{11}.H_2O(\alpha)$ and $C_{12}H_{22}O_{11}(\gamma)$. [illegible]malia and also

Occurrence.—Lactose has been [illegible]*chras Sapota*)
It occurs in the milk of the mam[illegible]tose constitutes
in the fruit of *Sapotillier* ([illegible] sheep, goats, and
(Bouchardat, *Bl.* [2] 16, 26). L[illegible]
3–5 p.c. of the milk of women. cows, 6 p.c. of asses' milk, and a slightly greater proportion of mare's milk (Fleischmann, *Das Molkereiwesen*, Braunschweig, 1875; Kühne, *Lehrb. d. physiol. Ch.* p. 573).

Preparation.—Skim milk, or, better, milk from which the fat has been separated by mechanical means, is coagulated with rennet and the whey digested for some time with calcium carbonate (chalk) and aluminium hydroxide. The insoluble matter is then filtered out and the filtrate concentrated in a vacuum to a syrup; this, on standing, yields crystals of lactose. During concentration some matter becomes insoluble; this should be filtered out before final concentration. The crystals are purified by repeated re-crystallisation from solutions concentrated at the temperature of boiling water; on cooling $C_{12}H_{22}O_{11}.H_2O$ crystallises. This is lactose α. If the saturated solution is evaporated rapidly on the water-bath with continual stirring, small crystals of $C_{12}H_{22}O_{11}$ are obtained; lactose γ. These are not hygroscopic. If the α modification is dried at 130° a hygroscopic mass is left, which is known as the β modification. There are said to be other modifications, but in solution after boiling they all have the same optical activity and are identical (Enling a. Rüf, *B. C.* 1882, 346; *Centbl. f. Ag. Ch.* 1885, 130; J. Kunz, *Ph.* [3] 15, 443).

Properties.—Ordinary lactose forms large, rhombic, hemihedral crystals, having a sp.gr. 1·53–1·54 (Schröder, *B.* 12, 562) and containing 1 mol. H_2O, which is lost by drying at 130°. It is soluble in six parts of cold water and in two and a-half or less of boiling water, from which on cooling it slowly crystallises. Its solutions rotate the plane of polarisation to the right, and its specific rotatory power for the D line is $[\alpha]_D = 52·53° + (20 - t) \times 0·055$ (Schmöger, *B.* 13, 1927; Hesse, *A.* 176, 98; Erdmann, *J.* 1855, 661; Denigès a. Bonnans, *J. Ph.* [5] 17, 363 a. 411). The variation with the concentration is very little, and, as is obvious from the above formula, the effect of temperature is slight. These numbers for the $[\alpha]_D$ are calculated for the crystals $C_{12}H_{22}O_{11}.H_2O$. For the dry sugar $C_{12}H_{22}O_{11}$ I have found $[\alpha]_D = 55·5°$ with a Jellet-Cornu instrument (Schmidt a. Hans, *Ch.*), sodium flame, and absolutely the same number $[\alpha]_j = 61·6°$ with a Soleil-Scheibler, taking 100 divs. = 38·4°.

α_j α_D
(24:21·67::61·6°:55·5°). 55·5°–5·25 p.c. = 52·59: my observations were made at 15·5°, Schmöger's at 20°. Freshly-prepared solutions of crystallised lactose exhibit the phenomenon of bi-rotation, the angle immediately after solution being in the proportion of 8:5 to the constant value (Urech, *B.* 16, 2270; Dubrunfaut, *C. R.* 42, 228; Schmöger, *l.c.*; Parcus a. Tollens, *A.* 257, 160). The rotatory power does not vary with the concentration. The dispersive power—that is, the ratio between the specific rotatory powers for the C and D lines—is 1:1·259 ($[\alpha]_C = 41·58$) (Grimbert, *J. Ph.* [5] 16, 295 a. 345). The modification γ when freshly dissolved in water exhibits the phenomenon of semi-rotation—that is, the specific rotatory power is only about ⅝ of the normal, to which it attains on standing a few hours (E. O. Erdmann, *Fortschritte der Physik*, 1855, 13; *B.* 13, 2180; Schmöger, *B.* 13, 1915). The modification β on solution has immediately the normal optical activity; the presence of alkali lowers the

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[1] *Journal des Fabricants de Sucre.*

activity (Schmöger, *l.c.*; Urech, *B.* 17, 1543). Schmöger give the specific gravity of solutions, containing given percentages of the crystals from which by calculation we get D = 3·956 for a solution containing 2·5 g. dry sugar in 100 c.c. at 20°, 3·921 for a 10 g. solution and 3·913 for a 15 g. one. My observations are, temperature 15·5°:—

1 gram	in 100 c.c.	sp.gr. $\frac{15·5}{15·5}$	1·0040;	D = 4·00
5 grams	”	”	1·0199;	D = 3·98
10	”	”	1·0397;	D = 3·97
20	”	”	1·0785;	D = 3·93

D = 3·99 for solution below 10 g. per 100 c.c. at 15·5°. The K = 79·2 for dry sugar, *i.e.* 0·5723 anhydrous lactose reduce 1 g. CuO from Fehling's solution (Jones, *Analyst*, 1889, 81). According to Soxhlet 0·5 g. sugar = 74 c.c. Fehling's solution, hence K = 74; in this case 1 g. CuO = ·6127 lactose: by weighing the precipitated CuO as Cu by Allihn's method, 1 g. sugar = 1·736 CuO, or 1 g. CuO = 0·5760 g. sugar, K = 78·8, agreeing with the number given by Jones. According to Roderwald a. Tollens (*B.* 11, 2076) the working number 1 g. CuO = ·5795 g. anhydrous sugar. I am inclined, when the conditions hereafter to be described are followed, to place the K at 78·9, *i.e.* 1 g. CuO = 0·5758 g. sugar. In this case 7·5 mols. CuO are reduced by 1 mol. sugar.

Action of heat. Hydrous crystallised lactose (*a*) remains constant at 100°; above this water is slowly given off, and at 130° the dehydration is complete without decomposition if the water is eliminated slowly. Anhydrous lactose commences to colour at 170°-180°, loses water, and forms the so-called lactocaramel $C_6H_{10}O_5$, which is easily soluble in water but insoluble in alcohol, and yields compounds with lead and copper oxide. Lactose melts at 203·5° to a brown liquid, and by further heating it is decomposed with separation of carbon (Lieben, *J. pr.* 68, 409). Heated in a sealed tube with water to 90°-100° it is coloured, and more so at 180°-200°, when a glucose is produced which may be precipitated by alcohol, and, by further heating, carbonic acid, a little pyrocatechin, and other bodies are formed (Vohl, *A.* 105, 334; Hoppe-Seyler, *B.* 4, 16; Munk, *H.* 1, 357).

Action of acids. By heating with dilute acids lactose is hydrolysed (inverted), yielding galactose and dextrose

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

one molecule of water being taken up. The reaction takes some hours to complete; during the hydrolysis the reducing power and optical activity increase (Pasteur, *C. R.* 42, 228; Fudakowski, *B.* 8, 559; 9, 42; 278 and 1602; 11, 1069; Bourquelot, *N. Ztschr. f. Rubenz-ind.* 16, 71; Kent a. Tollens, *A.* 227, 221; Rindell, *N. Ztschr. f. Rubenz-ind.* 4, 163). The chief products of the reaction are as stated, but the conditions have not yet been described by which the optical activity and K of the resulting substances will exactly correspond with those of a mixture of equal parts of galactose and dextrose. Other bodies are undoubtedly produced. By the continued action of acids for several days, aceto-propionic and formic acids are produced (Tollens a. Roderwald, *A.* 206, 231; Conrad a. Guthzeit, *B.* 19, 2575). Concentrated sulphuric acid does not blacken lactose in the cold.

Compounds with acids. A mixture of sulphuric and nitric acids give lactose pentanitrate $C_{12}H_{17}(NO_2)_5O_{11}$, insoluble in water but soluble in alcohol and ether, m.p. 139·2° and exploding when struck by a hammer on an anvil; lactose tri-nitrate $C_{12}H_{19}(NO_2)_3O_{11}$, very slightly soluble in water, but easily in alcohol and ether, m.p. 37°; and lactose tetranitrate $C_{12}H_{18}(NO_2)_4O_{11}$, m.p. 80°-81° (Gé, *J. R.* 1882, 253; *B.* 15, 2238). With chlorosulphonic acid lactose yields dextrose-tetra-sulphonic acid chloride (Claësson, *J. pr.* [2] 20, 1 and 18). Organic acids act very slowly on lactose, but by prolonged action they yield ethers of lactose or of dextrose and galactose (Berthelot, *Chim. org.* 2, 279, 295). A series of acetates, beginning with the mono- body and ending with the octo-one, have been described. $C_{12}H_{14}(C_2H_3O)_8O_{11}$ is obtained by boiling lactose with an excess of acetic anhydride or by heating a mixture in the proper proportions of the sugar, acetic anhydride, and fused sodium acetate at 100° (Herzfeld, *B.* 13, 265). This body is insoluble in water and in ether, soluble in benzene, acetic acid, and in alcohol. It crystallises from a mixture of alcohol and acetic ether. $[a]_D = +31°$ in alcoholic solution. The mono- and di- acetate are obtained by incompletely decomposing the octo-acetate by alkalis (Démole, *C. R.* 89, 481). Tetracetate is formed at the same time as the octo- acetate, when lactose is boiled with acetic anhydride (Schützenberger a. Naudin, *Bl.* 12, 208). It is easily soluble in water, $[a]_D = +50°$. Hexacetate $C_{12}H_{16}(C_2H_3O)_6O_{11}$ crystallises from a mixture of alcohol and acetic ether in white needles, m.p. 86° (Herzfeld, *N. Z. R.* 3, 156). It is doubtful whether or not lactose is reproduced when these bodies are saponified by treatment with alkalis. There seems to be no reason why it should not be so, if the alkali is carefully employed.

Action of alkalis. Hot alkalis colour solutions of lactose yellow to brown, and form lactic acid, pyrocatechin, and other products (Hoppe-Seyler, *B.* 4, 347; Nencki a. Sieber, *J. pr.* [2] 34, 503; Urech, *B.* 17, 1543). Fused with KHO it yields carbonic, oxalic, and a little succinic acids (Hlasiwetz a. Barth, *A.* 138, 76).

Compounds with alkalis. Lactoseates are formed by the action of potash or soda on lactose in alcoholic solutions, or by adding alcohol to the mixed aqueous solutions. They are amorphous, easily decomposed precipitates having a composition expressed by the formulæ $C_{12}H_{21}NaO_{11}$ and $C_{12}H_{21}KO_{11}$ (Fremy, *A.* 15, 278; Hönig a. Rosenfeld, *B.* 12, 45). Calcium, barium, and lead lactoseates are obtained by dissolving the base in lactose solution and precipitating with alcohol. The long-continued action of lime produces isosaccharin and metasaccharin (Cuisinier, *M. S.* [3] 12, 520; Kiliani, *B.* 16, 2625). By heating with ammonia, brown, amorphous, nitrogenous products are obtained (Thénard, *C. R.* 52, 444). Aniline yields two crystalline compounds, $C_{30}H_{49}NO_{21}$ and $C_{36}H_{54}N_2O_{20}$, which reduce Fehling's solution (Sachsse, *B.* 4, 835; *L. V.* 16, 441).

Oxidation.—Oxygen and ozone have no action on lactose in the cold; hot solutions are oxidised by oxygen in the presence of platinum black (Gorup-Besanez, *A.* 110, 86 a. 103; Reiset

a. Millon, *A. Ch.* [3] 8, 295). Alkaline permanganate solutions oxidise lactose easily (Laubenheimer, *A.* 164, 283). Chromic acid yields aldehyde (Guckelberger, *A.* 64, 98). Nitric acid first inverts lactose and then yields mucic and saccharic acids; from 36 to 40 p.c. of mucic acid is produced; by long-continued heating tartaric and oxalic acids, &c., are obtained (Liebig, *A.* 113, 1; Dubrunfaut, *C. R.* 42, 228; Kent a. Tollens, *A.* 227, 227). Alkaline solutions of copper oxide are reduced by lactose, and from amongst the products of the reaction Bödecker a. Struckmann (*A.* 100, 264) isolated gallactinic acid $C_{14}H_{10}O_9$; pectolactinic acid $C_{16}H_{16}O_{12}$, lactic and glycollic acids are also produced (Habermann a. Hönig, *B.* 17, 351). Silver oxide oxidises lactose solutions with production of oxalic, glycollic, and lactonic (galactonic) acids (Kiliani, *B.* 13, 2307). Chlorine or bromine in the presence of silver oxide yield lactonic (galactonic) acid $C_6H_{12}O_7$ (Barth a. Hlasiwetz, *A.* 119, 281; 122, 96). By very careful oxidation with bromine water Fischer a. Meyer (*B.* 22, 361) have obtained lactobionic acid $C_{12}H_{22}O_{12}$; it is a colourless, strongly acid syrup, easily soluble in water, but only sparingly in alcohol. It does not reduce Fehling's solution; it decomposes metallic carbonates, forming salts. The calcium $(C_{12}H_{21}O_{12})_2Ca$, barium $(C_{12}H_{21}O_{12})_2Ba$, lead $(C_{12}H_{21}O_{12})Pb$, and other salts may be prepared in this way; they are insoluble in alcohol, but soluble in water. When heated with dilute mineral acids, lactobionic acid is decomposed into galactose and gluconic acid. With iodine and sodium bicarbonate lactose yields a little iodoform (Millon, *C. R.* 21, 828).

Fermentation.—There is no known enzyme capable of inverting lactose; it does not ferment with yeast (Berthelot, *A. Ch.* [3] 50, 332 a. 362; Fitz, *B.* 11, 42). It easily undergoes lactic acid fermentation, especially in milk (Fitz, *l.c.*; Richet, *C. R.* 86, 550; Schmidt-Mülheim, *B.* 15, 2631). It undergoes alcoholic fermentation in kumys or kefir fermentation (Struve, *B.* 17, 314; Vieth, *A.* 12, 2), and also under the agency of certain bacteria (Rotondi a. Zechini, see v. Lippmann, *Deutsche Zuckerind.* 1887, 1091).

Phenylhydrazine yields lactose phenylhydrazide $C_{18}H_{28}O_{10}N_2$, soluble in water and alcohol, insoluble in ether and lævorotatory, and lactose osazone $C_{24}H_{32}N_4O_9$, crystallising in yellow needles; soluble to some extent in hot water, and m.p. 200° (Fischer, *B.* 17, 583; 20, 830; 20, 2566). By the action of hydrochloric acid it yields lactose osone (Fischer, *B.* 21, 2631).

Maltose. *Maltobiose*, *Amylon*, $C_{12}H_{22}O_{11}$; $C_{12}H_{22}O_{11}.H_2O$. De Saussure (*Bibl. Britannique*, 56, 1814, 333; *P.* 1819, 29, 58) may have obtained this sugar when studying the products of the spontaneous decomposition of starch-paste when exposed to the air at 20°–25°. Guérin-Varry (*A. Ch.* 60, 32; 61, 66) described accurately how the body could be prepared in the crystallised state and some of its properties, but failed to recognise it as a distinct substance; Jacquelain (*A. Ch.* 68, 167) added nothing to Varry's work; Dubrunfaut (*A. Ch.* [3] 21, 78) prepared the body according to Varry's method, observed that it was less soluble in alcohol than dextrose, and had an optical activity three times as great, *i.e.* $[\alpha]_j = 58 \times 3 = 174$, a figure so high as to lead one to believe that he had not a pure body in his hands. He recognised it as a distinct body, and called it *maltose*; he, however, looked upon it as a glucose, *triglucose*; O'Sullivan (*C. J.* 1872, 576; 1876, 478) showed that it was not an 'ose' but an 'on' sugar, and from this and a fuller description of its characters gave it a place among chemical entities.

Occurrence.—It is present in some commercial glucoses and in beer (Valentin, *J. S. A.* 24, 404); probably in bread; in *amé*, a rice-extract prepared in Japan (Yoshida, *C. N.* 43, 29), and in germinated cereals to the extent of 1 to 2 p.c. (O'Sullivan, *C. J.* 49, 58). After feeding with amylaceous substances it is found in the intestinal canal, but the blood of the mesenteries contains only dextrose. If injected into a vein it is found in the urine; if injected subcutaneously, it is partially converted into dextrose (Phillips, *B. C.* 1882, 127). Some of the reducing sugars of blood may be maltose.

Formation.—Diastase converts starch and the dextrins into maltose (O'Sullivan, *l.c.*). The ferment of saliva, ptyalin, of the pancreas, and of the liver, act in the same way (Nasse, *J. Th.* 1877, 62; Musculus a. v. Mering, *Z.* 2, 403). The same ferments act on glycogen, maltose being amongst the products; dextrose is present when saliva is employed (Kütz, *Pf.* 24, 8). All mineral acids and many organic acids act on starch and glycogen; maltose is amongst the products.

Preparation.—100 g. purified starch are mixed as completely as possible with 300 c.c. water at 40°, and then poured with continuous stirring into 2 litres of boiling water. The paste is cooled to 60° and the extract from 20 g. pale malt added to it; the mixture is kept at 60°–63° for four or five hours, and the solution may be allowed to cool and stand for a few days. At the end of that time it is evaporated, best in a vacuum, to 200 c.c., and then boiled with 2 litres alcohol, sp.gr. ·820. On cooling and standing, the clear liquid is decanted off the undissolved syrup and put aside in a corked flask; at the end of six days the sides of the flask will be found to be covered with a crystalline crust of maltose. Or the undissolved syrup may be treated with strong alcohol as long as any matter is taken up, the whole of the clear alcoholic solutions are mixed, the alcohol distilled off and the residue concentrated to a syrup; this on standing in a cool place becomes filled with crystals of maltose, especially if a few crystals from a previous preparation be stirred in. These may be washed with dry methyl alcohol; if this is used hot, a portion of the crystals dissolves and the solution soon yields much sugar. The crystallisation is hastened by adding half a volume of ethyl alcohol (·810 sp.gr.) or a little ether with some crystals of a previous preparation (O'Sullivan, *l.c.*; Schulze, *B.* 7, 1047; Soxhlet, *J. pr.* [2] 21, 277; Herzfeld, *A. Ch.* 220, 209; Cuisinier, *J.* 1884, 1803). The body may be purified by recrystallisation from methyl alcohol or water.

Properties.—Maltose crystallises out of water in plates which contain $C_{12}H_{22}O_{11}.H_2O$; out of alcohol (sp. gr. ·810) it crystallises in crusts and at times in cauliflower-like or warty aggregations which contain $C_{12}H_{22}O_{11}$. The hydrous body easily parts with its water at 100° in a current of dry air. The anhydrous body is but slightly soluble in strong ethyl alcohol; it is more soluble in methyl alcohol. The hydrous body dissolves more freely in both solvents. Both bodies are very soluble in water, but less so than dextrose. The solution is optically active, and the activity for a solution containing 10 g. in 100 c.c. is 15°–20° less when freshly prepared than after standing. The activity becomes constant in ten to twelve hours in the cold or immediately on boiling (Meissel, *J. pr.* [2] 25, 120).

The specific rotatory power for dry maltose is $[\alpha]_j = 154°–155°$, $[\alpha]_D = 139°–140°$ at 15·5° in solutions containing 10 g. per 100 c.c. and under (O'Sullivan, *C. J.* 35, 771; 45, 5); Meissel (*J. pr.* [2] 25, 114) gives the formula $[\alpha]_D = 140{\cdot}735 - {\cdot}01837\ P - {\cdot}095\ T$ to represent the specific rotatory power of dry maltose at 0°, in which P = percentage of maltose in solution and T the temperature of observation. On calculating the value of the sugar in a 10-g. solution at 15·5° from this formula we get $[\alpha]_D =$ 138·9 (*v.* also Soxhlet, *l.c.*, and Herzfeld, *A.* 220, 206). The dispersive power, *i.e.* the ratio of $[\alpha]_D : [\alpha]_C$, is 1·262 (Grimbert, *J. Ph.* [5] 16, 295). A solution of maltose containing 10 g. dry substance in 100 c.c. at 15·5° has a sp. gr. $\frac{15{\cdot}5°}{15{\cdot}5°} =$ 1·0395. Maltose reduces alkaline copper solution. O'Sullivan (*C. J.* 35, 771) gives its reducing power K = 62·5, *i.e.* 62·5 parts dextrose reduce as much copper oxide as 100 parts of maltose. Soxhlet (*J. pr.* 21, 227–317) says 0·5 g. maltose in 1 p.c. solution = 64·2 c.c. undiluted Fehling solution (1 c.c. = ·005 g. dextrose), *i.e.* K = 64·2, and 67·5 c.c. if the solution is diluted with four times its volume of water, *i.e.* K = 67·5. He further states that 100 parts of dry maltose = 113 parts Cu, hence 141 parts CuO; from this, we have K = 63·94. There appears to be fair evidence that the K varies within certain limits according to the mode of manipulation, but when we see that the K should be 63·17 if it be supposed that 1 molecule maltose reduces 6 molecules CuO, and that the observed numbers closely approach this, we may take it that this is the true number when errors of manipulation are avoided. If the Cu_2O be separated, the filtrate treated with acid gives a further reduction with Fehling's solution which, if added to the first, equals the reduction of dextrose (Herzfeld, *A. B.* 589, 220). Alkaline mercuric cyanide solutions are also reduced by maltose. Copper acetate is not reduced by it (Barfoed, *Org. Analysis*, 214); dextrose reduces this reagent. When maltose reduces copper oxide, glycollic and a mixture of acids of unknown composition are produced (Habermann a. Hönig, *M.* 5, 208).

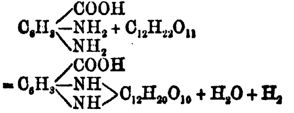
Maltose is hydrolysed to dextrose according to the equation $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$ by the following reagents: the mineral acids and many organic ones; pancreatic secretion and portions of the small intestine (Brown a. Heron, *C. N.* 42, 63; Bourquelot, *C. R.* 97, 1000 and 1822); a ferment developed in *Aspergillus niger* and in *Mucor mucedo*; the former contains also a ferment capable of inverting sucrose, the latter yields only the one (Bourquelot, *l.c.*). Under the action of ordinary beer yeasts maltose ferments, *i.e.* is broken down into carbonic acid, alcohol, &c., apparently without being previously inverted. Other organisms yield lactic acid and other products; *v.* FERMENTATION.

Maltose withstands the hydrolytic action of sulphuric acid with five times the power of sucrose; 3 hours' digestion with a 3 p.c. solution gives complete inversion (Meissel, *l.c.*). 0·5 p.c. solution of lactic acid does not hydrolyse it, even at 110°; 1 p.c. oxalic acid acts at that temperature; carbonic acid at 100°, and under a pressure of six atmospheres, is without action (Bourquelot, *J. de l'Anat. et de la Physiol.* 22, 161–204; Urech, *B.* 18, 3074).

Nitric acid converts maltose into saccharic acid and finally oxalic acid. Chlorine does not act on it as energetically as it does on dextrose or sucrose; the product is neither gluconic nor glycollic acids (Meissel, *l.c.*). Herzfeld (*B. C.* 1883) obtained an acid which he called maltonic acid, by the action of bromine on maltose; this is probably identical with Fischer and Meyer's (*B.* 22, 194) *maltobionic acid* $C_{12}H_{22}O_{12}$, which they prepared by acting on maltose in aqueous solution with bromine in the cold for two or three days. This acid is broken down into dextrose and gluconic acid by digestion with sulphuric acid. Treated at 110° with acetic anhydride and acetic acid, maltose yields *monacetyl maltose* $C_{12}H_{21}(C_2H_3O)O_{11}$ (Yoshida, *l.c.*, a. Steiner, *G. N.* 43, 52); with sodium acetate and acetic anhydride the *octacetyl* derivative $C_{12}H_{14}(C_2H_3O)_8O_{11}$ is produced, the optical activity of which is $[\alpha]_D = 81{\cdot}18°$ (Herzfeld, *A.* 200, 206). With benzyl chloride it yields penta-benzyl maltose, m.p. 110°–115° (Skraup, *M.* 15, 359).

Sodium $C_{12}H_{21}NaO_{11}$, calcium $C_{12}H_{20}CaO_{11}.H_2O$, strontium $C_{12}H_{20}SrO_{11}H_2O$, and barium $C_{12}H_{20}BaO_{11}.H_2O$ maltose are prepared as easily decomposable amorphous precipitates when alcoholic solutions of maltose and the corresponding bases are mixed (Herzfeld, *l.c.*). Compounds with the alkaline chlorides or bromides have not been prepared.

When 1 part maltose, 2 parts phenylhydrazine hydrochloride, 3 parts sodium acetate, and 15 parts of water are heated together for 1½ hours, *phenylmaltosazone* crystallises out on cooling in fine yellow needles, m.p. 190°–191°. The equation $C_{12}H_{22}O_{11} + 2N_2H_3.C_6H_5 = C_{24}H_{32}N_4O_9 + 2H_2O + H_2$ represents the reaction. Only 30 p.c. of the maltose employed is obtained as *osazone* (Fischer, *B.* 17, 583). With γ-diamido-benzoic acid, maltose yields *malto-γ-diamido-benzoic acid* according to the equation



$$C_6H_3\begin{cases}COOH\\NH_2\\NH_2\end{cases} + C_{12}H_{22}O_{11} = C_6H_3\begin{cases}COOH\\NH\\NH\end{cases}\!\!>C_{12}H_{20}O_{10} + H_2O + H_2$$

The body crystallises in white microscopic needles or narrow plates; its barium salt is a gummy mass (Griess a. Harrow, *B.* 20, 2212).

Isomaltose. Fischer (*B.* 23, 3687) prepared a saccharon by the polymerisation of dextrose. Previous attempts in this direction had been made by Musculus (*Bl.* 18, 66), Musculus a. Meyer (*C. R.* 92, 528), Hönig a. Schuber *M.* 7, 455), and they obtained by the action of strong sulphuric acid a dextrin-like body $C_6H_{10}O_5$, which slightly reduced Fehling's solution, did not ferment with beer yeast, and was reconverted into dextrose by the action of dilute sulphuric acid. Grimaux a. Lefèvre (*C. R.* 103, 146) obtained a like result by evaporating *in vacuo* dextrose with dilute hydrochloric acid. Gautier (*Bl.* 22, 145) obtained a body $C_{12}H_{22}O_{11}$ by the action of hydrochloric acid on an alcoholic solution of dextrose; this body reduces Fehling's solution but slightly, does not ferment with beer yeast, and could not be reconverted into dextrose. Grimaux and Lefèvre considered that in their product they could detect maltose by the osazone. Scheibler a. Mittelmeier (*B.* 23, 3075; 24, 301) isolated an unfermentable syrup from commercial glucose which reduces Fehling's solution and yields an osazone $C_{24}H_{32}N_4O_9$, m.p. 152°–153°. They find it is only produced when the heating with acid has been prolonged, and that it may be prepared by the action of acids on dextrose. This body has been previously named gallisin (Cobenzl, Roseneck a. Schmitt, *B.* 17, 1000 and 2456; Anthon, *D. P. J.* 151, 213; Mehring, *Deutsche Vierteljahrsschrift für öffentl. Gesundheitspflege*, 14, Heft 2). Fischer's substance also yielded the same osazone, m.p. 150°–153°; he calls the body isomaltose, and prepares it as follows: One hundred g. glucose (commercial dextrose) are digested with 400 g. hydrochloric acid solution sp. gr. 1·19 at 10°–15° for 15 hours. Alcohol throws out of the solution a small precipitate, which is not formed if the temperature of the reaction is kept below 10°. To the clear solution an excess of ether is added, when a colourless amorphous precipitate is obtained which is filtered out and washed with a mixture of alcohol and ether. This body is dissolved in water, neutralised, boiled to expel alcohol and ether, and fresh beer yeast added. After 18 hours all the dextrose is destroyed (?); the solution has still a high reducing power, and contains *isomaltose* and other bodies.

The isomaltose is separated as osazone; the solution is heated with phenylhydrazine acetate in the water-bath for 1¼ hours. A little glucosazone separates and is filtered out, and on cooling the filtrate deposits a yellow precipitate consisting of a mixture of glucosazone and isomaltosazone; the mother-liquor, by further heating and similar after-treatment, yields more osazone. The whole of the osazone obtainable is boiled with 100 c.c. water and the solution filtered, the filtrate contains isomaltosazone, which is deposited on cooling in needles; 2½ g. of this are obtained from 100 g. glucose, the actual yield is, no doubt, considerably higher than this. By the action of hydrochloric acid the osazone is converted into the osone, which, when boiled with 4 p.c. hydrochloric acid, yields glucosone and glucose.

Lintner claims to have found isomaltose amongst the transformation products of starch by diastase (*Woch. Brauerei*, 9, 245), and in wort and beer (*Zeit. ges. Brauw.* 1891, 281), but it is very doubtful if this is the same body as that above described. Schiffer (*C. C.* 1892, 2, 825) has also isolated isomaltose from the diastase transformation products of starch. But the whole evidence is unsatisfactory, as the factors upon which the identity of the bodies can be recognised are not stated. Lintner and Düll (*Zeit. ges. Brauw.* 1892, 145) prepare it as follows: 250 g. potato starch are mixed with 500 c.c. diastase solution at 55° containing 0·5 g. diastase (*J. pr.* 34, 378) and 2 litres water at 75°C. After complete solution another 0·5 g. diastase is added, and the reaction allowed to proceed for three hours at 65°–69°. $[a]_D = 170°$. for matter in solution. The solution is evaporated to a syrup, saturated with 80 p.c. alcohol, and poured into hot alcohol. Sufficient alcohol must be used so that every 100 parts of 80 p.c. alcohol do not contain more than 10 pts. dry substance. After cooling, the clear solution is decanted and the alcohol distilled off. The residue is diluted to a 20 p.c. solution and yeast added in order to destroy the maltose; this is found to take place in about 20 hours. The fermented solution is filtered, decolourised with animal charcoal, evaporated to a syrup, and precipitated with 85 p.c. alcohol; there must be 100 c.c. of 85 p.c. alcohol for every 5 g. of dry substance. The solution is evaporated and the syrup treated in the same way, but with 99 p.c. alcohol and so that 100 c.c. of alcohol are present for every 3 g. dry substance. The clear alcoholic solution contains isomaltose and but a trace of dextrin, which may be removed by fractionating with alcohol. In this way 20 p.c. of the starch is obtained as isomaltose.

Lintner (*Zeit. ges. Brauw.* 1892, 6) finds the reducing power of iso-maltose to be 84 p.c. of that of maltose, *i.e.* K = 53·1, and its optical activity to be $[a]_D = 139°$. He has not been able to crystallise it, and finds it under certain conditions fermentable by yeast and converted by diastase into maltose (*Zeit. ang. Ch.* 1892, 263).

Trehalose. *Mycose* $C_{12}H_{22}O_{11}.H_2O$.

Occurrence.—It has been isolated from ergot of rye (Wiggers, *A.* 1, 173; Mitscherlich, 56, 15); trehala-manna, the hollow cocoons of the larvæ of an insect (*Larinus maculatus*) (Berthelot *A. Ch.* [3] 53, 232; 55, 272 and 291); and from various fungi (Müntz, *C. R.* 76, 649). Berthelot at first considered it a new sugar and called it *trehalose*, but afterwards found it was identical with the mycose of Mitscherlich, and the *Saccharum spermodiæ* of Wiggers.

Preparation.—Any one of the materials mentioned is extracted with boiling alcohol of moderate strength; the alcohol is distilled off the clear solution. The residue is taken up with water and precipitated with basic lead acetate. The precipitate is washed with water and pressed; it is then suspended in water and submitted to a current of H_2S. The clear filtrate from the lead sulphide is evaporated to a syrup, when the sugar crystallises and can be purified by recrystallisation. I may say that I do not find this mode of treatment answer very well; the filtrate from the PbS is, no doubt, clear, but the precipitate with the lead salt is bulky and unwieldy. I much prefer in this case, as in others of the same kind, fractional precipitation with alcohol; a few experiments will show the strength of alcohol best suited to holding or precipitating the sugar. (See also Apping.)

Properties.—The sugar crystallises in rhombs ($C_{12}H_{22}O_{11}.H_2O$); it gives up its water at 100°, m.p. 109°; it is sweet, easily soluble in water and boiling alcohol, insoluble in ether. Specific rotatory power in aqueous solutions

$[\alpha]_j$ = 199° (Berthelot); $[\alpha]_j$ = 192·5° (Mitscherlich); $[\alpha]_D$ = 197·28° (Apping). These factors are unsatisfactory, and cannot be relied on to identify the sugar. It does not reduce Fehling's solution. Acids convert it very slowly into dextrose (Berthelot), there being no other product; but considering that five hours are required for complete hydrolysis, it is not possible that only pure dextrose could be formed. With strong nitric acid it yields a nitro- compound; with weaker acid no mucic acid is formed, but saccharic acid and finally oxalic acid. With acetic and butyric anhydrides it yields compounds identical with those produced from dextrose. Maquenne (*C. R.* 112, 947) says acetic anhydride yields $C_{12}H_{14}(C_2H_3O)_8O_{11}$. Alkalis do not act on it. On adding basic lead acetate, or an ammoniacal solution of the acetate, to its solutions a lead compound is precipitated. It appears to slowly undergo alcoholic fermentation in contact with beer yeast, but this has not been established with certainty. Phenylhydrazine does not form a compound with trehalose (Fischer, *B.* 17, 583).

Agavose $C_{12}H_{22}O_{11}$ (?) is obtained from the juice of *Agava americana*; it is crystalline, soluble in water, and optically inactive (?). It is hydrolysed to a sugar or mixture of sugars $[\alpha]_j = -14·4°$. It reduces Fehling's solution; K = 62·5, agreeing nearly with maltose in this respect. It does not yield mucic acid on treatment with nitric acid. It is probably fermentable under the influence of some saccharomyces and yields alcohol, &c. (Michaud a. Tristan, *Am.* 14, 548).

Cyclamose $C_{12}H_{22}O_{11}$. A sugar obtained from *Cyclamen europæum*, having a lævorotation $[\alpha]_D = -15·15°$ or $-11·4°$; it is hydrolysed by dilute acids, when the lævorotation increases to $[\alpha]_D = -66·54°$ (Michaud, *C. N.* 53, 232).

Parasaccharose $C_{12}H_{22}O_{11}$. This, together with another uncrystallisable sugar, is said to be obtained from cane sugar by the action of a yeast (Jodin, *C. R.* 53, 1252). It crystallises easily, and is easily soluble in water and difficultly in alcohol. It is dextrorotatory, having $[\alpha]_j$ = 108°, and it reduces Fehling's solution; K = 50 (about). Hot dilute sulphuric acid does not act on it, whilst hot dilute hydrochloric acid diminishes the optical activity and increases the K. On long digestion the solution becomes brown, and finally complete decomposition takes place.

Melibiose $C_{12}H_{22}O_{11}$ is obtained by the careful hydrolysis of raffinose by acids or invertase (see *Raffinose*). Its specific rotatory power is $[\alpha]_D = +126·8°$. It forms a hydrazide $C_{18}H_{28}O_{10}N$ as yellow microscopic crystals, m.p. 145°, and an octacetyl derivative $C_{12}H_{14}O_{11}Ac_8$ (Scheibler a. Mittelmeier, *B.* 23, 1438). Invertase converts it into galactose and dextrose.

Tewfikose $C_{12}H_{22}O_{11}$ occurs in the milk of the gamoose (*Bos Bubalus*). It is prepared by precipitating the milk by 4 p.c. acid mercuric nitrate (Wiley, *Am.* 6, No. 5 (?), neutralising the filtrate with NaHO, filtering out the precipitate, separating the mercury from filtrate by H_2S, and concentrating the slightly acid solution to the crystallising point. A slight precipitate formed during evaporation must be separated. It is purified by two or three recrystallisations. The solutions are dextrorotatory, $[\alpha]_D$ = 48·6°; it reduces Fehling's solution; K = 73·6, hence less than lactose; if 7 molecules CuO were reduced by 1 molecule of sugar, the K would be 73·4, a near approximation; and D = 3·94 for the crystals, hence they are anhydrous. Acids hydrolyse it very easily, the only product being dextrose (Pappel a. Richmond, *C. J.* 1890, 758). The substance is, no doubt, an '-on' sugar $C_{12}H_{22}O_{11}$, and is, like amylon, di-dextrose, and should not therefore yield mucic acid on treatment with nitric acid.

(*c*) *Trihexoses.*

Raffinose $C_{18}H_{32}O_{16}5H_2O$, first obtained from a Tasmanian *Eucalyptus manna* by Johnston (*C. J.* 1, 159). This was the *melitose* of Berthelot (*A. Ch.* [3] 46, 66), who now says (*C. R.* 103, 533) that this term should be applied only to a loose combination of raffinose with eucalin, which is decomposed by re-crystallisation. From the evidence it would appear that the body first described as melitose was impure raffinose, and that the impurity even was not eucalin. It occurs also in cotton seed (Berthelot, *l.c.*; Ritthausen, *J. pr.* [2] 29, 357; Böhn, *J. pr.* [2] 30, 87); in beetroot (Loiseau, *C. R.* 82, 1058; Tollens, *A.* 232, 169; *B.* 18, 26; Rischbieth a. Tollens, *A.* 232, 172; *B.* 18, 2611); in beet juice (v. Lippmann, *B.* 18, 3087); in barley (O'Sullivan, *C. J.* 1886, 70); in young wheat-buds (Richardson a. Crampton (*B.* 19, 1180); and again in *Eucalyptus manna* (Tollens, *A.* 232, 201); probably also in Soja beans. Loiseau considered it a product of the refining process, but v. Lippmann that it was ready formed in beet juice.

Preparation.—A molasses containing a fair quantity of raffinose is selected, and the chief part of the cane sugar removed as monostrontium saccharate; on heating the solution raffinose and cane sugar bistrontium saccharates are precipitated. The compounds are decomposed by CO_2 and the sugar solution obtained again precipitated with strontia, when the cane sugar is precipitated as monostrontium saccharate, and raffinose remains in solution and may be purified by crystallisation (Scheibler, *B.* 18, 1409). Raffinose may be extracted from cotton-seed cake and *Eucalyptus manna* by alcohol, and purified by crystallisation. See also Tollens (*l.c.*); Tenne (*Zeit. d. Ver.* 31, 795); Schaaf (*Z. V.* 33, 699); Wolff (*Deutsche Zuckerind.*, 1887, 1413); Berthelot (*l.c.*); Lindet (*C. R.* 110, 795); Gunning (*C. C.* 1891, ii. 798).

Properties.—Raffinose crystallises in cauliflower-like segregations consisting of thin microscopic rhombic prisms, which contain $C_{18}H_{32}O_{16}.5H_2O$. The H_2O is in greater part eliminated in a vacuum over sulphuric acid, and the remainder easily at 100° (O'Sullivan). If heated too quickly it melts, and then cannot be dried without decomposition. Berthelot obtained crystals containing $6H_2O$ (*C. R.* 109, 548; Scheibler, *B.* 18, 1779; Rinne in *Rischbieth Dissert. über Raffinose*, Göttingen, 1885). It is easily soluble in water, very slightly in strong alcohol, and slightly in methyl alcohol, being much more soluble than cane sugar in this solvent. The dry sugar melts at 118°–119° (Scheibler, *B.* 19, 2868). Its solutions are optically active, the specific rotatory power of crystallised raffinose for the D line being $[\alpha]_D$ = 104·5° in 10 p.c. solution; $[\alpha]_j$ = 114·7° or $[\alpha]_j$ =

185·1° for the dry sugar. O'Sullivan observed $[\alpha]_j = 185·8°$. No bi-rotation has been observed. It does not reduce Fehling's solution. D = 3·712 (Tollens, *B.* 18, 2616), but this is due to some misunderstanding; D = 3·956 (O'Sullivan, *C. J.* 1886, 70).

Action of acids. Hot dilute acids hydrolyse raffinose; galactose, lævulose, and probably dextrose are formed (Hädicke a. Tollens, *Z. V.* 37, 17; *A.* 238, 308; Beythien a. Tollens, *A.* 255, 214; Maquenne, *C. R.* 112, 799). By very careful hydrolysis, Scheibler a. Mittelmeier (*B.* 22, 1678) have obtained a saccharose and lævulose as the products of the reaction; the saccharose is a new body, which they have called *melibiose* (*q. v.*). The mixture of saccharose and lævulose has a specific rotatory power $[\alpha]_D = 50°$. Complete inversion of raffinose takes some hours. Invertase also hydrolyses raffinose (O'Sullivan). The products of hydrolysis are at first lævulose and melibiose (Scheibler a. Mittelmeier, *B.* 22, 3118), and melibiose is slowly acted on. When heated for some time with sulphuric acid, lævulinic acid is a product (Rischbieth a. Tollens, *A.* 232, 195).

Action of alkalis. By boiling aqueous solutions of strontia and raffinose, di-strontia raffinose $C_{15}H_{32}O_{16}(SrO)_2.H_2O$ is produced. Other compounds with baryta $C_{18}H_{32}O_{16}.BaO$, lime $C_{18}H_{32}O_{16}.3CaO.2H_2O$, lead oxide $C_{18}H_{32}O_{16}.3PbO$, and soda, $C_{18}H_{31}NaO_{16}$ and $C_{18}H_{31}NaO_{16}.NaOH$, have been prepared (Beythien a. Tollens, *B.* 22, 1047; *A.* 255, 195; Rischbieth a. Tollens, *A.* 232, 172).

Oxidation.—Nitric acid oxidises raffinose, producing 30 p.c. mucic acid, also saccharic and oxalic acids.

Fermentation.—Raffinose is slowly fermented by beer yeast (Rischbieth a. Tollens, *A.* 232, 242; Tollens, *A.* 232, 169; O'Sullivan, *C. J.* 1886. 73). Weak yeast only partially ferments it (Tollens, *l.c.*; Berthelot, *C. R.* 109, 548); the melibiose being with difficulty hydrolysed and fermented.

With phenylhydrazine a compound is formed, m.p. 187°–189° (Rischbieth a. Tollens, *l.c.*).

Melezitose $C_{18}H_{32}O_{16}.2H_2O$ is obtained from Persian manna, a product of *Alhagi maurorum* (DC.), it crystallises in rhombic prisms, m.p. 147–148° (when anhydrous); the specific rotatory power of the anhydrous body is $[\alpha]_D = 87·7°$. On inversion it yields *turanose* and dextrose. Turanose $C_{12}H_{22}O_{11}$ $[\alpha]_D = 65°–68°$, yields dextrose by the further action of acid (Alekhin, *J. R.* 21, 407).

(*d*) *Hexahexoses.*

Gentianose $C_{36}H_{62}O_{31}$. Obtained by A. Meyer (*H.* 6, 135), from the root of *Gentiana lutea*, by extraction with alcohol, precipitation with ether and re-crystallisation from alcohol. It has a sweet taste, dissolves easily in water, m.p. 210°, does not reduce Fehling's solution, and ferments with yeast. It is hydrolysed by dilute acids; before inversion the optical activity is $[\alpha]_D = 33·6°$; after, it is 20·2°, and has a reducing power equal to that of dextrose. Strong sulphuric acid chars it, like cane sugar.

Stachyose is obtained from the root of *Stachys tuberifera*. It has a sweet taste, is dextrorotatory, having $[\alpha]_D = 148·1°$ in 9 p.c. solution. It forms triclinic crystals. When inverted it yields galactose, dextrose, and lævulose. Its formula appears to be $C_{36}H_{64}O_{32} + 6H_2O$ (Planta a. Schulze, *B.* 23, 1692; 24, 2705), the products of the hydrolysis being the same as those of raffinose.

QUALITATIVE AND QUANTITATIVE DETERMINATION OF SUGARS.

If the material to be examined is a solution, it must be made neutral, clear, and colourless if it is not already so.

If the material is a dry substance, it must be ground fine. If not sufficiently dry to admit of grinding, it must, if possible, be dried in vacuum over sulphuric acid, or, where this is not possible, in the open, at a low, gradually increasing temperature.

The finely-ground substance is extracted with alcohol sp. gr. ·860–·880. The solution is neutralised and the alcohol distilled off. The residue is taken up with water. The examination then comes under the head of a *solution*, and the treatment is the same.

The solution is turbid and coloured after neutralisation. The turbidity may be removed by simple filtration; if not, a little aluminium hydroxide (prepared by precipitating a solution of alum with excess of ammonia and washing free from ammonia and sulphuric acid) may be employed. A little (well washed) Swedish filter paper-pulp is at times found useful. The turbidity and colour may be removed together by animal charcoal, lead sulphide, barium sulphate, &c. Animal charcoal, either prepared from blood or bones, the former by preference, thoroughly extracted with hydrochloric acid and washed free therefrom, is best employed in all cases of investigation. The crude substances are employed to remove the colour, &c., from sugar syrups in the manufacture of refined cane sugar. These decolouring agents must always be used in the least possible quantity, and with the understanding that the charcoal especially is capable of taking up some sugar as well as colouring matter. Dried, freshly-made bone charcoal does not take up more than ·006 p.c. of its own weight from pure cane-sugar solution (Casamajor, *C. N.* 41, 66). In quantitative work, when the decolourising agents have to be used it is well to have a knowledge of the influence of the agent on the sugar or sugars under examination. Charcoal retains sugar, other substances influence the optical activity. Part of the sugar is again given up on washing the agent with water, or the agent is placed on a filter and a portion of the solution to be examined passed through it and rejected before the portion intended for examination is collected. This is done on the supposition that the charcoal is sooner saturated with sugar than with colouring matter.

Having thus the sugars in clear solution, the means at our disposal for identification are:—

1. Taste of solution.
2. Form of crystals and melting-point thereof.
3. Depression of the freezing-point (Raoult's method of determining molecular weights).
4. Specific rotatory power.
5. Reducing power.
6. Action of unorganised ferments: enzymes.
7. Action of organised ferments.

8. **Action of acids.**
9. **Action of alkalis.**
10. **Action of phenylhydrazine, and melting-points of the resulting osazones and hydrazides.**

1. The solution tastes sweet if a sugar is present. It must not be forgotten, however, that some other bodies are also more or less sweet.

2. On evaporating this solution (best in a vacuum) to a syrup, if there is no preventive material present, crystallisation takes place. The microscopic appearance of the crystals will often be sufficient to identify the sugar; indeed, the habit of crystallisation will often suffice. A substance or substances may be present which altogether prevent the crystallisation of the syrup, although it may contain a crystallisable sugar. This substance may be an inorganic or organic salt, or another body, or, indeed, another sugar. Treatment with strong or absolute ethylic or methylic alcohols may at times eliminate some or the whole of the substances preventing the crystallisation, and dissolve the sugar in so clean a state as to admit of the formation of crystals on concentration.

3. *Depression of the freezing-point* (Raoult's method). For references to Raoult's work see Victor Meyer, *B.* 21, 536; Auwers, *id.* 701; Tollens a. Meyer, *id.* 1566; and Brown a. Morris, *C. J.* 1888, 610. When crystals are obtainable from the solution as described above, a determination of the molecular weight by this method will decide to which group it belongs: a hexose or a pentose, a dihexose or dipentose, a trihexose. In the recorded observations water of crystallisation appears not to have received proper attention. Tollens a. Meyer record observations for dextrose $C_6H_{12}O_6$, so do Brown a. Morris. Water of crystallisation is not taken into account; the former treat of $C_{12}H_{22}O_{11}.H_2O$ for lactose, the latter omit the H_2O, while both employ crystallised raffinose $C_{18}H_{32}O_{16}.5H_2O$, mol. = 594, with the result that T. a. M. find the observed molecular weight between 544 and 644, and B. a. M. between 518 and 533. In these experiments with raffinose and lactose, it is not possible to say whether it is intended that the crystallisation water functions with the solid sugar or with the water; the calculations make it function with the sugar, but the results, as might have been expected, are unsatisfactory—it does not function with the sugar. It is perfectly clear that water of crystallisation of a sugar must be looked upon as water in observations with this method—that the quantity of *dry* sugar should be the factor dealt with. If the crystals contain water of crystallisation it should be determined and allowed for. A determination of the D will give some information as to whether a dry sugar or one containing water of crystallisation is being dealt with. The D of the different sugars in the dry state is given under each sugar. Between 8 and 15 g. dry substance is dissolved in water and the solution made up to 100 c.c. at 15·5°. A determination of the specific gravity of this will give a means of calculating the D, and the number of g. of water to substance employed in the solution. About 60 c.c. of this solution are introduced into a thin glass (120 c.c.) beaker. The mouth of the beaker is loosely closed with an indiarubber plug, in which three holes are bored. One of these, in the middle, admits of the introduction of a thermometer; the second, at the side, carries a stirrer, of very thin glass rod or platinum, best in the form of a flat coil, so that when the stirrer is moved up and down in the liquid the thermometer will be in the middle of the coil; and the third, also at the side, to admit of the introduction of a small solid particle of the frozen solution or of ice. The thermometer must be graduated for 2° or 3° above and below 0° to the 20th of a degree. By means of a telescope, if the divisions are open, and they should be so, readings to ·005° can be made with a fair amount of accuracy. The beaker thus charged and fitted is placed in a freezing mixture of ice and salt—which should not be at too low a temperature, −4° to −5°, not more than 2°–3° below the freezing-point of the solution—contained in a strong beaker of 500–600 c.c. capacity. In a short time the temperature in the inner beaker will be observed to sink below 0°, and, on rapidly moving the stirring rod up and down, to go gradually lower and lower until a point is reached when the solution begins to freeze. This may be accelerated by adding a particle of the solution previously frozen; when freezing begins the mercury of the thermometer rapidly rises and soon becomes stationary. This is the freezing-point of the solution *c*, and is the observation upon which the molecular weight of the substance employed is calculated.

$$M = \frac{19}{A}, \qquad A = \frac{c \times y}{x \times 100},$$

x = g. substance; y = g. water, and 19 is a number calculated by Raoult for water as a solvent from observations with well-defined compounds. As examples, Brown a. Morris (*l.c.*) with a solution containing 8·258 g. sucrose and 94·93 g. water observed a freezing-point $c = 0\cdot490°$, thence

$$M = \frac{19}{\frac{\cdot 49 \times 94\cdot 93}{8\cdot 258 \times 100}} = 337\cdot 5. \quad C_{12}H_{22}O_{11} = 342.$$

Hence, if an unknown sugar were under observation there would be no doubt left as to the molecular weight. O'Sullivan (*C. J.* 1890, 59) observed for arabinon: sp.gr. sol. 1·02554, $y = 96\cdot088$ g., $x = 6\cdot466$ g., $c = 0\cdot535°$; thence

$$19 \div \frac{96\cdot 088 \times \cdot 535}{6\cdot 466 \times 100} = 239\cdot 2,$$

the molecular weight of the new sugar. A dipentose requires 282. The indications agreed with further confirmatory observations. When the solution contains more than 12 g. per 100 c.c. the results are low; with most sugars a solution containing from 5 to 8 g. substance per 100 c.c. gives the best results, and with more dilute solutions the results are again low. Raoult's latest observations (*C. R.* 114, 264) for sucrose, made with apparatus constructed to meet the exact requirements of the case, the concentration of the solution being 5·839 g. sucrose in 100 g. water, work out M = 323, against 342, the true molecular weight. The results are, even under the best conditions, low; but the indication is sufficiently good to enable us to decide to which group the sugar we are dealing with belongs. If, instead of the factor 19, 19·8 were substituted, the results would agree with the accepted molecular weight of sucrose, and it is probable that this number or 20 will be finally decided upon as the constant.

4. *Specific rotatory power.* If the form of the crystals or their habitat does not indicate the sugar present, a determination of the specific rotatory power may give the desired information. This is the quantitative expression of a property possessed by the sugars in common with many other substances. When light from any source is examined through a Nicol prism—*i.e.* polarised—no change is evident; but if the light, after passing through one prism (the *polariser*) is examined by another, it is found that in certain positions of the examining prism—or *analyser*, as it is called—no light passes. If the analyser is made to carry an index, and is so mounted as to rotate with its axis at right angles to a disc graduated to degrees, it will be found that, if the position of the two prisms is so arranged that the index is at 0° on the graduated circle when no light passes, light will pass on the least rotation of the analyser to the right or left, and if the movement is continued another position is found on the disc in which the light is again cut off. This is at 180°, so that the circle should be graduated to 180° right and 180° left. Now, if a cell or tube with flat glass caps be filled with a solution of, say, sucrose and introduced between the two Nicols, and the source of light be a Bunsen burner flame coloured yellow with sodium chloride, when the index of the analyser is at 0° it will be observed that the light passes, and that on rotating the analyser a certain number of degrees to the right a point is found (which is not 180°) at which the light is cut off; and if note be taken of the exact number of degrees, and the analyser rotated further, it is found that the light is not again cut off at 180°, but the same number of degrees beyond 180° as the first extinction was beyond 0°. This is the *optical activity* of the sugar solution. It is the power of rotating the plane of polarisation of the ray passing through the polariser so as to admit of its passing through the analyser when it would not pass had the sugar solution not been introduced. The amount of rotation of the analyser to again find the direction of the plane of polarisation, as indicated by the index on the graduated disc, is the measure of the activity of the sugar solution, and the direction of the movement of the index is the direction in which the rotation has taken place; in the present case (*i.e.* when the index is moved on the disc in the direction of the hands of a watch) *right* or +. If the sugar solution be now hydrolysed by dilute acids or invertase, and again introduced between the Nicols, it is found that the analyser must be rotated to the left in order to find the position of extinction—*i.e.* the direction of the plane of polarisation of the rotated ray. This is *left* rotation, and is indicated by the sign −. On further rotation of the analyser light again passes, and finally there is a second extinction as far beyond 180° as the first extinction was beyond 0°. From this it is clear that the second reading may indicate right-handed rotation as well as left. Say the first extinction was 10° left of 0° (−10°), the second would be +170°, 10° less than 180°; then the activity might be −10° or +170°. On diluting the solution say one-half, if the activity is − the readings will be −5° and +175°, if + they will be +85° and −95°. The exact measurement of this activity has been the subject of much investigation, and many plans have been devised to facilitate the operation. It is, however, beyond the scope of this article to deal more fully with the subject (for details see *Das optische Drehungsvermögen organischer Substanzen*, Landolt, Braunschweig, 1879, *Engl. Trans.*; *Handbook of the Polariscope*, Macmillan & Co., 1882; Watts' *Dictionary*, *Suppl.* 3, art. LIGHT). In the experiments above described the light of a sodium flame was employed; it was observed early in the investigation of the phenomena that readings sufficiently accurate, especially if the amount of activity was small, could not be obtained. Hence other devices were introduced. In the literature we find the activity expressed $[\alpha]_R$, $[\alpha_j]$, or $[\alpha]_D$ and $[\alpha]_B$, $[\alpha]_C$, $[\alpha]_{Li}$, &c.

$[\alpha]_R$ values are not now used. They were obtained by employing white light, and interposing between the polariser and the source of light a plate of red glass. They are of no value for our purpose, and may be neglected.

$[\alpha]_j$ values are frequently used, but unless they are referred to a definite standard they, too, are of no value. If any ordinary source of white light be substituted for the sodium flame in the experiments above described, it will be observed that on rotating the analyser to find the effect produced by the sucrose solution no position of the analyser can be found in which all the light is cut off, but at one stage marked blue light passes, and, on further rotation of the analyser, red. This is due to the fact that the sugar solution acts unequally on the different rays of which the beam of white light is composed, the red rays being rotated least and the violet most, so that when the analyser is rotated the ray the plane of polarisation of which is rotated least is first cut off. The first cut off rays are the red, the complement of those cut off passing, the dominant being blue; on further rotation the dominant becomes red. On rotating the analyser carefully it is found that the *transition* from the blue to the red is well marked; this is the α_j value; it is the, so-called, *transition* tint, the ray complementary to the median yellow, *jaune moyen*; hence α_j. For the same strength of sugar solution the position of the analyser is not the same for every source of white light. The stage at which the transition appears with candle-light is different from that at which it appears with gas-light; the stage in this case differs again from that obtained with the electric light, and even the position for direct sunlight differs from that of the light reflected from a cloud. Hence, when a pair of Nicols are employed as described above, even when the source of light is given, α_j cannot be looked upon as a standard value. This value has, however, been given to it by the French instrument makers.

Soleil invented an instrument with which lamp- or gas- light is employed (afterwards improved by Duboscq, and known as the Soleil-Duboscq (see Watts' *Dictionary*, 1st ed. 3, 674, a. *Suppl.* 8, 1199), by which the activity of a solution is measured by *divisions* of a scale instead of degrees; 100 of these divisions were made equal to the amount of rotation produced by 1 mm. quartz for the α_j; this was *considered* to be 24°. Of course, if this is taken as a standard it is of full value; it may not be truly α_j even for the quartz, but it is α_j referred to a definite measure, the 100 divisions of the instrument being 24°. This was complicated by the fact, since pointed out by Scheibler, that quartz from different sources has not the same optical activity; hence we have various observers giving different values for the amount of sucrose in 100 c.c. solution, which when observed with the Soleil-Duboscq instrument, in a tube 200 mm. long, equals the activity of 1 mm. quartz. If, however, we look upon the 100 divisions of the instrument as $=24° \alpha_j$, we have a standard value for the expression. I believe this is the value given to it by the French observers. The writer employed it in the same way. Another instrument of much the same construction is the Soleil-Ventzke-Scheibler (*v.* Watts, *l.c.*). In this the 100 divisions of the scale are made to represent the activity of 26·048 g. saccharon in 100 c.c. solution; we have only to inquire as to the $[\alpha]_j$ and $[\alpha]_D$ of cane sugar to arrive at a value in degrees of the 100 divisions for these two expressions. From these two factors we get 100 divisions, Soleil-Duboscq $=24° \alpha_j$ and $21·67° \alpha_D$, and 100 divs. S.V.S. $=38·34° \alpha_j$ and $34·55° \alpha_D$. The angular value for any other instrument in use in which the scale is given in divisions can be calculated for α_j or α_D by ascertaining the number of divisions required to compensate a solution of sucrose containing 10 g. in 100 c.c. at 15·5°, and taking the apparent specific rotatory power of the sugar for the concentration to be $[\alpha]_j = +73·8°$ and $[\alpha]_D = 66·6°$, the value of the divisions in degrees for both rays can be calculated. The direction of the rotation is indicated in these instruments by the direction of the movement of the 0 point to find the compensation necessary; if from left to right it is right or +, if in a contrary direction left or −. With the other instruments in use sodium flame is the source of light employed; the readings are therefore α_D. The scale is a circle graduated to degrees on a disc, beginning with 0 at the top and graduated in half degrees and degrees to 180° to the right, and in the same way to the left. The analyser rotates in the axis of this disc, and carries an index with vernier, which admits of readings being made to minutes. The arrangement is such that the polarised ray before entering the active solution has the appearance of a circular disc divided into halves by a perpendicular diameter. The position of the plane of polarisation is not the same in both semi-discs, so that when the light is completely cut off at one side it passes at the other, and *vice versâ*. To find these positions the analyser has to be rotated several degrees, but between the two positions of complete cut off there is a position of the analyser in which the two semi-discs are equally illuminated; this is a well-marked position distinctly ascertainable. The 0 point of the index and of the graduated scale are made to correspond exactly with it. It can always be found to within less than a minute. When the active substance is introduced the equality of the illumination of the semi-discs is destroyed; the analyser is rotated until it is again restored. The amount of rotation as shown by the graduations gives the activity in degrees and minutes, or degrees and decimals, according to the make of the vernier. These are the *half-shadow* instruments, of which the *Jellet-Cornu* and *Laurent* are examples (see Watts, *l.c.*). Other devices have been employed to facilitate an accurate determination of the position of the plane of polarisation of the ray before and after rotation; a description will be found in Landolt and in Watts (*l.c.*). Recently an instrument has been introduced in which the half-shadow contrivance is adopted, white light (a strong gas-flame) being employed. The scale is the same as that of the Soleil-Ventzke-Scheibler instrument; readings with it can be made with great accuracy. It is manufactured by Schmidt & Haensch, Berlin.

When it is necessary to determine the activity for rays of other refrangibility, say for the lithium or the thallium flame, it is only necessary to colour the Bunsen flame with these metals in the same way as in the case of sodium above. The readings are then α_{Li} and α_{Th}. The α_B, α_C, α_D, &c. for any active substance can be found by employing a pair of ordinary Nicols as described above—white light, best a ray of sunlight, being employed—and examining the light after passing the analyser, with a spectroscope. If the positions of the lines of the solar spectrum are marked, the amount of rotation for the active substance introduced between the polariser and the analyser is found, when on rotating the analyser the thickest part of the black band is on the marked position of the line of the spectrum. This is read off on the scale connected with the analyser.

With any of these instruments we can determine the optical activity of a sugar and thus identify it. The sugar is crystallised; it is dried, and 10 g. or thereabouts carefully weighed out. This is dissolved in water, and the solution made up to 100 c.c.[1] at 15·5°. A portion of this is introduced into a tube of definite length, and an observation made with any of the instruments mentioned above. The formula $[\alpha] = \frac{\alpha \cdot 100}{l.c}$ gives the apparent specific rotatory power for the concentration. α = the angular disturbance observed, l = length in decimetres of tube employed, and c = grams substances in 100 c.c. Let us take an example, 10 g. sucrose, dissolved and made up to 100 c.c. Disturbance observed in a 200 mm. tube, with a Soleil-Duboscq instrument, $=61·5$ divs.; now for α_j 100 div. = 24°. Then, substituting the values in the above formula we have

$$\frac{61·5 \times ·24 \times 100}{2 \times 10} = [\alpha]_j = +73·8°$$

100 divs. $= 21·67° \alpha_D$; then

$$\frac{61·5 \times ·2167 \times 100}{2 \times 10} = [\alpha]_D = +66·6°.$$

The scale of the Soleil-Ventzke-Scheibler instrument is so graduated that 100 divisions = the activity of a solution of sucrose containing

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[1] This is practically the usual 100 c.c. of a volumetric analysis. For more accurate manipulation see Landolt. This is, however, unnecessary for the identification of the sugar—our purpose.

26·048 g. in 100 c.c. in a 200 mm. tube. The apparent specific rotatory power of sucrose in a solution of this concentration is $[\alpha]_D = 66·33°$ and $[\alpha]_j = 73·61°$. Substituting these values in the formula we get

$$\frac{x\,.\,100}{2 \times 26·048} = 66·33\,;$$

x = the value of 100 divisions in degrees α_D = 34·55°, and

$$\frac{x'\,.\,100}{2 \times 26·048} = 73·61\,;$$

x' = the value of 100 divisions α_j = 38·34°.

It is of importance that the values in degrees of the scales of these two instruments should be clearly understood. We find it stated that a quantity of sugar varying from 16·49 to 16·35 g. in 100 c.c. require, in a 200 mm. tube, a compensation with a Soleil-Duboscq instrument = 100 divisions; 16·35 g. is the best-recognised factor; from my observations it is still too high.

$$\frac{100 \times ·24 \times 100}{2 \times 16·35} = [\alpha]^j = 73·39°, \text{ and}$$

$$\frac{100 \times ·2167 \times 100}{2 \times 16·35} = [\alpha]_D = 66·27°,$$

figures slightly too low for the apparent specific rotatory power of sucrose for the *c*, hence 16·35 g. is too high. The number, no doubt, should be 16·28, and this gives factors agreeing well with the observed $[\alpha]_D$ and $[\alpha]_j$ for the *c*.

A solution containing 10 g. sucrose in 100 c.c. requires a compensation in a 200 mm. tube of 38·5 divisions f a Soleil-Ventzke-Scheibler instrument.

$$\frac{38·5 \times ·3834 \times 100}{2 \times 10} = [\alpha]_j = 73·8° \text{ and}$$

$$\frac{38·5 \times ·3455 \times 100}{2 \times 10} = [\alpha]_D = 66·5°,$$

numbers agreeing accurately with the specific rotatory power for the *c*. The optical arrangements of these instruments admit of the employment of white light.

If either of the sodium-flame instruments is employed the angular disturbance is introduced directly into the formula. With the 10 g. in 100 c.c. solution of sucrose, the reading in a 200 mm. tube is $\alpha_D = +13·3°$, then $\frac{13·3 \times 100}{2 \times 10} = [\alpha]_D = 66·5°$. The use of this factor is obvious. We have a solution of a known sugar of unknown strength, and want to find the *c* (g. in 100 c.c.). An observation is made in a tube of known length, α_D or α_j; then $\frac{\alpha\,.\,100}{l\,.\,c}$ = the determined value of $[\alpha]_D$ or $[\alpha]_j$, α the ray for which the observation is made, and $[\alpha]$ the specific rotatory power for that ray, according to the light employed and concentration, $c = \frac{\alpha\,.\,100.}{[\alpha]\;l}$

It has been shown that if a solution contains two or more active substances, the observed activity is the algebraic sum of the activities of the constituents. The specific rotatory power of each individual sugar is given in the description of it.

5. *The reducing power.* As has been stated, most of the sugars possess the power of reducing the oxides of the higher metals and some organic colouring matters. Various propositions have been made to employ this property as a means of qualitatively and quantitatively determining the sugars, and various solutions have been proposed for that purpose; but speaking with many years' experience I may say that they may all be discarded in favour of alkaline copper solution, *Fehling's solution*; and even with regard to the value of this a great diversity of opinion exists. But there is a general agreement that if the conditions under which it is used are constant the results are constant. For literature see Becquerel, *A. Ch.* [2] 47, 15; Trömmer, *A.* 38, 360; Müller a. Hagen, *Pf.* 23, 221; Neubauer, *Fr.* 1, 378; Maly, *Fr.* 10, 383; Seegen, *C. C.* 1875, 223; Fehling, *A.* 72, 106; Claus, *J. pr.* [2] 4, 63; Neubauer, *Ar. Ph.* [2] 71, 278; Patterson, *C. N.* 25, 149; Loiseau, *C. R.* 1873. 26; Soxhlet, *J. pr.* [2] 21, 227; Krause a. Städeler, *C. C.* 1854. 936; Gräger, *Fr.* 7, 490; Buswitz, *B.* 11, 1445; O'Sullivan, *C. J.* 1876, 2, 125; Märcker, *O.*[1] 7, 699; Brunner, *Fr.* 11, 32; Bayley, *C. N.* 37, 211; Allihn, *J. pr.* [2] 22, 55; Salomon, *B.* 14, 2711; Digener, *Z.V.* 31, 349; Schwarz, *A.* 84, 84; Mohr, *Fr.* 12, 296; Perrot, *B.* 9, 19; Ulbricht, *B.* 10, 128; Jean, *C. R.* 73, 1397; Scheibler, *Z.* 9, 820; Weil, *Fr.* 11, 284; Arnold, *Fr.* 20, 331; Volhard, *A.* 190, 1; Soldaini, *B.* 9, 1126; Possoz, *C. R.* 1874, 721; Pellet, *J. Fabr.*[2] 19, 22; Pavy, *C. N.* 39, 1004; Löwe, *Fr.* 9, 20; Vogel, *J. Ph.* [2] 1, 245; and others of less value. As a result of a study of all this literature, I may say that I have come to the conclusion that if the Fehling's solution is carefully made with pure materials, and employed as described below, the reducing power of any sugar can be determined with constancy and accuracy, and when the conditions are fulfilled the reduction is molecular—*i.e.* a definite number of copper oxide molecules are reduced by a definite number of molecules of the sugar.

Fehling's solution is made as follows: 34·61 g. pure recrystallised copper sulphate are dissolved in 400 c.c. H_2O or thereabouts, 173 g. sodium potassium tartrate (Rochelle salt), and 74[3] grams freshly-prepared sodium hydroxide (commercial stick soda) are dissolved to 450 H_2O; when the solution is cold it is gradually added to the copper solution in small portions at a time, so that the pp. at first formed is re-dissolved. When both solutions are mixed the volume is made up to 1 litre. It is very generally stated that this solution does not keep very well. I found it constant in its properties for more than twelve months when kept in carefully-stoppered bottles, sealed with paraffin in a cool, dark place. Some recommend that both the solutions be made up to 500 c.c., kept separately and mixed in equal volumes when required for use. This is probably the better plan but unless the solutions are kept in well-stoppered bottles sealed they will deteriorate as badly as if mixed. This solution is used as (a) a qualitative test for the reducing sugars. I is also used (*b*) quantitatively, to determine the reducing power and the quantity of a sugar.

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[1] *O.* = *Organ des Centralvereins für Rübenzuckerfabrication in der österreichisch-ungarischen Monarchie.*

[2] *Journal des Fabricants de Sucre.*

[3] Redewald a. Tollens (*B.* 11, 2076) employ 60 g and they say the increase of alkali to 70 g. diminishes the reducing power of lactose about 1 p.c.

(*a*) *Qualitatively.* A portion of the solution supposed to contain sugar, prepared as described, is heated to boiling in a small beaker or test-tube, and is added to 5 c.c. of the alkaline copper solution previously diluted with its own bulk of water, and heated to boiling. The production of a red pp. of Cu_2O indicates the presence of a reducing sugar. There are substances besides the sugars capable of reducing Fehling's solution. The absence of these must be established before it can be inferred that the reduction is due to sugar.

(*b*) *Quantitatively.* The reducing power of a sugar, or of a solution containing reducing sugars, can be determined *volumetrically* or *gravimetrically*, with Fehling's solution. It is now very generally admitted that the gravimetric method gives the only reliable results.

Volumetrically. The sugar solution, prepared as described, should be diluted (0·5 to 1·0 g. reducing sugar in 100 c.c.). This is introduced into a burette, and the Fehling's solution into a second one. Of the latter a definite quantity, say 10 c.c., is measured into a porcelain dish of about 60 to 100 c.c. capacity, and diluted with four times its own bulk of water. The dish is then placed over a small Bunsen, and the contents heated to boiling. The sugar solution is then run in a c.c. at a time until the blue colour of the copper solution has nearly all disappeared, then drop by drop until it has quite gone. The first experiment may only give approximate results; in a second a quantity of sugar slightly less than was found necessary in the first experiment is measured into a small beaker, heated to boiling, and mixed rapidly with the boiling dilute copper solution. If the whole of the copper is reduced, a few drops more of the Fehling's solution are added from the burette. A few experiments of this kind will give fairly approximately the amount of copper solution a certain quantity of the sugar solution is capable of reducing. That the Fehling's solution is not in excess is seen by the absence of blue on subsidence of the Cu_2O, and may be confirmed by filtering a little and testing for copper with a dilute solution of potassium ferrocyanide in acetic acid. The absence of a brown colouration indicates the absence of CuO. If the sugar is in excess, more CuO solution is decolourised, but after boiling the sugar in the alkaline solution the amount reduced is not a measure of the quantity of sugar. The final experiment must be performed after two or more observations, when the relative value of the two solutions has been approximately ascertained, as described above, by adding the whole, or nearly the whole, of the sugar at a boiling temperature to the copper solution *at once.* If only a few drops of the sugar solution are required to remove the last traces of CuO, the error is not great; 10 c.c. of the Fehling's solution, made as directed, contain ·1100 g. CuO; 396 CuO = 180 dextrose, *i.e.* 5 mols. CuO (79·2 + 5 = 396) are reduced by 1 mol. dextrose 180, then 396:110 = 180:050 grams dextrose = 10 c.c. Fehling's solution. Soxhlet (*l.c.*) states that the value of the CuO solution in dextrose varies with the way in which the experiment is performed; that 10 c.c. undiluted Fehling's solution are reduced by 0·04753 g. dextrose, while it takes 0·0494 to reduce the same bulk diluted with four measures of water. The same applies to the other reducing sugars, only in the case of lactose dilution has no effect, while in that of maltose dilution diminishes the amount of sugar required. This is, no doubt, correct under the conditions stated, but it is not necessary in dealing with a reaction of this kind to deviate from recognised conditions such as those laid down above. When these are adhered to it is found that the reducing power of the sugar very closely approaches molecular interaction; in fact, so much so that the molecular relation most closely approximated to by the experimental data may be taken as the *normal reducing* power of a sugar. These normals for the better-known sugars are:—

10 c.c. Fehling's solution = 0·0500 g. dextrose.*
" " 0·0500 g. galactose.
" " 0·0500 g. lævulose.
" " 0·06334 g. lactose.†
" " 0·07196 g. maltose.†
" " 0·04630 g. arabinose.
" " 0·08701 g. arabinon.

* Soxhlet says the reducing power of lævulose is different from that of dextrose. This is not supported; his error is due to his mode of preparing invert sugar.

† Sugar free from water of crystallisation.

Gravimetrically. The Fehling's solution is prepared as described; 25-30 c.c. of it are measured into a beaker of 130-140 c.c. capacity, and about 50 c.c. well boiled water added. The beaker is then placed in a boiling-water bath, consisting of a larger beaker in which water is kept boiling. At the end of five or six minutes, when the dilute copper solution has acquired the temperature of the bath, a known weight or measure of the sugar solution is heated to boiling, and added. If at the end of a few minutes the blue colour is completely destroyed, it can be restored by adding more Fehling's solution, but it is much better to so arrange matters by a few experiments that the amount of sugar solution employed will reduce the Fehling's as nearly as possible, leaving only sufficient blue, on subsidence of the Cu_2O, to make it evident that the copper solution is in slight excess. After twelve to fourteen minutes' boiling the clear supernatant liquid is decanted on to a filter, the Cu_2O is washed by decantation, and finally on the filter. If the Fehling's solution is in large excess it is difficult to wash the filter free from unreduced copper oxide (blue colouration), but if the excess is only slight there is no indication that the filter retains copper compounds other than Cu_2O. Ignition for four or five minutes in an open porcelain crucible converts the red precipitate into black copper oxide CuO, in which form it is weighed. From this the sugar is calculated by multiplying by the constants (see next page). It may be again pointed out that the factors given by various authorities differ more or less from these (see the K of individual sugars), but I believe these are the constants, the differences amongst the authors being due to manipulation, to the state of dilution and alkalinity of the solutions, and to the temperature of the mixed sugar and CuO solution. An imperfect knowledge of the composition of the material is a source of error. In dealing with some solutions, other

1 mol. sugar to 5 mols. CuO : 1 g. CuO = 0·4545 g. dextrose : K = 100
" " 5 " " 1 g. " = 0·4545 g. galactose : K = 100
" " 5 " " 1 g. " = 0·4545 g. lævulose : K = 100
" " 7·5 " " 1 g. " = 0·5758 g. lactose : K = 77·67
" " 6 " " 1 g. " = 0·7196 g. maltose : K = 63·16
" " 4·5 " " 1 g. " = 0·4209 g. arabinose : K = 108·8
" " 4·5 " " 1 g. " = 0·7910 g. arabinon : K = 57·5

substances may be precipitated with the Cu_2O. These should be ascertained, determined, and allowed for. In dealing with solutions in which ammonia is found, or liberated by the alkali, Cu_2O is retained in solution. Sundry propositions have been made to avoid the disturbing influence of the alkali in Fehling's solution, but they seem to have met with no favour. Soldaini (*B.* 9, 1126) proposed copper carbonate in potassium bicarbonate; Possoz (*C. R.* 1874, 721) and Pellet (*J. fb.* 19, 22) other solutions of copper in alkaline carbonates. Löwe (*Fr.* 9, 20) recommends the use of a solution of CuO in glycerol, but so far little can be said of the value of the solution. In cases where the sugar solution contains other substances than reducing sugars capable of giving a precipitate with Fehling's solution without reduction, the whole precipitate may be dissolved in hydrochloric acid, made strongly alkaline, and added to an excess of ammoniacal solution of silver nitrate. The copper suboxide reduces an equivalent quantity of silver oxide. The silver in the precipitate may be estimated as chloride (Jean, *C. R.* 73, 1397). As has been stated above, many other solutions and modifications of Fehling's solution, have been proposed for employment in determining the sugars, but they appear to be of no value.

Pavy (*l.c.*) recommends the addition of sufficient ammonia to the Fehling's solution to hold the Cu_2O in solution; the disappearance of the blue is then the indicator of the reaction. The reducing powers for sugars other than dextrose for this solution have not been ascertained; even for dextrose it is doubtful (*v.* Hehner, *An.* 6, 218).

Three solutions of mercury salts have been proposed as agents by which sugars can be determined by their reducing power—the one known as *Knapp's* solution, the other as *Sachsse's* solution, and the third as *Hager's* solution. Neither of them are of high value, except in certain circumstances, but Hager's least of all.

Knapp's solution is made by dissolving 10 g. $HgCy_2$ in about 600 c.c. water, then adding gradually 100 c.c. sodium hydroxide solution, specific gravity 1·145, and diluting the clear solution to 1 litre; 10 c.c. of this solution equal 0·025 g. dextrose; but according to Soxhlet (*l.c.*) this is not true, and the quantity varies with the conditions under which the reducing solution and reducible one are brought in contact, and even with the indicator used in determining the absence of mercury. The solution is used as follows:—40 c.c. of it are heated to boiling in a flask, and the sugar solution, which should not contain more than 0·5 p.c. reducing sugar calculated as dextrose, run in as quickly as possible until the whole of the mercury is ppd. as such, the mixed liquids being kept continually boiling. The complete precipitation of the Hg is ascertained by testing for it with ammonium sulphide, or alkaline tin solution. Less mercury is reduced by adding the sugar gradually than when the addition is made all at one time (Brunner, *J. pr.* [2] 21; Soxhlet. *l.c.*). According to the latter, when the reducing solution is added all at one time, and alkaline tin solution employed as a test for the absence of Hg from the solution, 0·200–·202 g. dextrose reduce 100 c.c. of Knapp's solution.

Sachsse's solution is made to contain in 1 litre 18 g. mercuric iodide, 25 g. potassium iodide, and 80 g. potassium hydroxide. The mercury salt is dissolved in a solution of the potassium iodide, the solution of the potassium hydroxide added, and the mixture made up to the litre. A measured quantity, 40 c.c., of the solution is boiled in a porcelain dish, and the sugar solution, containing not more than 0·5 g. per 100 c.c., run in until a drop of the supernatant liquid ceases to give a brown colour with an alkaline solution of tin chloride. It is said that in using this reagent more mercury is reduced by adding the sugar slowly than by adding it all at one time, the reverse being the case with Knapp's solution. Soxhlet (*l.c.*) compares the value of these solutions for the reducing sugars as follows:—

Taking the reducing power of dextrose = 100, the reducing powers (K) of the other sugars are:

	Fehling (undiluted)	Knapp	Sachsse
Dextrose . . .	100	100	100
Invert sugar . .	96·2	99	124·5
Lævulose . .	92·4	102·2	148·6
Galactose . .	93·2	83·0	74·8
Lactose (hydrated?)	70·3	64·9	70·9
Maltose (dry?) . .	61·0	63·8	65·0

These relations for the K of the sugars for Fehling's solution do not agree at all with the generally recorded numbers (*v.* K of individual sugars); there are no data to enable one to form an opinion on the value of the K for the other solutions.

Potassium ferricyanide has been proposed as an agent for determining the reducing power of the sugars by Gentele (*Fr.* 9, 453), but although Stahlschmidt (*B.* 1, 141), Stammer (*D. P. J.* 158, 40), and Sostmann (*V. Z.* 22, 170) have worked with it, we know nothing very definite about its value. It should yield definite results, as the complete reduction is definitely recognisable.

6. *The action of unorganised ferments. Enzymes.* Sucrose is converted by invertase into lævulose and dextrose; the only other sugar acted upon by this enzyme is raffinose (Kjeldahl, *Fr.* 22, 588; O'Sullivan, *C. J.* 1886. 70; and O'Sullivan a. Tompson, *C. J.* 1890. 834), and, as it has been shown, the invertive action is most active at a temperature at which yeast, from which the invertase is prepared, has no fermentative action on the products of the inversion; yeast can be employed instead of prepared invertase. The products of the action of invertase

on raffinose are lævulose and melibiose, the latter yielding finally dextrose and galactose. Raffinose is but very sparely distributed. It may be considered that sucrose is present if the optical activity of a solution is materially altered by treatment with invertase and the copper oxide reducing power at the same time increased. The absence of raffinose can be determined by the non-production of mucic acid on treatment with nitric acid. Before applying the invertase test the solution to be tested must be boiled. If this is not done, and active diastase and any of the high-starch transformation products are present, the latter would be acted upon by the diastase, the opticity lowered, and the cupric reducing power increased. Diastase does not appear to act on any of the sugars, except isomaltose (?)

Other organisms, such as the moulds which grow on steamed rice, contain an enzyme capable of acting on maltose, but this substance has not been employed in the detection or estimation of maltose. There is no doubt, however, it is available for the purpose.

7. *Organised Ferments* (see FERMENTATION). The *hyphomycetes*, *saccharomycetes*, and *schizomycetes* act on the sugars and yield various products, and, no doubt, can be made available for the detection and estimation of them; but we have only to concern ourselves here with the action of ordinary beer yeast (*saccharomyces cerevisiæ*); the changes effected by the other organisms come under art. FERMENTATION. On adding pressed yeast to a very slightly acid solution, and keeping the mixture at a temperature of 20° or thereabouts, if a fermentable sugar be present, a frothy head will form on the surface of the liquid, carbon dioxide will be evolved, and alcohol formed. The specific gravity and optical activity of the solution diminishes. Certain substances known as antiseptics prevent this reaction—they must be proved to be absent. The fermentable sugars, in this sense, are described as such under the respective heads.

The quantitative value of this phenomenon has been studied by many workers, but it is still unsatisfactory. It has been made available with approximate accuracy in determining the total fermentable sugars in presence of other substances from which they cannot otherwise be conveniently separated. The solution should be of about sp.gr. 1·050–1·060, slightly acid, and should not contain much foreign matter. A measured quantity of this is taken, best 100 c.c. if available, introduced into a 150 c.c. flask, and 0·5 to 1 g. freshly-pressed yeast added. If necessary, a little yeast ash dissolved in the least possible quantity of hydrochloric acid, together with a little ammonium tartrate, should be added. A temperature of from 20° to 22° is best suited for the process. The gas evolved is washed by being made to pass through a few c.c. water in two successive wash-bottles. In some cases the fermentation is very slow and takes many days to complete itself, in others it is rapid and is finished in a few days; but in all cases it should be continued as long as gas bubbles through the wash-bottles on shaking the flask in which the fermentation is going on. As soon as this point is arrived at, the contents of the flask are washed with the water of the wash-bottles into a distilling flask, and submitted to distillation. Dilute alcohol distils over and is collected in a 100 c.c. flask. If only 20–25 c.c. wash-water were used, the distillate, when it amounts to 80–85 c.c., will contain all the alcohol produced. This is then made up to 100 c.c. and its specific gravity taken. On referring to the alcohol tables, the weight of alcohol in the 100 c.c. is ascertained. From this a knowledge of the amount of fermentable sugars is arrived at. Sucrose yields 51 p.c. alcohol, dextrose 48–49 p.c. (Pasteur, *A. Ch.* [3] 58, 330), maltose 50·4–51·8 p.c. (O'Sullivan, *C. J.* 1876, 479). Hofmann, Graham, and Redwood (*C. J.* 5, 229) gave expression to the value of the specific gravity of distillate, in points or degrees of specific gravity lost by the saccharine solution fermented for various sugars. These factors are still employed in determining the original specific gravity of beer, from the alcohol it contains and the specific gravity of the residue after distillation. The residue left in the distilling flask mentioned above is with the washings made up to 100 c.c., the specific gravity of this solution subtracted from that of the solution before the yeast was added + 1—or 1000 if water be taken at 1000 instead of 1—will give approximately the specific gravity of a solution containing the amount of sugars or sugar fermented in 100 c.c. The average D of the sugars being known, the quantity fermented within 2 or 3 p.c. can be calculated from this. Inasmuch, however, as the value in specific gravity of the non-volatile products of the fermentation of the sugars has not been accurately determined, this mode of estimation can only be approximate.

It has been proposed to estimate the amount of sugar or sugars by determining the amount of carbon dioxide evolved during fermentation. Pasteur (*l.c.*) gives 0·4665 g. CO_2 as the product of 1 g. dextrose. Jodlbauer (*Z. V.* 25, 308) states that dry maltose yields 49·54 p.c. CO_2 and dextrose 46·54 p.c. These figures are, no doubt, true also for all the fermentable '-on' and '-ose' sugars.

Some of the sugars when in the pure state are not fermented by yeast, but the presence of a small quantity of an easily fermentable sugar sets up the action. Pure galactose is not fermented by yeast; the presence of a little dextrose, lævulose, or maltose sets up the process (Bourquelot, *C. R.* 106, 283; Tollens a. Stone, *B.* 21, 1572; Stone a. Tollens, *A.* 249, 257), the fermentation of galactose being as complete as that of dextrose if the suitable nourishment is present. Under the same condition sorbose ferments more slowly and less completely, arabinose and lactose very slowly and incompletely. Pure arabinose behaves like pure galactose. Sucrose is inverted by yeast, dextrose ferments easily, lævulose less so, maltose still less, and raffinose less still. The other sugars ferment only when these are present; hence it should be possible to detect the presence of individual sugars from the specific rotatory power and K by fractional fermentation. With some varieties of yeast lævulose ferments before dextrose (Dubourg, *C. R.* 110, 868). Again, some organisms are found to ferment the '-ose' sugars and to be incapable of fermenting the '-on' ones. A study of the action of these organisms will yield results valuable in the identification and estimation of the sugars.

8. *Action of acids.* All the di- and tri- sugars are converted into mono- sugars by the action of dilute mineral acids; this is accompanied by an alteration in the K and [α] of the solution. If this took place only with the high sugars, the reaction would be applicable in distinguishing the '-on' and '-ose -on' sugars from the '-ose;' but the K and [α] of these sugars are also affected by digestion with mineral acids, but much more slowly, so that the reaction is only available when carefully performed. If the sugar solution increase in K, and there is a material alteration in [α] on ten or twelve minutes' boiling with 2–3 p.c. sulphuric acid or hydrochloric acid, it may safely be inferred that a high sugar (di- or tri-) is present. Some organic acids act differently on the high sugars. Dilute citric acid inverts sucrose; it is without action, at least material action, in a short time on lactose (Jones, *l.c.*).

The invertive action of acids—except under well-defined conditions, such as the employment of hydrochloric acid by Clerget in hydrolysing sucrose—cannot, for the reason mentioned above, be employed in estimating these sugars.

Dextrose and substances capable of yielding it can be detected by acting on the material with nitric acid (1 pt. mat. 1 pt. H_2O and 5 pts. nitric acid, sp.gr. 1·15). Saccharic acid, recognisable by the microscopic appearance of its acid potassium salt, is produced (Sohst a. Tollens, *A.* 245, 1). Lævulose, galactose, sorbose, and arabinose do not yield this acid (Gans, Stone, a. Tollens, *B.* 21, 2148). Galactose, lactose, and raffinose, on treatment with nitric acid in the same way, yield mucic acid. This reaction has some quantitative value. Pasteur (*C. R.* 42, 349) obtained 75 to 78 p.c. mucic acid from galactose. The yield, however, varies very considerably with the quantity and strength of the acid employed. Kent a. Tollens (*A.* 227, 221) find on employing 1 pt. sugar, 12 pts. nitric acid, sp.gr. 1·15, allowing to crystallise in 1·5 to 2·0 pts. solution, and washing with 5 pts. water that galactose gives 77·4 p.c. mucic acid. Lactose treated in the same way gives 40 p.c., and raffinose (Rischbieth a. Tollens, *A.* 232, 172) 22–23 p.c. By using 1 g. dry sugar, or a quantity equal thereto, in a concentrated syrup, 4 g. nitric acid sp.gr. 1·25–1·24, heating gently until red fumes began to be evolved, then allowing the reaction to proceed until the violence was over, heating on a water-bath until red fumes ceased to be evolved, allowing to stand for 24 hours to crystallise, I obtained 73 p.c. mucic acid from galactose, 36·9 p.c. from dry lactose, and 28–30 p.c. from dry raffinose (O'Sullivan, *C. J.* 1886, 73). The mucic acid was collected on a tared filter, washed carefully with 50 c.c. water, dried in a vacuum over sulphuric acid, then at 100°, and weighed. By treating 0·5 g. mucic acid in the same way, the loss was 0·04–0·05 g. Corrected for this the above numbers become 80–81 p.c. for galactose and 40·5–41·5 p.c. for lactose. The number for raffinose was corrected.

The pentoses, and bodies from which they can be obtained, yield on digestion with strong hydrochloric acid, furfural, the detection of which is simple and definite. This reaction has been employed in the estimation of these sugars. It must not, however, be forgotten that the hexoses also yield furfural, although, no doubt, in very small quantities (Günther a. Tollens, *B.* 23, 1751; de Chalmot a. Tollens, *B.* 24, 694; Stone, *B.* 24, 3019). The first difficulty to overcome was to determine the conditions under which the greatest yield of furfural was obtainable, the next to accurately determine the furfural. 2 to 5 g. of the material are digested with 100 c.c. hydrochloric acid, sp.gr. 1·06, and then distilling, returning the distillate until the reaction is complete; or the mixture of material and acid is submitted to distillation in a flask over a small flame, so that not more than 10 c.c. distillate pass over in five minutes, fresh acid being regularly added until a sample of the distillate ceases to give the reaction for furfural. The distillate is then neutralised with soda, acidified with a few drops of acetic acid, and made up to a definite volume. In this the furfural is estimated by a standard solution of phenylhydrazine, made by dissolving 2 g. phenylhydrazine chloride with 6 g. sodium acetate in 1 litre water. This is standardised with a solution of furfural of known strength (1 g. pure furfuramide in a little acetic acid to 1 ltr. water). Standardisation must be made before each set of determinations, as the phenylhydrazine solution loses its value in a short time. The titration is performed as follows: 25 c.c. of the distillate are mixed with a measured quantity of the phenylhydrazine solution, the mixture rapidly boiled and cooled; a little of the solution is filtered and boiled with twice its volume of Fehling's solution; if the phenylhydrazine is in excess reduction takes place, but if furfural is in excess there is no reduction. Trials are made until the equivalent amount of phenylhydrazine solution is found (Stone, *l.c.*). The dilute acidified solution is precipitated with phenylhydrazine acetate, the hydrazide collected on an asbestos filter and dried in a vacuum in a specially-constructed apparatus at 50°–60° until the weight becomes constant. The precipitation is always effected in the same volume of solution, so that allowance can be made for the solubility of the hydrazide. Arabinose yields on an average 48·72 p.c. and zylose 56·25 p.c. furfural (de Chalmot a. Tollens).

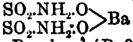
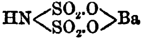
9. *The action of alkalis.* This can only be applied as a rough qualitative test. All the hexoses yield a brown colouration when boiled for a few minutes with a 3-4 p.c. solution sodium hydroxide. The '-on' sugars are not affected.

10. *The action of phenylhydrazine.* The melting-point of the osazones and hydrazides and composition thereof give good indication of the nature of the sugar whence they are prepared. For preparation and melting-point see individual sugars. Maquenne (*C. R.* 112, 799) finds that different sugars yield, with excess of phenylhydrazine, very different quantities of osazones. By heating 1 g. each sugar for one hour at 100° with 100 c.c. water, and 5 c.c. of a solution of phenylhydrazine acetate, containing in 1 litre 400 g. phenylhydrazine and 400 g. glacial acetic acid, cooling, collecting the precipitate, washing with 100 c.c. water and drying at 110°, he found sorbose gave 0·82 g., lævulose 0·70, xylose 0·40, dry dextrose 0·32, arabinose 0·27, galactose 0·23, rhamnose 0·15, lactose 0·11, maltose 0·11. There must, however, be some error or misunderstanding here, as there is no difficulty in getting 120

c. osazone from arabinose and more than 130 p.c. rom lævulose. C. O'S.

SULPHACETIC ACID *v.* Sulphoacetic acid.

SULPHAMIC ACID and **SULPHAMATES** $SO_2.NH_2.OH$ and $SO_2.NH_2.OM^I$. (*Amidosulphonic acid* and *Amidosulphonates.*) By passing dry NH_3 over SO_3, Rose (*P.* 33, 81; 47, 471; 49, 183) obtained a compound $SO_3.2NH_3$. This compound, called by Rose '*sulphatammon*,' is generally described as ammonium sulphamate $SO_2.NH_2.ONH_4$, but Divers a. Haga (*C. J.* 61, 948) have shown, fairly conclusively, that the compound is tri-ammonium imidosulphonate $(N(NH_4)(SO_2.ONH_4)_2$ $[=2SO_3.4NH_3]$; this salt is described under *Imidosulphonic acid and its salts* (*v.* Sulphonic acids and derivatives, p. 600).

Barium sulphamate  $\left.\begin{matrix}SO_2.NH_2.O\\SO_2.NH_2.O\end{matrix}\right>Ba$ seems to have been obtained by Berglund (*B.* 9, 1896) by boiling an aqueous solution of barium imidosulphonate  $HN\left<\begin{matrix}SO_2.O\\SO_2.O\end{matrix}\right>Ba$ (*v. Imidosulphonic acid* under Sulphonic acids and derivatives, p. 600) till the solution reacted strongly acid, adding excess BaOAq, boiling so long as NH_3 came off, filtering, removing excess of Ba by passing in CO_2, filtering, evaporating the filtrate to a small bulk, and allowing to stand. The salt crystallises in long, lustrous needles; it is not changed by heating to 200°, nor by boiling in solution, even in presence of HClAq.

Berglund (*l.c.*) says that a solution of *potassium sulphamate* is obtained by the reaction of nascent hydrogen with potassium oxyamidosulphonate (*v. Oxyamidosulphonic acid* under Sulphonic acids and derivatives, p. 602), thus: $NHOH.SO_2.OKAq + 2H = NH_2.SO_2.OKAq + H_2O$. B. was unable to isolate the salt. Raschig (*A.* 241, 176) obtained the *potassium salt* $SO_2.NH_2.OK$ by boiling potassium imidosulphonate $NH(SO_2.OK)_2$ with a little water for some time, removing the H_2SO_4 that was produced by $CaCO_3$, filtering from $CaSO_4$, evaporating, pouring off from K_2SO_4 that separated, and allowing the syrupy mother-liquor to crystallise. The salt separated in large colourless, rhombic crystals. In 1878 Berglund prepared several sulphamates, viz. the salts of NH_4, Cd, Ca, Co, Cu, Pb, Li, Mn, Ni, Ag, Na, Sr, Tl, and Zn (*Lunds Universitets Årsskrift*, 13; abstract in *Bl.* [2] 29, 422).

Sulphamic acid $SO_2.NH_2.OH$. This acid was obtained by Berglund (*l.c.*) by passing H_2S into a solution of the silver salt, filtering from Ag_2S, and evaporating over H_2SO_4. It forms large, translucent, rhombic crystals; the ratio *a*:*b*:*c* = ·9945:1:1·056 (Raschig, *A.* 241, 178). Easily sol. water, less sol. alcohol; aqueous solution only slowly decomposed to $NH_4.H.SO_4$ on boiling; more rapidly decomposed if HClAq is added; not decomposed by heating to 190° (B., *l.c.*). A solution of the acid gives no pp. with BaOAq; on boiling with HClAq and $BaCl_2Aq$ a pp. of $BaSO_4$ gradually forms. Raschig (*l.c.* p. 209) obtained sulphamic acid by saturating a solution of hydroxylamine hydrochloride with SO_2, allowing to stand for a little, and then evaporating on a water-bath $(NH_2OH.HClAq + H.SO_2.OHAq = NH_2.SO_2.OHAq + HClAq + H_2O)$.

SULPHAMIDE $SO_2(NH_2)_2$. (*Sulphonamide. Sulphurylamide.*) The neutral amide of sulphuric acid is obtained by passing dry NH_3 into cooled SO_2Cl_2, diluted with 15 to 20 vols. $CHCl_3$, to complete saturation, dissolving the pp. so produced in water, making strongly acid by HNO_3Aq, ppg. Cl as AgCl by addition of $AgNO_3Aq$, filtering, neutralising by KOHAq, and again ppg. by $AgNO_3Aq$, filtering from SO_2NAg (*v.* Sulphimide, p. 587), adding more $AgNO_3Aq$ and then KOHAq, warming and then cooling quickly, and collecting the pp. that forms. This pp. consists chiefly of $SO_2(NHAg)_2$, but there is a small quantity of another Ag salt which must be removed. This is done by washing well, adding exactly enough HClAq to convert all Ag into AgCl, neutralising by NH_3Aq, adding $AgNO_3Aq$, filtering from the pp. of the foreign Ag salt, adding more $AgNO_3Aq$ and then excess of NH_3Aq, when pure $SO_2(NHAg)_2$ is ppd. The salt is decomposed by exactly the proper quantity of HClAq, AgCl is filtered off, the filtrate is evaporated *in vacuo* at a temperature not above 40°, and the liquid is allowed to remain *in vacuo* over H_2SO_4, when $SO_2(NH_2)_2$ separates in large, colourless crystals (W. Traube, *B.* 26, 607). Sulphamide is very sol. water, less sol. dilute alcohol, insol. alcohol, ether, and other ordinary organic solvents; it softens at 75° and melts at 81°, begins to give off NH_3 below 100°, no further decomposition occurring to 250°; above 250° gives off acid vapours, and is completely decomposed. An aqueous solution of sulphamide is neutral; boiled with acids it gives H_2SO_4Aq and NH_3. Solutions of alkalis split off NH_3 and form alkali salts of $SO_2.OH.NH_2$. Small quantities of H_2SO_4Aq are formed after prolonged boiling. By adding $AgNO_3Aq$ to solutions of sulphamide, and then NH_3Aq, a pp. of $SO_2(NHAg)_2$ is formed; other metallic derivatives of $SO_2(NH_2)_2$ exist, but have not yet been isolated satisfactorily.

Imido-sulphamide $NH(SO_2.NH_2)_2$ *v.* Sulphimido-amide (p. 587). M. M. P. M.

SULPHAMINE-BENZOIC ACID *v. Amide of o*-sulpho-benzoic acid.

SULPHAMMONIC ACIDS AND SALTS *v.* Sulphur oxyacids, nitrogen derivatives of, p. 619.

SULPHANILIC ACID *v.* vol. i. p. 154.

SULPHANTIMONATES, &c. For such salts as *sulphantimonates*, *sulpharsenates*, *sulphophosphates* *v.* *Thio-antimonates* &c., under Antimonates &c.

SULPHATAMMON and **PARASULPHATAMMON** *v. Tri-ammonium imidosulphonate* and *Di-ammonium imidosulphonate* under *Imidosulphonic acid and salts*, a section of Sulphonic acids and derivatives, p. 600.

SULPHATES *and allied salts. Salts of sulphuric acid* H_2SO_4. The compositions of the normal sulphates are expressed by the general formulæ $M_2^ISO_4$, $M^{II}SO_4$, $M^{III}_2(SO_4)_3$, and $M^{IV}(SO_4)_2$; the greater number of the acid sulphates come under such formulæ as M^IHSO_4, $M^{II}H_2(SO_4)_2$, $M^{III}H(SO_4)_2$, $M^{IV}H_2(SO_4)_3$. All sulphates, whether normal, acid, or basic, may be represented by the formula $nMO.mSO_3.xH_2O$, where MO stands for a basic oxide. The sulphates are prepared (1) by the interaction of H_2SO_4Aq with metals, metallic oxides, or hydroxides; some metals react with dilute H_2SO_4Aq, giving sulphates and H, others react only with not conc. H_2SO_4, giving sulphates and SO_2, or SO_2 and H_2S, and sometimes H also; (2) by the interaction of H_2SO_4Aq with salts of volatilisable or decomposable acids, e.g. with chlorides, nitrates, or carbonates; (3) by the direct combination of SO_3 with metallic oxides; (4) by oxidising sulphides, by boiling with HNO_3Aq, or by reacting with Cl in presence of water, or sometimes by heating in air, e.g. $FeSO_4$, $CuSO_4$, and $ZnSO_4$; (5) by double decomposition from other sulphates, e.g. $BaSO_4$, $PbSO_4$. Most of the metallic normal sulphates are soluble in water; $BaSO_4$ is insol. water, $PbSO_4$ and $SrSO_4$ nearly insol., and $CaSO_4$ very slightly soluble. The basic sulphates are generally insoluble in water. Sulphates of metals whose oxides are strong bases—the alkali and alkaline earth metals—are not decomposed by heat alone; the sulphates of metals whose oxides are weak bases are decomposed by heating, giving off SO_3, or SO_2 and O, and leaving oxides, or metals if the oxides are reducible by heat. Sulphates are reduced by heating with charcoal, either to sulphides or oxides, with evolution of CO and CO_2, and also SO_2 from the sulphates of weak bases. Many sulphates are decomposed completely by heating with HCl gas, giving chlorides (*v.* Hensgen, *B.* 9, 1671; 10, 259). Fusion with excess of alkali carbonate produces alkali sulphate and carbonate of the metal of the original sulphate. Many sulphates are reduced by strongly heating in a stream of NH_3, yielding sulphides, oxides, metal, or mixtures of these (*v.* Hodgkinson a. Trench, *C. N.* 66, 223). Several sulphates occur as minerals; *e.g.* $BaSO_4$ (*heavy spar*), $CaSO_4$ (*gypsum*), $SrSO_4$ (*celestine*), $MgSO_4$ (*Epsom salts*), &c.

Aluminium sulphates. The *normal salt* $Al_2(SO_4)_3.18aq$ occurs native as *feather alum*; it is prepared by heating clay with conc. H_2SO_4Aq and boiling down the solution; also, according to Persoz (*A. Ch.* [3] 56, 102), by adding solution of alum or $AlCl_3$ to a large excess of conc. boiling H_2SO_4, when anhydrous $Al_2(SO_4)_3$ separates as a white powder. Gawalovski (*C. C.* 1885. 721) says that perfect octahedral crystals of $Al_2(SO_4)_3.17aq$ are obtained by saturating H_2SO_4Aq with freshly ppd. AlO_3H_3 and allowing to stand for some months. Crystallises with difficulty from water; crystallisation hastened by adding alcohol in which the salt is insol. (P., *l.c.*). Concerning ppn. of $Al_2(SO_4)_3.xH_2O$ from aqueous solutions by H_2SO_4 *v.* Eremin, *J. R.* 20, 468 (abstract in *C. J.* 56, 347). When heated gives off all water; heated to redness gives off SO_3 and leaves Al_2O_3. Various *basic salts* are known; they are obtained by heating solution of $Al_2(SO_4)_3$ with AlO_3H_3, or by partially ppg. solution of the normal salt by NH_3Aq, or by partial reduction of the normal salt by Zn (*v.* Maus, *P.* 11, 80; Debray, *Bl.* [2] 7, 1; Athanasesco, *C. R.* 103, 271; Crum, *A.* 89, 156; Marguerite, *C. R.* 90, 1354; Löwe, *J. pr.* 79, 428; Bley, *J. pr.* 89, [illegible]).

The *double salts* $Al_2(SO_4)_3.M_2SO_4.24aq$, where $M = NH_4$, Na, K, Rb, Cs, Ag, or Tl, are *alums*. For expansions of alums *v.* Spring, *B.* 15, 1254, 1739; 17, 408.

Ammonia alum $Al_2(SO_4)_3.(NH_4)_2SO_4.24aq$, prepared by adding $(NH_4)_2SO_4$ or NH_4Cl to $Al_2(SO_4)_3Aq$, so that the salts are in equivalent quantities, crystallises in octahedra; S.G. 1·56; S. 5·22 [illegible] at 100°. Heated to 190°, $23H_2O$ is given off and $Al_2(SO_4)_3.(NH_4)_2SO_4.aq$ remains; NH_3 begins to come off at c. 193° (Lupton, *C. J.* [2] 13, 201).

Potash alum $Al_2(SO_4)_3.K_2SO_4.24aq$, prepared by mixing solutions of the two sulphates and evaporating, crystallises in regular octahedra; S.G. 1·7; S. 3·29 at 0°, 9·52 at 10°, 22 at 30°, 31 at 60°, 90 at 70°, 357 at 100°. The crystals effloresce in air. At 190°, $23H_2O$ is given off (L., *l.c.*). Also obtained in cubical crystals (*v.* Polis, *B.* 13, 360). Solution in water has an acid reaction, and dissolves Zn and Fe, giving off H.

Cæsium and rubidium alums *v.* Bunsen, *P.* 119, 1; Godeffroy, *B.* 181, 176; Redtenbacher, *J. pr.* 95, 148. Setterberg (*A.* 211, 100) gives S. in water from 0° to 80° (cf. CÆSIUM, vol. i. p. 658).

Silver alum *v.* Church a. Northcote, *C. N.* 9, 155.

Sodium alum *v.* Pouisin, *Polytech. Centralbl.* 1852. 774; Zellner, *S.* 36, 183; and especially Augé, *C. R.* 110, 1139 (abstract in *C. J.* 58, 1059).

Thallium alum *v.* Lamy, *Bl.* [2] 11, 210. The double salts of $Al_2(SO_4)_3$ with $FeSO_4$, $MgSO_4$, $MnSO_4$, and $ZnSO_4$ also crystallise with $24H_2O$. For double salts with $Fe_2(SO_4)_3$, $Mn_2(SO_4)_3$, and $Cr_2(SO_4)_3$ *v.* Étard (*Bl.* [2] 31, 200). For a double salt with $PbSO_4$ *v.* Bailey (*C. S. I.* 6, 415).

Ammonium sulphates. The *normal salt* $(NH_4)_2SO_4$ is found in certain volcanic districts; it is prepared by neutralising H_2SO_4Aq by NH_3Aq or $(NH_4)_2CO_3Aq$ and evaporating. Crystallises in clear rhombic forms, is isomorphous with K_2SO_4 (Mitscherlich, *P.* 18, 168). S.G. 1·761 (Playfair a. Joule, *C. S. Mem.* 2, 401); for S.G. from 10° to 100° *v.* Spring (*B.* 15, 1940). Melts at c. 140° (Marchand, *P.* 42); decomposes above 280°; according to Johnson a. Chittenden (*Am. S.* [3] 15, 131), gives NH_4HSO_4 and $(NH_4)_2S_2O_7$, and at incipient redness gives SO_3, H_2O, and NH_3. Absorbs dry HCl, forming some NH_4Cl (*v.* Thomas, *C. J.* 33, 372). S. 71 at 0°, 73·65 at 10°, 76·3 at 20°, 78·95 at 30°, 81·6 at 40°, 84·25 at 50°, 86·9 at 60°, 89·55 at 70°, 92·2 at 80°, 94·85 at 90°, 97·5 at 100° (Alluard, *C. R.* 59, 500). Insol. absolute alcohol. For S.G. of $(NH_4)_2SO_4Aq$ from 1 to 50 p.c. $(NH_4)_2SO_4$ *v.* Schiff (*A.* 108, 338; 110, 74). H.F. $[N^2,H^8,S,O^4] = 284,800$ (Thomsen, *J. pr.* 21, 477). The *acid salt* NH_4HSO_4 crystallises from solution of $(NH_4)_2SO_4$ in hot conc. H_2SO_4 in long rhombic prisms, S.G. 1·787 (Schiff, *A.* 107, 83). S. 100 in cold water. Two other acid salts have been isolated: (1) $(NH_4)_3H(SO_4)_2$ $[= 3(NH_4)_2SO_4.SO_3.H_2O$ or $3(NH_4)_2O.4SO_3.H_2O]$ by adding the proper quantity of H_2SO_4 to $(NH_4)_2SO_4Aq$ (Marignac, *Ann. M.* [5] 12, 38); (2) $(NH_4)_2SO_4.7SO_3$ $[= (NH_4)_2O.8SO_3]$ by heating dry $(NH_4)_2SO_4$ with SO_3 to 100° in a closed tube and distilling off excess of SO_3 at c. 60° (Weber, *B.* 17, 2501).

Antimony sulphates. The *normal salt* $Sb_2(SO_4)_3$ is obtained by dissolving Sb_2O_3 in boiling conc. H_2SO_4Aq (c. 98 p.c. H_2SO_4), recrystallising from conc. H_2SO_4, and drying on a porous tile over H_2SO_4. (Adie, *C. J.* 57, 540; where an account of the action of H_2SO_4Aq of different concentrations, and of SO_3, on Sb_2O_3, will be found, with references to older papers).

Barium sulphates. The *normal salt* $BaSO_4$ occurs native as *heavy spar.* Prepared by adding dilute H_2SO_4Aq or dilute solution of a sulphate to solution of a salt of Ba, washing, and drying. A white solid; S.G. 4·525 (G. Rose, *P.* 75, 409; *v.* also Schröder, *P.* 106, 226; a. Wiedemann, *P. M.* [5] 15, 371). Obtained as a crystalline powder by fusing 1 part K_2SO_4 with $4\frac{1}{3}$ parts dry $BaCl_2$ in a closed crucible, and washing with water (Manross, *A.* 82, 348); also by heating dilute $BaCl_2Aq$ with slight excess of H_2SO_4Aq to 245° (Scheerer a. Drechsel, *J. pr.* [2] 7, 63). H.F. $[Ba,O^4,S]$ = c. 338,000 (*Th.* 3, 516). Insol. water; 1 part dissolves in c. 23,000 parts cold, and in c. 4,900 parts hot, HClAq S.G. 1·03, and in c. 9,200 parts HNO_3Aq S.G. 1·02. Struve (*Fr.* 9, 34) gives S. of $BaSO_4$ in conc. H_2SO_4 as 5·69, and 15·89 in Nordhausen acid. $BaSO_4$ is partly decomposed by boiling with conc. solution of an alkali carbonate, or by fusion with alkali carbonate; Spring (*Bl.* [2] 44, 166) found that some $BaCO_3$ was formed by compressing $BaSO_4$ and Na_2CO_3 at a pressure of c. 6,000 atmospheres.

An *acid salt* $BaSO_4.H_2SO_4$ is formed by dissolving $BaSO_4$ in hot conc. H_2SO_4 S.G. 1·843, and heating to 100° (*v.* Garside, *C. N.* 31, 245).

Beryllium sulphates. The *normal salt* $BeSO_4.4aq$ is formed by dissolving $BeCO_3$ in dilute H_2SO_4Aq and concentrating the slightly acid liquid. For crystalline form *v.* Topsöe (*W. A. B.* 66 [2nd part], 5). According to Klatzo (*J. pr.* 106, 233) the salt crystallises with $7H_2O$. Various *basic salts* are obtained by the action of $BeCO_3$ or Zn on solution of the normal salt.

Bismuth sulphates. The *normal salt* $Bi_2(SO_4)_3$ is best prepared by dissolving Bi_2S_3 in conc. H_2SO_4 heated to commencing vaporisation; on cooling the salt separates in lustrous, very deliquescent, needles (Hensgen, *R. T. C.* 4, 401; *cf.* Schultz-Sellack, *B.* 4, 13). For the action of heat on $Bi_2(SO_4)_3$ *v.* Bailey (*C. J.* 51, 680). An *acid salt* $BiH(SO_4)_2.3aq$ was obtained by Leist (*A.* 160, 29) by dissolving Bi_2O_3 in dil. H_2SO_4Aq under definite conditions. *Basic salts* are also formed by the reaction of dilute H_2SO_4Aq with Bi_2O_3 (*v.* Heintz, *P.* 63, 55, 567), and by the action of H_2O on the normal salt (*cf.* Hensgen, *l.c.*).

According to R. H. Adie (*priv. comm.*), acid salts $BiH(SO_4)_2.xaq$ (x = probably $1\frac{1}{2}$ and 3) crystallise from solutions of Bi_2O_3 or $Bi_2(SO_4)_3$ in H_2SO_4Aq of concentrations varying from $H_2SO_4.H_2O$ to c. $H_2SO_4.5H_2O$; from acid of the concentration $H_2SO_4.6H_2O$, a basic salt crystallises, probably $Bi.OH.SO_4.H_2O$.

Cadmium sulphates. The *normal salt* $CdSO_4.aq$ is obtained by dissolving Cd in dilute H_2SO_4Aq, and concentrating, by boiling, the acid solution (von Hauer, *J. pr.* 72, 372). Various other hydrates have been isolated. H.F. $[Cd,S,O^4]$ = 221,550 (*Th.* 3, 516). $CdSO_4$ combines with NH_3 to form various compounds (*v.* H. Rose, *P.* 20, 152; Malaguti a. Sarzeau, *A. Ch.* [3] 9, 431; Isambert, *C. R.* 70, 456; Müller, *A.* 149, 70). Forms *double salts* with $(NH_4)_2SO_4$, $MgSO_4$, and Na_2SO_4; these salts crystallise with 6aq (von H., *l.c.*) The double salt with $Al_2(SO_4)_3$ is an alum.

Cæsium sulphates. *Normal salt* Cs_2SO_4; by neutralising H_2SO_4Aq by Cs_2CO_3 and evaporating. Short needles, not hygroscopic; insol. alcohol; S. 158·7 at −2°. The *acid salt* $CsHSO_4$, formed by reacting on Cs_2SO_4 with excess of H_2SO_4, crystallises in small rhombic prisms (Bunsen a. Kirchoff, *P.* 113, 342).

Calcium sulphates. The *normal salt* $CaSO_4$ occurs native as *anhydrite*, and the dihydrate $CaSO_4.2aq$ as *gypsum*, *alabaster*, and *selenite*. $CaSO_4$ is obtained in crystals by fusing K_2SO_4 with excess of $CaCl_2$ and washing (Manross, *A.* 82, 348; *cf.* Mitscherlich, *P.* 21, 321). $CaSO_4.2aq$ is formed by ppg. fairly conc. $CaCl_2Aq$ by dil. H_2SO_4Aq or solution of a sulphate, evaporating, and washing the solid that separates. $CaSO_4.2aq$ is said to be formed by the interaction of $CaCO_3$ and S moistened with water (Polacci, *G.* 1874. 177, 245). $CaSO_4$ has S.G. 2·964, and $CaSO_4.2aq$ has S.G. 2·31 (*v.* also McCaleb, *Am.* 11, 35). S. for $CaSO_4$, ·19 at 0°, ·206 [illegible]0°, ·214 at 40°, ·208 at 60°, ·195 at 80°, ·174 at 100° (Marignac, *A. Ch.* [5] 1, 274); S. for $CaSO_4.2aq$ ·2119 at 16·5°, ·2352 at 22° (Cossa, *G.* 1873. 135); S. for $CaSO_4.2aq$ in glycerin, ·957 at ordinary temperature, S. increases as temperature rises (Asselin, *C. R.* 76, 884). According to Raupenstauch (*C. C.* 1888. 821) the solubility in water of gypsum increases to 32°, is constant from 32° to 38°, and decreases above 38°. Gypsum loses $2H_2O$ when heated to 80° in a stream of dry air; when the $CaSO_4$ thus produced is moistened it takes up $2H_2O$, becomes crystalline, and expands. The dehydrated $CaSO_4$ obtained by heating gypsum to 160° takes up water very slowly; if the gypsum is heated to c. 300° the $CaSO_4$ formed combines with water with extreme slowness (*v.* Schott, *D. P. J.* 202, 52, 355, 513; *cf. Plaster of Paris*, under CEMENTS, in DICTIONARY OF APPLIED CHEMISTRY, vol. i. p. 468).

According to Potilitzin (*J. R.* 1893 [1] 201, 207) $CaSO_4.2aq$ slowly gives off water at 62°–65° till the hydrate $2CaSO_4.aq$ is formed; $CaSO_4$ prepared by heating $CaSO_4.2aq$ to 130°–170° absorbs H_2O from ordinary air until $2CaSO_4.aq$ is formed when absorption of water ceases. The hydrate $2CaSO_4.aq$ absorbs water from air saturated with moisture, forming $CaSO_4.2aq$. The water of crystallisation of gypsum is not equally firmly retained; P. writes the formula $2CaSO_4.4aq$; three-quarters of the H_2O is much more readily given off than the other fourth. The hydrate $2CaSO_4.aq$ is more soluble in water than the dihydrate $CaSO_4.2aq$.

An *acid salt* $CaH_2(SO_4)_2$ is said by Berzelius to be formed by digesting $CaSO_4$ with H_2SO_4Aq at 80°–100°; it is decomposed by moist air to the normal salt and H_2SO_4. For *double salts* with alkali and alkaline earth sulphates *v.* Fassbender (*B.* 9, 1356; 11, 1968); Struve (*Bl.* [2] 12, 348); Ditte (*C. R.* 84, 86); Popp (*A. Suppl.* 8, 1); Hannay (*C. J.* 32, 399).

Cerium sulphates. The *normal cerous sulphate*, $Ce_2(SO_4)_3.xH_2O$ (x being probably 6, 8, 9, and 12) is obtained in colourless crystals by evaporating a solution of $Ce_2(CO_3)_3$ in dilute H_2SO_4Aq, or a solution of CeO_2 in H_2SO_4Aq saturated with SO_2. The *normal ceric salt* $Ce(SO_4)_2.4aq$ forms, in yellow crystals, from a solution of CeO_2 in dilute H_2SO_4Aq. *Ceroso-ceric sulphates*, $xCe_2(SO_4)_3.yCe(SO_4)_2.2aq$, are obtained by dissolving CeO_2 in conc. H_2SO_4, and evaporating. *Basic salts* are formed by the interaction of water with the normal salts. *Double salts* of $Ce_2(SO_4)_3$ with $(NH_4)_2SO_4$, K_2SO_4, and Na_2SO_4 are known (*v.* Marignac, *A. Ch.* [4] 30, 57; Czudnowicz, *J. pr.* 30, 19; Hermann, *J. pr.* 92, 126; Zschiesche, *J. pr.* 107, 65; Rammelsberg, *B.* 6, 85; Jolin, *Bl.* [2] 21, 523; Wyrouboff, *Bl.* [3] 2, 745; Wing, *Am. S.* [2] 40, 356).

Chromium sulphates. The *normal chromous salt* $CrSO_4.7aq$ was obtained by Moissan (*Bl.* [2] 37, 296) by dissolving the acetate in warm dilute H_2SO_4Aq, crystallising, and drying between paper, all operations being conducted in an atmosphere of CO_2 (for directions for making $Cr(C_2H_3O_2)_2$ *v.* Nitrogen, *Preparation*, vol. iii. p. 557). Blue crystals; isomorphous with $FeSO_4.7aq$. S. 12·35 at 0°; sl. sol. alcohol. Absorbs O rapidly from air, and acts as a strong reducer. A monohydra[illegible]rSO_4.aq was obtained as a white crystalline powder by adding the acetate to excess of conc. H_2SO_4 (M., *l.c.*). Forms a *double salt*, $CrSO_4.K_2SO_4.6aq$ (Péligot, *A. Ch.* [3] 12, 539).

The *normal chromic salt* $Cr_2(SO_4)_3.xH_2O$ exists in two forms. (1) Violet, $x=15$ (Schrötter, *P.* 53, 516), $=18$ (Siewert, *A.* 126, 97); by digesting 1 pt. CrO_3H_3 dried at 100° with 1 to 1¼ pts. conc. H_2SO_4, in a closed vessel, till a mass of greenish-blue crystals is formed, dissolving these crystals in water, ppg. by absolute alcohol, dissolving again in water, adding alcohol till ppn. just begins, covering the vessel with moist parchment-paper, and allowing to crystallise slowly. Regular octahedra; red-violet in reflected light, garnet-red in transmitted light; S. 120 in cold water (Schrötter, *P.* 53, 516; Löwel, *A. Ch.* [3] 40, 42). (2) Green, $x=5$. By heating the violet salt to 100°; the salt melts, gives off water, and then solidifies to a green amorphous mass. Also formed by dissolving CrO_3H_3 in conc. H_2SO_4 at 50°–60°, and evaporating quickly. Easily sol. alcohol; whereas the violet salt is insol. alcohol.

Addition of a cold solution of a Ba salt ppts. all SO_4 from a solution of the violet form, but boiling is needed to complete the ppn. from the green variety. According to Ét[illegible]d (*C. R.* 84, 1089), the difference between the two forms is one of hydration only (but *v.* Chromium salts, vol. ii. p. 167; and *v.* also Recoura, *C. R.* 113, 857).

Basic salts are obtained by adding a little NH_3Aq to solution of the normal salt, also by digesting the normal salt with CrO_3H_3, or excess of CrO_3H_3 with H_2SO_4Aq (*v.* Schrötter, *P.* 53, 516; Siewert, *A.* 126, 97; Schiff, *A.* 1[illegible]4, 167, 172; Recoura, *C. R.* 112, 1439). According to Traube (*A.* 66, 87), an *acid salt*, $Cr_2(SO_4)_3.H_2SO_4$, is formed by heating either variety of the normal salt with excess of H_2SO_4 till vaporisation of the acid begins, and allowing to cool (Schrötter [*l.c.*] regarded this as an insoluble variety of the normal salt); insol. water, not acted on by cold KOHAq, heated strongly gives Cr_2O_3, SO_2, and O.

$Cr_2(SO_4)_3$ forms many *double salts*; those with the alkali sulphates have the composition $Cr_2(SO_4)_3.M_2SO_4.24aq$, and are alums.

Ammonia chrome-alum is ppd. by adding $(NH_4)_2SO_4$ to a saturated solution of violet $Cr_2(SO_4)_3$; also formed by mixing $(NH_4)_2SO_4Aq$ and $Cr_2(SO_4)_3Aq$, and evaporating; also by mixing $Cr_2(SO_4)_3Aq$ (violet) with $(NH_4)_2CrO_4Aq$, adding a little H_2SO_4, and allowing to evaporate. Crystallises in ruby-red octahedra; S.G. 1·738. Effloresces slowly in air. Solution in water is violet; at 75° it becomes green, but slowly returns to violet on standing for some weeks (regarding this change *v.* Chromium salts, vol. ii. p. 167).

Potash chrome-alum is produced similarly to the ammonia salt; also by heating $K_2Cr_2O_7$ with conc. H_2SO_4, more quickly in presence of a reducer, *e.g.* SO_2. Crystallises in large dark-purple octahedra; S. 14·5 in cold water. Solution in water is grey-blue with tinge of red; heated to 70°–80° it becomes green and non-crystallisable, but returns to violet after standing for some weeks. For Soda chrome-alum *v.* Schrötter (*P.* 53, 513). For double salts of $Cr_2(SO_4)_3$ with $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $Mn_2(SO_4)_3$ *v.* Étard (*Bl.* [2] 31, 200); for double salts of the form $Cr_2(SO_4)_3.3M_2SO_4$, where M = Li, K, or Na, *v.* Warnicke (*P.* 159, 572).

For description of other *double salts* of $Cr_2(SO_4)_3$ with alkali sulphates, *v.* Klobb, *C. R.* 117, 311 (Abstract in *C. J.* 64 [ii.], 573).

Cobalt sulphates.—The *normal cobaltous salt* $CoSO_4.7aq$ occurs native as *biberite*; prepared by dissolving Co, CoO, or $CoCO_3$ in dilute H_2SO_4Aq, and evaporating. Forms carmine-red crystals, isomorphous with $FeSO_4.7aq$; S.G. 1·918 at 15° (Thorpe a. Watts, *C. J.* 37, 102). Unchanged in air; loses all water by heating, and gives $CoSO_4$ as a red powder, not decomposed easily by heat; S.G. 3·472 at 15° (T. a. W., *l.c.*). Klobb (*C. R.* 114, 836) obtained the anhydrous salt in crystals by mixing $CoSO_4.7aq$ with excess of $(NH_4)_2SO_4$ and heating in a partly-closed crucible, out of contact with the gases of the flame, till $(NH_4)_2SO_4$ was all volatilised. The hexahydrate $CoSO_4.6aq$ separates from solutions of Co or $CoCO_3$ in H_2SO_4Aq at 40°–50°; it is isomorphous with the corresponding salts of Mg, Ni, and Zn (Marignac). For other hydrates, with 4aq and aq, *v.* Fröhde (*J.* 1866. 244); Vortmann (*B.* 15, 1888). $CoSO_4.7aq$ is insol. alcohol; S. water 30·5 at 10°, 36·4 at 20°, 40 at 29°, 46·3 at 35°, 55·2 at 50°, 60·4 at 60°, 65·7 at 70° (stated as parts $CoSO_4$ dissolved by 100 parts water; Tobler, *A.* 95, 193). Thomsen (*Th.* 3, 516) gives H.F. $[Co,S,O^4,7H_2O]=234,000$. By electrolysing $CoSO_4Aq$ in presence of K_2SO_4 and H_2SO_4, under special conditions, Marshall obtained $Co_2(SO_4)_3$ along with $K_2S_2O_8$ (*C. J.* 59, 760).

Basic salts are formed by addition of a little NH_3Aq to hot $CoSO_4Aq$, also by digesting $CoSO_4Aq$ with $CoCO_3$ (*v.* Habermann, *M.* 5, 442; Athanasesco, *C. R.* 103, 271).

For *double salts* with $FeSO_4$, $MgSO_4$, $MnSO_4$, and $ZnSO_4$ *v.* Vohl (*A.* 94, 57).

Normal cobaltic sulphate $Co_2(SO_4)_3$ was obtained by Marshall (*C. J.* 59, 767) by electrolysing $CoSO_4Aq$ in presence of H_2SO_4, under special conditions. A blue crystalline powder, unchanged in a stoppered bottle in ordinary air, but decomposes rapidly in dry air; sol. water, with evolution of O; sol. conc. H_2SO_4; in HClAq forms $CoCl_2$ and gives off Cl.

Copper sulphates. Only salts corresponding with the oxide CuO have been isolated. The *normal salt* $CuSO_4$ is obtained by dissolving Cu in hot conc. H_2SO_4, decanting the hot solution, and allowing to cool; also by adding conc.

H_2SO_4 to $CuSO_4$.aq, also by heating powdered crystals of $CuSO_4$.5aq to c. 230° as long as they lose weight. Klobb (*C. R.* 114, 836) obtained $CuSO_4$ in crystals by heating a mixture of the hydrated salt and excess of $(NH_4)_2SO_4$ in a partly closed crucible till all $(NH_4)_2SO_4$ had volatilised. A white crystalline powder; S.G. 3·606 at 15° (Thorpe a. Watts, *C. J.* 37, 102). Partly decomposed at red heat, wholly at white heat, to SO_2, O, and CuO. Reduced by heating to redness with charcoal, giving Cu, SO_2, and CO_2. At a higher temperature some CuS is said to be formed; also reduced to Cu by heating in H; heated in PH_3 gives off H_2O, and leaves a mixture of sulphide and phosphide of Cu. HCl gas forms $CuCl_2$ and H_2SO_4. $CuSO_4$ acts as a powerful dehydrating agent; it rapidly absorbs water, forming $CuSO_4$.5aq. H.F.$[Cu,S,O^4]$ = 182,500 (*Th.* 3, 516).

The *pentahydrate* $CuSO_4$.5aq (*blue vitriol*) is prepared by dissolving Cu in hot conc. H_2SO_4, evaporating, and recrystallising from water the solid that separates. At. c. 20° there is a very slight reaction, with formation of Cu_2S and $CuSO_4$; at c. 270° the reaction is $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$ (Pickering, *C. J.* 33, 112). According to Anthion (*R. P.* 81, 344), $CuSO_4$.5aq free from nitrate, is obtained by dissolving Cu in a warm mixture of dilute H_2SO_4Aq and HNO_3Aq, and crystallising. (For preparation of commercial blue vitriol *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. i. p. 608.) Large blue, triclinic crystals; S.G. 2·284 at 15° (Thorpe a. Watts, *C. J.* 37, 102). Solubility in water is given by Poggiale (*A. Ch.* [3] 8, 463) as follows:—

	S.	
Temp.	$CuSO_4$.5aq	$CuSO_4$
0°	31·61	18·20
10	36·95	20·92
20	42·31	23·55
30	48·81	26·63
40	56·90	30·29
50	65·83	34·14
60°	77·39	38·83
70	94·40	45·06
80	118·03	53·15
90	156·44	64·23
100	203·32	75·25

Gerlach (*D. P. J.* 181, 129) gives the following table:—

Percentage $CuSO_4$.5aq	S.G. of solution
2	1·0126
4	1·0254
6	1·0384
8	1·0516
10	1·0649
12	1·0785
14	1·0933
16	1·1063
18	1·1208
20	1·1354
22	1·1501
24	1·1659

Insol. absolute alcohol; S. in 40 p.c. alcohol at 15° = ·25 (Schiff). Fairly sol. glycerin. Effloresces in dry air, giving off $2H_2O$; heated for some time to 100° loses $4H_2O$, the last H_2O is removed at c. 230°. For dissociation-pressures of water given off at various temperatures *v.* Lescœur (*C. R.* 102, 1466). Solution in HClAq gives $CuCl_2.2H_2O$ on evaporation. The dry salt, in powder, absorbs HCl, the water of crystallisation being set free (Kane, *A.* 19, 1); several compounds of $CuSO_4$, HCl, and H_2O are formed according to Latschinoff (*J. R.* 1888 [1] 586, 657, 707; abstract in *B.* 22 *Ref.* 192). Combines with NH_3, forming $CuSO_4.5NH_3$, all water of crystallisation being removed (L., *l.c.*).

Other hydrated copper sulphates are (1) $CuSO_4$.6aq and (2) $CuSO_4$.7aq, obtained by Lecoq de Boisbaudran (*C. R.* 65, 1240), the former by placing a crystal of $NiSO_4$.4aq in a warm supersaturated solution of $CuSO_4$.5aq, to which a few drops of H_2SO_4Aq had been added, and the latter by placing a crystal of $FeSO_4$.7aq in the mother-liquor from the first-named hydrate; (3) $CuSO_4$.3aq, by keeping $CuSO_4$.5aq in dry air at 25°–30° (Magnier de la Source, *C. R.* 83, 899); also by pouring cold conc. $CuSO_4$Aq into H_2SO_4Aq, S.G. 1·7, and washing the pp. with small quantities of absolute alcohol (Thorpe a. Watts, *C. J.* 37, 104); (4) $CuSO_4$.2aq by keeping the pentahydrate *in vacuo* at 20° for some days, or by pouring conc. $CuSO_4$Aq into cold conc. H_2SO_4, and washing the pp. with absolute alcohol (T. a. W., *l.c.*); (5) $CuSO_4$.aq by heating powdered pentahydrate at 110° till it ceases to lose weight (T. a. W., *l.c.*). T. a. W. (*l.c.*) give the S.G. of these hydrates, at 15°, as: monohydrate, 3·289; dihydrate, 2·953; trihydrate, 2·663. Lescœur (*C. R.* 102, 1466) obtained only the penta-, tri-, and monohydrates.

Double salts with the alkali sulphates, of the form $CuSO_4.M_2SO_4$.6aq, are obtained by crystallising mixtures of the constituents in the proper proportions (*v.* Graham, *P. M.* 1835. 327, 417; Brunner, *P.* 15, 476; 32, 221; Pickering, *C. J.* 49, 1). Vohl (*A.* 94, 57) has described several *triple salts* of the form $CuSO_4.MSO_4.2X_2SO_4$.12aq, where M = Fe, Zn, &c., and X = an alkali metal; and also *quadruple salts* $CuSO_4.2MSO_4.3X_2SO_4$.18aq. Double salts of the form $CuSO_4.MSO_4.x$aq, x being 5 and 7, and M being Co, Fe, Mg, Ni or Zn, are described (*v.* Rammelsberg, *P.* 91, 321; also Lefort, *A. Ch.* [3] 23, 95; von Hauer, *P.* 125, 638). Several *basic salts* of the form $CuSO_4.xCuO$.aq are known:—$x = 1$, *v.* Roucher (*J. Ph.* [3] 37, 249); $x = 2$, *v.* Reindel (*J. pr.* 100, 1; 102, 204), Persoz (*A. Ch.* [3] 25, 257), Shenstone (*C. J.* 47, 375); $x = 3$, *v.* Smith (*J.* 25, 280), Pickering (*C. J.* 43, 336; 49, 1), Grimbert a. Barré (*J. Ph.* [5] 21, 414), Kühn (*Ph. C.* 1847. 595), Kane (*A.* 19, 1); $x = 4$, *v.* Smith (*l.c.*); $x = 7$, *v.* Pickering (*l.c.*). For other basic sulphates *v.* Steinmann (*B.* 15, 1411), Brunner (*P.* 15, 476; 32, 221), Becquerel (*C. R.* 67, 1081), Casselmann (*Fr.* 4, 24).

Didymium sulphates (*v.* Marignac, *A. Ch.* [3] 58, 148; Cleve, *Bl.* [2] 21, 246; 39, 151; Hermann, *J. pr.* 82, 385; Frerichs a. Smith, *A.* 191, 348). The *normal salt* $Di_2(SO_4)_3$.8aq crystallises in red, lustrous, monoclinic crystals from a solution of Di_2O_3 or $Di_2(CO_3)_3$ in excess of H_2SO_4Aq; S.G. 2·878; S.H. ·1948 (Nilson a. Pettersson, *B.* 13, 1459). Heated to 300° loses all water of crystallisation, leaving $Di_2(SO_4)_3$ as a red powder; S.G. 3·735; S.H. ·1187 (N. a. P., *l.c.*); S. 43·1 at 12°, 11 at 50°, 2 at 100° (Marignac). For effect of heat at various temperatures *v.* Bailey (*C. J.* 51, 682). Hydrates with 6aq and aq crystallise from cold saturated solutions of $Di_2(SO_4)_3$; Marignac (*l.c.*) also obtained a hydrate with 9aq. *Double salts* of the form $Di_2(SO_4)_3.M_2SO_4$.8aq, where M is an alkali metal, are known. *Basic salts* are formed by heating the normal salt, also by adding a little NH_3Aq to solutions of the normal salt.

Gold sulphates. The *normal auro-auric sulphate* $AuSO_4$ was obtained by Schottländer (*A.* 217, 312) by evaporating solution of

AuO.H.SO₄ (*v. infra*) nearly to dryness at 250°, and drying in a desiccator over lime. Lustrous, scarlet prisms, that rapidly absorb moisture from the air, with partial decomposition. A *basic salt* $AuO.H.SO_4$ (*auryl sulphate*) was obtained (S., *l.c.*), as a yellow crystalline powder, by heating $AuO.NO_3$ with conc. H_2SO_4 at c. 200° ($AuO.NO_3$ was formed by dissolving AuO_3H_3 in HNO_3Aq S.G. 1·4, filtering through asbestos, and evaporating under reduced pressure over lime and soda). A *double salt* $AuK(SO_4)_2$ was formed by dissolving $KHSO_4$ in solution of $AuO.H.SO_4$, and evaporating at 200° (*v.* also Allen, *C. N.* 25, 85).

Indium sulphates (*v.* Winkler, *J. pr.* 94, 1; 95, 414; 98, 344; 102, 273; B. Meyer, *A.* 150, 429). The *normal salt* $In_2(SO_4)_3$ is obtained by dissolving In or InO_3H_3 in excess of H_2SO_4Aq, evaporating to dryness, and heating till excess of acid is removed; a white, very hygroscopic powder; S.H. ·129 (Nilson a. Pettersson, *B.* 13, 1459). S.G. 3·438 (N. a. P., *C. R.* 91, 232). By dissolving in water and evaporating, a hydrate with 9aq is obtained as a gummy solid. The solution of In or InO_3H_3 in excess of H_2SO_4Aq yields a syrupy liquid on evaporation which probably contains an *acid salt* (? $In_2(SO_4)_3.H_2SO_4$). By adding $(NH_4)_2SO_4$Aq to solution of $In_2(SO_4)_3$, and evaporating, the *double salt* with the composition $In_2(SO_4)_3.(NH_4)_2SO_4.24aq$ is obtained; this salt is an alum; it is sol. in ½ part water at 16°, and in ¼ part water at 30°. On evaporating the mother-liquor, the salt $In_2(SO_4)_3.(NH_4)_2SO_4.8aq$ is obtained (Rössler, *J. pr.* [2] 7, 13). *Double salts* with K_2SO_4 and Na_2SO_4, crystallising with 8aq, have also been obtained.

Iridium sulphates. By treating IrS_2 with conc. HNO_3Aq, Birnbaum (*A.* 136, 179) obtained an amorphous, brownish-yellow solid, easily sol. water, probably a sulphate of Ir. The *double salt* $Ir_2(SO_4)_3.3K_2SO_4$ was obtained by Lecoq de Boisbaudran (*C. R.* 96, 1406, 1551) by fusing $KHSO_4$ with Ir compounds, treating with water containing $KHSO_4$, dissolving the residue in hot water, and crystallising; green, translucent crystals, probably regular octahedra; almost insol. saturated $KHSO_4$Aq.

Iron sulphates. I. *Ferrous salts.* The *normal salt*, $FeSO_4$, is obtained by heating powdered $FeSO_4$. 7aq very carefully to 300° till it ceases to lose weight (the heating is best done in a stream of H); at a slightly higher temperature SO_2 and O begin to be given off, and finally Fe_2O_3 remains. $FeSO_4$ is a white powder; S.G. 3·346 (Thorpe a. Watts, *C. J.* 37, 102). Several hydrates of $FeSO_4$ are known, ordinary *green vitriol* being the most common and best examined of these; this *heptahydrate*, $FeSO_4$. 7aq, is best prepared by adding iron filings to warm dilute H_2SO_4Aq until the acid is saturated and a little iron remains undissolved, boiling for a little, filtering into a vessel that has been rinsed with a very little conc. H_2SO_4, allowing to crystallise, washing the crystals two or three times with very small quantities of cold water, and then with alcohol till all acid is removed, drying at c. 30°, powdering the dry crystals, and strongly pressing between paper or linen. As thus prepared the salt does not readily oxidise in the air. If alcohol is added to the hot solution, filtered from undissolved iron, $FeSO_4$.7aq is ppd. in minute crystals; if this pp. is washed with alcohol till acid is removed and then spread on filter paper, in dry air, till the alcohol has evaporated, the salt is obtained as a bluish white powder, which does not oxidise except in very moist air. Blue-green, monoclinic crystals; S.G. 1·8889 at 4° (Playfair a. Joule, *C. J.* 1, 138), 1·9854 at 16° (Pape, *P.* 120, 372). H.F. $[Fe,S,O^4,7H^2O] = 240,100$ (*Th.* 3, 516). Heated to 100° gives off $6H_2O$, and at c. 300° leaves $FeSO_4$ (*v. supra*). S. 60·9 at 10°, 70 at 15°, 114·95 at 25°, 227·27 at 46°, 263·15 at 60°, 270·27 at 84°, 370·37 at 90°, 333·33 at 100°. Gerlach (*D. P. J.* 181, 129) gives the following data (*v.* also Schiff, *D. P. J.* 1858. 38):—

S.G. $FeSO_4$Aq	Pctge. $FeSO_4$. 7aq	Pctge. $FeSO_4$
1·0267	5	2·811
1·0537	10	5·784
1·0823	15	8·934
1·1124	20	12·[illegible]
1·1430	25	15·834
1·1738	30	19·622
1·2063	35	23·672
1·2391	40	27·995

Insol. glacial acetic acid and absolute alcohol. $FeSO_4$. 7aq is fairly easily oxidised; exposure to air produces basic ferric sulphates. $FeSO_4$Aq absorbs NO, forming $FeSO_4.xNO$ (x probably $=1$ or ½; *v.* Gay, *A. Ch.* [6] 5, 145, and *cf.* NITRIC OXIDE, vol. iii. p. 563). *Other hydrates of ferrous sulphate* are (1) $FeSO_4$. 4aq, formed by crystallising $FeSO_4$Aq at 80° (Regnault, *A. Ch.* [3] 1, 201), also by exposing finely-powdered $FeSO_4$. 7aq over H_2SO_4, in an atmosphere of CO_2, until it ceases to lose weight (Thorpe a. Watts, *C. J.* 37, 102); S.G. 2·227 (T. a. W.); (2) $FeSO_4$. 3aq, by evaporating $FeSO_4$Aq made strongly acid by H_2SO_4 (Kühn, *S.* 61, 235), also by dissolving $FeSO_4$. 7aq in hot HClAq and crystallising (Kane, *A.* 19, 7); (3) $FeSO_4$. 2aq by boiling the heptahydrate with successive quantities of alcohol; S.G. 2·773 (T. a. W., *l.c.*); (4) $FeSO_4$. aq, by heating powdered $FeSO_4$. 7aq to 120° in H; S.G. 2·994 (T. a. W.; *v.* also Mitscherlich, *P.* 18, 152). Several *double salts of ferrous sulphate* are known; they are generally prepared by crystallising a mixture of the constituent sulphates in the proper proportions. The salts $FeSO_4.M_2SO_4.6aq$, where $M = NH_4$, K, Na, or Tl, form blue-green monoclinic crystals (*v.* Marignac, *Ann. M.* [5] 9, 19; Schiff, *A.* 108, 326; Tobler, *A.* 95, 193; Wilm, *A. Ch.* [4] 5, 56). For the salts $FeSO_4.MSO_4.14aq$, where $M = Mg$ or Zn, *v.* Schiff (*l.c.*), and Murmann (*W. A. B.* 27, 172). For various *triple* and *quadruple salts* containing $FeSO_4$, alkali sulphates, and sulphates of Mn, Mg, Zn, &c., *v.* Bette (*A.* 14, 278) and Vohl (*A.* 94, 57).

II. *Ferric salts.* The *normal salt* $Fe_2(SO_4)_3$ is obtained by adding 1 part conc. H_2SO_4 to 5 parts $FeSO_4$. 7aq dissolved in water, warming, and adding HNO_3Aq little by little till oxidation is complete, evaporating to a syrup, and then heating very cautiously so long as acid fumes are given off; on cooling $Fe_2(SO_4)_3$ remains as a white amorphous solid; S.G. 3·097 at 18° (Pettersson, *Upsala, Nova acta,* 1874). Fairly large quantities of $FeSO_4$. 7aq should be used, as evaporation of a dilute solution containing $Fe_2(SO_4)_3$ produces ppn. of basic sulphates. The hydrate $Fe_2(SO_4)_3$. 9aq occurs native as [illegible] on one occasion Bertels obtained rhombic leaflets of a hydrate with 10aq (*J.* 1874. 268). $Fe_2(SO_4)_3$ is slowly sol. in water; the presence of a very small quantity of $FeSO_4$ causes $Fe_2(SO_4)_3$ to dissolve rapidly in water (Barreswil, *Ph. C.* 1845. 604). $Fe_2(SO_4)_3$ is insol. in conc. H_2SO_4; it is reduced to $FeSO_4$ by most metals, more quickly if a little H_2SO_4 is present. $Fe_2(SO_4)_3$ forms several *double salts*. The compounds $Fe_2(SO_4)_3.M_2SO_4.24aq$, where $M = NH_4$ or K, are alums. **Potash iron alum** $Fe_2(SO_4)_3.K_2SO_4.24aq$ is prepared by dissolving 28 parts $FeSO_4.7aq$ in water, adding 5 parts conc. H_2SO_4, oxidising by HNO_3Aq, adding 8·75 parts K_2SO_4, and crystallising; or by mixing 10 parts powdered $FeSO_4.7aq$ with 4 parts KNO_3, slowly adding 5 parts conc. H_2SO_4, warming so long as NO_2 is given off, dissolving the residue in 4 times its weight of water at 80°, and allowing to stand at 0° for some time (Heintz, *A.* 44, 271). The salt slowly decomposes in the air; heated to 80° it gives $Fe_2(SO_4)_3$, basic ferric sulphate, and H_2SO_4; a similar decomposition occurs when an aqueous solution of the salt is heated (Rose, *P.* 94, 459). Addition of KOHAq to a conc. solution of the salt till a slight permanent pp. is formed, followed by evaporation, produces a double salt of K_2SO_4 with a basic ferric sulphate (*v.* Richter a. Scheerer, *P.* 87, 73). **Ammonia iron alum** is formed similarly to the K salt; loses $23H_2O$ at 150° (*v.* Lupton, *C. J.* 28, 201). For double salts with $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, $Mn_2(SO_4)_3$ and $MnSO_4$, *v.* Étard (*Bl.* [2] 31, 200). Some double compounds of $Fe_2(SO_4)_3$ with $(NH_4)_2SO_4$, and with $FeSO_4$ and $(NH_4)_2SO_4$, are described by Lachaud a. Lepierre (*C. R.* 114, 915).

A great many *basic salts* have been described; generally prepared by the action of air on solutions of $FeSO_4.7aq$, or by heating $Fe_2(SO_4)_3Aq$ in sealed tubes (*v.* Athanasesco, *C. R.* 103, 271). Pickering (*C. J.* 37, 807) gives very full references to all the memoirs on those basic salts, and comes to the conclusion that only one exists, viz. $2Fe_2O_3.SO_3$; in a later paper (*C. J.* 43, 182) he gives reasons for writing the formula rather as $6Fe_2O_3.3SO_3.xH_2O$, or $Fe_2(SO_4)_3.5Fe_2O_3.xH_2O$.

Lanthanum sulphates. The *normal salt* $La_2(SO_4)_3$ is obtained by dissolving La_2O_3 in excess of H_2SO_4Aq, evaporating, drying the crystals of $La_2(SO_4)_3.9aq$ that separate, and heating to dull redness; a white powder, S.G. 3·6 (Nilson a. Pettersson, *C. R.* 91, 232); S.H. ·1182 (N. a. P., *B.* 13, 1459). Much more sol. cold than hot water; Mosander (*P.* 11, 406) gives S. 16·6 at 2°–3°, 2·35 at 25°, ·87 at 100°. The *hydrate* with 9aq, formed by the slow evaporation of La_2O_3 in excess of H_2SO_4Aq, crystallises in large, lustrous, hexagonal prisms (Topsoë); S.G. 2·853 (N. a. P., *C. R.* 91, 232). A hydrate with 6aq was obtained by Frerichs a. Smith (*A.* 191, 331). Several *double salts* with the alkali sulphates have been obtained; the principal are $M.(NH_4)_2SO_4.8aq$, $M.3K_2SO_4$, and $M.4K_2SO_4$, where $M = La_2(SO_4)_3$ (*v.* Cleve, *Bl.* [2] 39, 151; 43, 56). A *basic salt* was obtained by F. a. S. (*l.c.* p. 360).

Lead sulphates. The *normal salt* $PbSO_4$ occurs in various lead ores. It is obtained as a white, heavy powder, by heating Pb with conc. H_2SO_4, by the interaction of warm H_2SO_4Aq and PbO, or of PbO_2 and SO_2, and by ppg. solutions of lead salts by dilute H_2SO_4Aq or solution of a sulphate. $PbSO_4$ is prepared in small rhombic crystals by melting $PbCl_2$ with K_2SO_4, and washing with water. S.G. 6·2 (Schröder, *P. Ergänz. Bd.* 6, 622); 5·96 at 17° (Pettersson, *Upsala, Nova Acta*, 1874). H.F.$[Pb,S,O^4] = 216,200$ (*Th.* 3, 516). Nearly insol. water; Rodwell (*C. N.* 11, 50) says that 31,062 parts water at 15° dissolves 1 part $PbSO_4$. Struve (*Fr.* 9, 34) gives S. in conc. H_2SO_4 as ·13, and S. in Nordhausen acid as 4·19 (*v.* also Kolb, *D. P. J.* 209, 268). For solubility in dilute HClAq and HNO_3Aq *v.* Rodwell (*C. J.* 15, 59); for S. in various salt solutions *v.* Löwe (*J.* 1859. 6[illegible]); Staedel (*J.* 1863. 245); Storer (*C. N.* 21, 17); Dibbits (*Fr.* 1874. 137). Heated to redness, $PbSO_4$ melts without decomposition, but at a white heat it gives PbO, SO_2, and O (Boussingault, *C. R.* 64, 1159). Heated in a stream of H, it is reduced to Pb with evolution of SO_2, H_2S, and steam; heated with charcoal, PbO, PbS, or Pb is formed according to the proportions of the reacting substances. Reduced by Fe or Zn in contact with water. Rubbed with K_2CrO_4 produces $PbCrO_4$; with KIAq yields PbI_2, and with NaCl is partly decomposed to $PbCl_2$ (*v.* Matthey, *Ar. Ph.* [3] 13, 233). For reaction when heated in NH_3 *v.* Rodwell (*C. N.* 15, 137). A *double salt* $PbSO_4.(NH_4)_2SO_4$ is formed by adding excess of H_2SO_4Aq to $Pb(C_2H_3O_2)_2Aq$, neutralising excess of acid by NH_3Aq, boiling, and allowing to cool. *An acid salt* $PbSO_4.H_2SO_4.aq$ was obtained by Schultz (*P.* 133, 137) by dissolving $PbSO_4$ in conc. H_2SO_4 and setting aside. A *basic salt* $PbSO_4.PbO$ is formed by digesting $PbSO_4$ with NH_3Aq (Kühn, *Ar. Ph.* [2] 50, 281).

Lithium sulphates. The *normal salt* Li_2SO_4 is obtained by dissolving Li_2CO_3 in H_2SO_4Aq, evaporating, drying the crystals of $Li_2SO_4.aq$ that separate, and heating them to c. 135°. S.G. 2·21 at 15° (Brauner, *P. M.* [5] 11, 67). Melts at 818° (Carnelley, *C. J.* 33, 280). S. 35·34 at 0°, 34·36 at 20°, 32·8 at 45°, 30·3 at 65°, 29·24 at 100° (Kremers, *A.* 99, 47). Easily sol. alcohol; insol. SO_3 (Weber). H.F.$[Li^2,S,O^4] = 333,200$ (*Th.* 3, 516). Heated in HCl gas below redness gives LiCl (Hensgen, *B.* 8, 125). The *monohydrate* $Li_2SO_4.aq$ crystallises in monoclinic forms (Rammelsberg, *P.* 128, 311). S.G. 2·052 at 21° (Pettersson, *Upsala, Nova Acta*, 1874). Effloresces a little in air, gives up water at a little above 130°. An *acid salt* $LiHSO_4$ is obtained by dissolving Li_2SO_4 in H_2SO_4Aq S.G. 1·6 to 1·7 (Schultz, *P.* 130, 149); prismatic crystals, melting at c. 120° (Lescœur, *Bl.* [2] 24, 516). *Double salts* with K_2SO_4 are obtained by evaporating mixed solutions of the constituent salts (*v.* Rammelsberg, *A.* 128, 311; Schabus, *J.* 1854. 323). For double salts with Rb_2SO_4 and Na_2SO_4 *v.* Wyrouboff (*Bull. soc. minéral. de France*, 1882. part 2). Wernicke (*P.* 159, 576) describes a salt $3Li_2SO_4.Cr_2(SO_4)_3$ formed, in green needles, by adding Cr_2O_3 to molten $LiHSO_4$. Li_2SO_4 does not form alums, nor does it combine with the magnesian sulphates (Rammelsberg, *l.c.*; Scheibler, *J. pr.* 67, 485).

Magnesium sulphates. The *normal salt* $MgSO_4$ is obtained by dissolving MgO or $MgCO_3$ in H_2SO_4Aq (or by heating *dolomite* till CO_2 is removed, treating with HClAq, which dissolves CaO, and dissolving the residual MgO in H_2SO_4Aq), evaporating, crystallising out $MgSO_4$.7aq, drying this salt, and heating it gradually to c. 300° till it ceases to lose weight. A white solid; S.G. 2·709 at 15° (Thorpe a. Watts, *C. J.* 37, 102); 2·77 to 2·795 at 14° (Pettersson, *Upsala, Nova Acta*, 1876). H.F. [Mg,S,O^4] = 302,300 (*Th.* 3, 516). [$MgSO^4$,Aq] = 20,765 (Pickering, *C. J.* 47, 100). Decomposed to MgO, SO_2, and O at c. 360° (*v.* Bailey, *C. J.* 51, 682). Not acted on by HCl gas below incipient red heat (Hensgen, *B.* 9, 1671; 10, 259). The *heptahydrate* $MgSO_4$.7aq (*Epsom salts*) occurs in many mineral springs, in sea water, and in some rocks. It crystallises at the ordinary temperature from solutions of MgO or $MgCO_3$ in H_2SO_4Aq. Translucent, rhombic prisms; from supersaturated solutions crystallises in hexagonal forms, and from solutions containing some $FeSO_4$ in monoclinic forms (*v.* Marignac, *Ann. M.* [5] 12, 50). S.G. 1·678 at 15° (Thorpe a. Watts, *C. J.* 37, 102); 1·683 at 4° (Playfair a. Joule, *C. J.* 1, 138). H.F. [$Mg,S,O^4,7H^2O$] = 326,400 (*Th.* 3, 516). Melts at 70° (Tilden, *C. J.* 45, 267); gives up $6H_2O$ by prolonged heating at 150°–160°, and all water of crystallisation at c. 280° (*v.* Pickering, *C. J.* 47, 100). The following data for solubility in water are calculated by Mulder from observations by Gay-Lussac, Tobler, and others:—

Temp.	S.	Temp.	S.
0°	25·76	60°	55·0
5	29·3	65	57·3
10	31·5	70	59·6
15	33·8	75	61·9
20	36·2	80	64·2
25	38·5	85	66·5
30	40·9	90	68·9
35	43·3	95	71·4
40	45·6	100	73·8
45	48·0	105	76·2
50	50·3	108·4	77·9
55	52·7		

Gerlach (*Fr.* 8, 287) gives the following:—

P.c. $MgSO_4$	S.G. $MgSO_4$Aq	P.c. $MgSO_4$	S.G. $MgSO_4$Aq
1	1·01031	14	1·15083
2	1·02062	15	1·16222
3	1·03092	16	1·1[illegible]20
4	1·04123	17	1·18618
5	1·05154	18	1·19816
6	1·06229	19	1·21014
7	1·07304	20	1·22212
8	1·08379	21	1·23465
9	1·09454	22	1·24718
10	1·10529	23	1·25972
11	1·11668	24	1·27225
12	1·12806	25	1·28478
13	1·13945		

S. at 15° in 10 p.c. alcohol 39·3, 20 p.c. alcohol 21·3, 40 p.c. alcohol 1·62 (Schiff, *A.* 118, 365). Heated with NaCl gives off HCl, leaving Na_2SO_4, $MgCl_2$ and some $MgSO_4$ (Ramon de Luna, *J. pr.* 66, 256). Decomposed, almost entirely, by heating in steam, giving off H_2SO_4 and leaving MgO (Clemm, *J.* 1864. 764). Strongly heated with charcoal gives off SO_2 and CO_2 (or CO), and leaves MgO. Mixed with NaCl and heated in steam gives Na_2SO_4, MgO, and HCl.

Other hydrates of magnesium sulphate. (1) $MgSO_4$.aq occurs native as *kieserite*, S.G. 2·281 at 16° (Pape, *P.* 120, 369); dissolves slowly in cold water, easily in boiling water, forming $MgSO_4$.7aq; prepared by heating the heptahydrate for a long time at 150°–160° (Pickering, *C. J.* 47, 100); S.G. 2·445 (Thorpe a. Watts, *C. J.* 37, 102). (2) $MgSO_4$.6aq, by crystallising a solution of the heptahydrate above 40°; S.G. 1·734 (T. a. W., *l.c.*). (3) $MgSO_4$.5aq, by drying the heptahydrate over conc. H_2SO_4; S.G. 1·869 (T. a. W., *l.c.*). (4) $MgSO_4$.2aq, by boiling powdered $MgSO_4$.7aq with absolute alcohol; S.G. 2·373 (T. a. W., *l.c.*). (5) According to Jacquelain (*A. Ch.* [3] 32, 201), the hydrates 4M.7aq, 4M.9aq, and 2M.5aq exist (M = $MgSO_4$).

Acid salts. Schiff (*A.* 106, 115) obtained deliquescent, hexagonal plates, $MgSO_4.H_2SO_4$, from a solution of $MgSO_4$ in hot conc. H_2SO_4; according to Schultz (*P.* 130, 149), the crystals are $MgSO_4.3H_2SO_4$.

Double salts. With K_2SO_4, or $(NH_4)_2SO_4$, to form compounds $MgSO_4.M_2SO_4$.6aq; by crystallising mixtures of the component salts in proper proportion. For solubility and S.G. of solution of the K_2SO_4 compound, *v.* Tobler (*A.* 95, 193), Schiff (*A.* 113, 183), Gerlach (*Fr.* 8, 287). The compound of $MgSO_4$ and Na_2SO_4 contains 4aq (*cf.* van't Hoff a. Deventer, *B.* 19, 2144). The compound $MgSO_4$.KCl.3aq occurs native as *kainite* (*v.* Reichardt, *Ar. Ph.* 159, 204; Erlenmeyer, *B.* 2, 289). A double salt $MgSO_4.Al_2(SO_4)_3.xH_2O$ occurs as *feather alum*, and *pickeringite*. Some *triple salts* of $MgSO_4$ with $CaSO_4$ and K_2SO_4 occur as minerals (*v.* Reichardt, *Ar. Ph.* 159, 204; Precht, *B.* 14, 2138).

Manganese sulphates. I. *Manganous salts.* The *normal salt* $MnSO_4$ is obtained by dissolving $MnCO_3$ or Mn in warm dilute H_2SO_4Aq, crystallising out $MnSO_4$.5aq, drying this salt, and heating to c. 280° until it ceases to lose weight. A white salt, with very faint rose tint; S.G. 3·282 (Thorpe a. Watts, *C. J.* 37, 113). H.F. [Mn,S,O^4] = 249,900 (*Th.* 3, 516). S. 56·5 at 6·3°, 60 at 18·7°, 68·7 at 37·5°, 67 at 75° (Brandes, *P.* 20, 575). Decomposed by heating to full redness, giving off SO_2 and O, and leaving Mn_3O_4; heated in steam is said to give an oxysulphide Mn_2OS (Arfvedson, *P.* 1, 50).

Hydrates of manganous sulphate. (1) $MnSO_4$.7aq separates from solutions of Mn or $MnCO_3$ in H_2SO_4Aq below 6° (Mitscherlich, *P.* 25, 287; Claassen, *Ar. Ph.* [3] 25, 310). Very pale rose-coloured, monoclinic crystals; isomorphous with $FeSO_4$.7aq. Very sol. water; S. at 18·5° c. 200 (Jahn, *A.* 28, 110). According to Étard (*C. R.* 86, 1399), solubility increases from 0°–55°, and decreases from 55°–145°; the changes are probably due to the formation of different hydrates. (2) $MnSO_4$.5aq, obtained by crystallising between 7° and 20°, or by treating a conc. solution of $MnSO_4$ with 95 p.c. alcohol and allowing to crystallise slowly (Claassen, *Ar. Ph.* [3] 25, 310). S.G. 2·103 (Thorpe a. Watts, *C. J.* 37, 113). H.F. [$Mn,S,O^4,5H^2O$] = 263,600 (*Th.* 3, 516). (3) $MnSO_4$.4aq, obtained by crystallising between 20° and 30° (C., *l.c.*; Mitscherlich, *P.* 25, 287). S.G. 2·261 (Topsoë, *C. C.* 4, 76). This is the main constituent of ordinary manganese sulphate. Mulder gives solubilities as follows:—

Temp.	S. $MnSO_4.4aq$
0°	55·4
5	58·2
10	63·8
20	66·3
25	68·5
30	70·4
35	71·9
40	73·1
45	74·0
50°	74·8
54	75·3
63·5	61·3
64	61·5
85	61·3
90	60·3
95	57·9
100	52·9

Insol. absolute alcohol (*cf.* Schiff, *A.* 118, 365). (4) $MnSO_4.2aq$, obtained by boiling the powdered pentahydrate with absolute alcohol; also by pouring a saturated solution of the pentahydrate into conc. H_2SO_4; S.G. 2·526 (T. a. W., *l.c.*). (5) $MnSO_4.aq$, obtained by heating the pentahydrate at 100° till it ceases to lose weight; S.G. 2·845 (T. a. W., *l.c.*).

Linebarger (*Am.* 15, 225) has obtained hydrates of $MnSO_4$ with 1, 2, 3, 4, 5, 6, and 7 H_2O. Below −10° mixtures of the heptahydrate and ice separate from $MnSO_4Aq$; above 117° only $MnSO_4$ separates. The solubilities of the various hydrates are discussed; the more water in the hydrate, the more soluble it is.

Acid salts $MnSO_4.H_2SO_4$ and $MnSO_4.3H_2SO_4$ were obtained by Schultz (*P.* 130, 149) by dissolving the normal salt in hot conc. H_2SO_4.

Basic salts are formed by adding a little warm KOHAq to a large excess of boiling $MnSO_4Aq$ (*v.* Gorgeu, *C. R.* 94, 1425).

Double salts; (1) with sulphates of Cu, Fe, Mg, and Zn to form salts $MnSO_4.MSO_4.xH_2O$ (*v.* Rammelsberg, *P.* 91, 321; Vohl, *A.* 94, 73). (2) With $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $Cr_2(SO_4)_3$ *v.* Étard (*C. R.* 86, 1399; 87, 602). (3) With alkali sulphates to form $MnSO_4.M_2SO_4.4aq$ or 6aq (*v.* Marignac, *Ann. M.* [5] 9, 1; Pierre, *A. Ch.* [3] 16, 239; von Hauer, *J. pr.* 74, 431). For various *triple salts* of $MnSO_4$ with alkali sulphates and $CuSO_4$, $MgSO_4$, &c.; *v.* Vohl (*A.* 94, 57).

II. *Manganic salts.*—The *normal salt* $Mn_2(SO_4)_3$ is obtained by the action of hot conc. H_2SO_4 on MnO_2. Carius (*A.* 98, 53) recommends to prepare pure MnO_2 by passing Cl into NaOHAq containing $MnCO_3$ in suspension, to wash and dry the MnO_2, to rub up to a paste with conc. H_2SO_4, and heat gradually to 110° till O is given off and the mass becomes grey-violet, then to heat to c. 135°-140° till the whole is liquid, to pour the solid that forms as the liquid partially cools on to warm unglazed porcelain, after H_2SO_4 has become absorbed to mix with a little conc. HNO_3Aq and allow to drain on the porcelain, to repeat this treatment with HNO_3 six or eight times, and finally to heat at 150° till all HNO_3 is removed. Franke (*J. pr.* [2] 36, 451) obtained $Mn_2(SO_4)_3$ by heating 8 g. $KMnO_4$ with 100 c.c. conc. H_2SO_4 at 100° for some time. A dark-green powder; Franke describes it as green crystals. Decomposed above 160°, giving $MnSO_4$. Insol. conc. H_2SO_4 or conc. HNO_3Aq. Sol. conc. HClAq to a brown liquid, which gives off Cl when warmed. $Mn_2(SO_4)_3$ is very hygroscopic; quickly decomposed by water, with separation of $MnO_2.xH_2O$ (Carius, *l.c.*).

Forms *double salts* with $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and $Cr_2(SO_4)_3$ (*v.* Étard, *C. R.* 86, 1399). The double compounds of $Mn_2(SO_4)_3$ with alkali sulphates—$Mn_2(SO_4)_3.M_2SO_4.24aq$—are alums. According to Fremy (*C. R.* 82, 1231), the salt $Mn(SO_4)_2$, *manganese disulphate*, corresponding with MnO_2, is formed by decomposing $KMnO_4$ by a considerable excess of cold conc. H_2SO_4 (*cf.* Franke, *J. pr.* [2] 36, 453).

Mercury sulphates. I. *Mercurous salts.* The *normal* salt Hg_2SO_4 is obtained by gently warming equal weights of Hg and conc. H_2SO_4, removing the white solid so produced before the whole of the Hg is changed, washing with cold water, and drying at a low temperature. Divers a. Shimidzu (*C. J.* 47, 639) recommend to mix Hg with fuming sulphuric acid rich in SO_3 in a covered dish, in a cool place, adding a little more Hg from time to time till there is sufficient to saturate the SO_3 in the acid, but avoiding excess, and when the Hg is all converted into Hg_2SO_4 to set the dish in a warm place to expel SO_2. Hg_2SO_4 is also obtained by adding 6 pts. water to 18 pts. $HgSO_4$ and rubbing with 11 pts. Hg (Planche, *A.* 66, 168). Also by ppg. $HgNO_3Aq$ by dilute H_2SO_4Aq or solution of a sulphate; or by rubbing together $HgNO_3$ and Na_2SO_4 and washing with cold water (H. Rose; Stoedeler, *A.* 87, 129). A white powder, consisting of monoclinic prisms (S., *l.c.*); S. G. 7·56 (Playfair a. Joule, *C. S. Mem.* 2, 401). Sl. sol. water; S. in cold water ·2, in boiling water ·33; more sol. dilute HNO_3Aq; sol. conc. hot H_2SO_4, crystallising out on cooling. Hg_2SO_4 becomes grey on exposure to light (*v.* Buchner, *Chem. Zeitung*, 10, 759): hence the salt should be kept in the dark. Hg_2SO_4 melts to a reddish liquid, and decomposes at a higher temperature, giving off SO_2 and O, and also partially subliming. Slowly changed by boiling water to an acid salt, and a yellow powder which is probably a basic salt (*v.* Kane, *P.* 42, 367). An *acid salt* $Hg_2SO_4.H_2SO_4$ is said to be formed by the prolonged reaction of conc. H_2SO_4 containing a drop of HNO_3Aq on Hg (Braham, *C. N.* 42, 163). A *double salt* $Hg_2SO_4.2HgSO_4$ was obtained by Brooks (*P.* 66, 63) by gently warming mercuro-mercuric nitrate (formed by warming 2 pts. Hg with 3 pts. HNO_3Aq S.G. 1·2) with Na_2SO_4Aq.

II. *Mercuric salts.* The *normal salt* $HgSO_4$ is obtained by the reaction of 6 pts. boiling conc. H_2SO_4 with 5 pts. Hg, till SO_2 ceases to be evolved, and a little of the white solid produced gives no pp. of HgCl when dropped into dilute HClAq; the white mass is gently warmed till acid fumes cease to be given off. A white powder; S.G. 6·466 (Playfair a. Joule, *C. S. Mem.* 2, 401). Becomes yellow, then red when heated; decomposes at red heat to Hg, O, and SO_2, a little $HgSO_4$ subliming (Mohr, *A.* 31, 180). Decomposed by water to a yellow basic salt and H_2SO_4Aq. Hot $HgSO_4$ absorbs HCl and HBr gases; according [illegible] Ditte (*A. Ch.* [5] 17, 120) the compounds $HgSO_4.2HCl$ and $HgSO_4.2HBr$ are formed; these bodies are said to be sol. water without formation of basic salts, and $HgSO_4.2HCl$ is said to sublime unchanged when heated. Solution of $HgSO_4$ in H_2SO_4Aq is said to react with PH_3 to form the compound $2(3HgO.SO_3).Hg_3P$ (H. Rose, *P.* 40, 75). *Monohydrated mercuric sulphate* $HgSO_4.aq$ was obtained by Eisfeldt (*Ar. Ph.* [2] 76, 16) by covering a thin layer of $HgSO_4$ with the calculated quantity of water. The *basic salt* $HgSO_4.2HgO$

($=3HgO.SO_3$) is obtained by the action of hot water on $HgSO_4$, also by adding Na_2SO_4Aq to bot $Hg(NO_3)_2Aq$; a citron-yellow powder, S.G. 6·44; nearly insol. water (*v.* Cameron, *An.* 880. 144). *Decomposed by Cl at the ordinary* emperature. Absorbs HCl and HBr, forming $IgSO_4.2HgO.6HCl$ (or 6HBr) (Ditte, *l.c.*). This asic salt was formerly known as *minerale* *irpethum* or *turbith mineral* (from its resemblance to a coloured gum obtained from an Oriental creeping plant [*Ipomœa turpethum*]). Hopkins (*Am. S.* 18, 364) described another basic salt $3HgSO_4.HgO = 4HgO.3SO_3$. *Double salts.* — (1) $HgSO_4.(NH_4)_2SO_4.xH_2O$ and $HgSO_4.K_2SO_4.xH_2O$ (*v.* Hirzel, *J.* 1850. 322). (2) $HgSO_4.HgI_2$ (*v.* Souville, *J. Ph.* 26, 474). (3) $2HgSO_4.HgS$ (*v.* Jacobsen, *P.* 68, 411).

Molybdenum sulphates. By evaporating a solution of MoO_3 in conc. H_2SO_4, Schultz-Sellack (*B.* 4, 14) obtained white lustrous crystals of $MoO_3.SO_3$; the compound $MoO_3.3SO_3.2aq$, described by Anderson (*B. J.* 22, 161), could not be obtained by S-S.

Nickel sulphates. The *normal salt* $NiSO_4$ is formed, as a clear yellow powder, by heating powdered $NiSO_4.xaq$ (*v. infra*) to c. 300°. The salt is obtained in crystals, regular octahedra, by heating $NiSO_4$, NiO, or $NiCO_3$ with five or six times its weight of fused $(NH_4)_2SO_4$, separating the yellow crystals of the double salt $3NiSO_4.2(NH_4)_2SO_4$ that form, and heating these in presence of some $(NH_4)_2SO_4$ in a partly closed crucible out of contact with the gases of the flame till all the ammonium salt is removed; S.G. of crystals 3·67 at 20° (Lepierre a. Lachaud, *C. R.* 115, 115; Klobb, *C. R.* 114, 836). Tobler (*A.* 95, 193) gives solubilities of $NiSO_4$ as follows:—

Temp.	S.	Temp.	S.
2°	30·4	41°	49·1
16	37·4	50	52·0
20	39·4	53	54·4
23	41·0	60	57·2
31	45·3	70	61·9

The *hexahydrate* $NiSO_4.6aq$ is obtained by dissolving Ni, NiO, or $NiCO_3$ in excess of H_2SO_4Aq, evaporating, and crystallising. At the ordinary temperature; bluish tetragonal pyramids separate (Brooke a. Phillips, *P.* 6, 193); greenish monoclinic crystals separate from warm solutions (Pierre, *A. Ch.* [3] 16, 252). The salt is, therefore, dimorphous (Marignac, *A.* 97, 294; *cf.* Mitscherlich, *P.* 12, 144; also Lecoq de Boisbaudran, *A. Ch.* [4] 9, 173). By dissolving this hydrate in water, and crystallising at 15°–20°, emerald-green rhombic prisms of the *heptahydrate* $NiSO_4.7aq$ are obtained, isomorphous with $MgSO_4.7aq$; melts at 98°–100° (Tilden, *C. J.* 45, 267). When this hydrate is heated to 103° it loses [illegible]H_2O and leaves the *monohydrate* $NiSO_4.aq$. By passing NH_3 into $NiSO_4Aq$, compounds of the form $NiSO_4.xNH_3.yH_2O$ are obtained ($x=4$, 5, and 6; *v.* F. Rose, *Ammon. Kobaltverbind.* [Heidelberg, 1871] 27; also *P.* 20, 156).

Double salts. (1) With $(NH_4)_2SO_4$, K_2SO_4, and Tl_2SO_4 to form $NiSO_4.M_2SO_4.6aq$ (*v.* F. Rose, *l.c.*; Link, *Crell's Ann.* 1796 [1] 32; Werther, *J. pr.* 92, 132). (2) With $BeSO_4$ to form various compounds (Klatzo, *Über die Constant. der Beryllerde*, Dorpat, 1868). (3) With $CuSO_4$, $CoSO_4$, $FeSO_4$, $MgSO_4$, $MnSO_4$, and with some of these and also alkali sulphates (*v.* Pierre, *A. Ch.* [3] 16, 253; Lecoq de Boisbaudran, *C. R.* 66, 497).

Basic salts are formed by the gradual reaction of $NiSO_4Aq$ with $NiCO_3$, and by adding a little NH_3Aq to boiling $NiSO_4Aq$ (Habermann, *M.* 5, 440).

Palladium sulphates. The *normal palladous salt* $PdSO_4.2aq$ is obtained in brown crystals by evaporating a solution of Pd in H_2SO_4Aq containing HNO_3. Addition of a little KOHAq to a conc. solution in water of the normal salt ppts. a *basic salt* $PdSO_4.7PdO.6aq$ (*v.* Kane, *B. J.* 24, 236).

Platinum sulphates. By dissolving PtO_2H_2 in dilute H_2SO_4Aq, Berzelius (*Lehrbuch* [5th ed.] 3, 987) obtained a dark syrup which probably contained *platinous sulphate* $PtSO_4$. *Platinic sulphate* $Pt(SO_4)_2$ was obtained by Berzelius (*l.c.*, p. 989) by evaporating $PtCl_4$ with conc. H_2SO_4 (1 part acid for 1 part Pt), as an almost black solid. E. Davy (*T.* 1820) obtained the salt by oxidising PtS_2 by fuming HNO_3. Prost (*Bl.* [2] 46, 156) obtained a *basic salt* by allowing an acid solution of $Pt(SO_4)_2$ to stand for some days; Prost also describes several *double salts* of $Pt(SO_4)_2$ with alkali sulphates.

Potassium sulphates. The *normal salt* K_2SO_4 is found in the *lava* from Vesuvius, in small quantities in sea water, and in some mineral springs, in combination with $MgSO_4$ and $MgCl_2$ as *kainite* ($K_2SO_4.MgSO_4.MgCl_2.6aq$), in combination with $MgSO_4$ and $CaSO_4$ as *polyhalite* ($K_2SO_4.MgSO_4.2CaSO_4.2aq$), and as *alum.* K_2SO_4 is prepared by decomposing KCl by H_2SO_4, by neutralising H_2SO_4Aq by KOH or K_2CO_3, and evaporating (for the preparation of K_2SO_4 on the large scale *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 279). K_2SO_4 forms in white, hard, four-sided, trimetric prisms, unchanged in air. S.G. 2·656 at 4° (Playfair a. Joule, *C. J.* 1, 132); for S.G. at various temperatures from 0° to 100° *v.* Spring, *B.* 15, 1940. Melts above 861° (Carnelley, *Melting- and Boiling-Point Tables*, 1, 33); melts at 1073° according to V. Meyer a. Riddle (*B.* 26, 2443). H.F. $[K^2,S,O^4]=344,600$ (*Th.* 3, 516); $[K^2SO^4,Aq]=-6167$ (Pickering, *C. J.* 47, 98). Mulder (*Scheikund. Verhandg.* 1864. 49) gives solubilities in water as follows:—

Temp.	S.	Temp.	S.
5°	9·1	55°	16·8
10	9·7	60	17·8
15	10·3	65	18·8
20	10·9	70	19·8
25	11·6	75	20·8
30	12·3	80	21·8
35	13·1	85	22·8
40	14·0	90	23·9
45	14·9	95	25·0
50	15·8	100	26·2

Gerlach (*Fr.* 8, 827) gives S.G. of K_2SO_4Aq as follows:—

Pctge. K_2SO_4	S.G. K_2SO_4Aq	Pctge. K_2SO_4	S.G. K_2SO_4Aq
1	1·00829	6	1·04947
2	1·01635	7	1·05790
3	1·02450	8	1·06644
4	1·03277	9	1·07499
5	1·04105	9·92 (satd.)	1·08305

Insol. absolute alcohol; sol. aqueous alcohol in proportion to amount of water present (*v.* Schiff, *A.* 118, 362). Insol. KOHAq 1·32 S.G.; sl. sol. KOHAq 20 p.c. S. in saturated NH_3Aq = ·0365 (Giraud, *Bl.* [2] 43, 552). S. in glycerin (S.G. 1·225) at ordinary temperature = 1·32 (Vogel, *N. R. P.* 16, 557). More sol. in solution of $CuSO_4$, $MgSO_4$, or Na_2SO_4 than in water. Reacts with strong acids to give $KHSO_4$ (for thermal measurements *v.* Berthelot, *Essai de méc. chimique*, 1, 389). Dissolves in hot conc. HNO_3Aq, $KHSO_4$ separates on cooling, then KNO_3, and then a compound of K_2SO_4 with HNO_3; H_3PO_4Aq reacts similarly (*v.* Jacquelain, Biedermann's *Techn. Chem. J.* 4, 62). Absorbs HCl gas when heated, forming KCl and $KHSO_4$ (Thomas, *C. J.* 33, 372; Hensgen, *B.* 9, 1671; 10, 259). Decomposed by heating with NH_4Cl, giving KCl (H. Rose, *P.* 64, 568). Heated to redness with iron filings gives KOH mixed with Fe_2O_3 and FeS (d'Heureuse, *P.* 75, 255). Reduced to sulphide (or KSH) by heating in CO; to KSH and KOH by heating in H (*v.* Berthelot, *C. R.* 110, 1106). Sulphur reacts at full red heat, giving SO_2 and polysulphides of K (Berthelot, *C. R.* 96, 303). SO_2 is without action at a red heat.

Double salts. (1) With $Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, and $Fe_2(SO_4)_3$ to form $K_2SO_4.M_2(SO_4)_3.24aq$; *v. potash alum*, *potash chrome-alum* and *potash iron-alum*, under ALUMINIUM SULPHATES (p. 568), CHROMIUM SULPHATES (p. 570), and IRON SULPHATES (p. 572). (2) With sulphates of Ce and Di respectively, to form $3K_2SO_4.M_2(SO_4)_3$ (*v.* Cleve, *Bl.* [2] 43, 359; Czudnowitz, *J. pr.* 82, 129; Hermann, *J. pr.* 82, 385); also the salt $2K_2SO_4.Ce(SO_4)_2.2aq$ (Marignac, *Ann. M.* [5] 15, 275). (3) With sulphates of Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn to form $K_2SO_4.MSO_4.6aq$ (*v.* Graham, *P. M.* 1835. 327, 417; Brunner, *P.* 15, 476; 32, 221; Pickering, *C. J.* 49, 1; Tobler, *A.* 95, 193; Schiff, *A.* 108, 326; 113, 183; Gerlach, *Fr.* 8, 287; Marignac, *Ann. M.* [5] 9, 19; Wilm, *A. Ch.* [4] 5, 56; Pierre, *A. Ch.* [3] 16, 239; von Hauer, *J. pr.* 74, 431; Werther, *J. pr.* 92, 132). (4) $K_2SO_4.BeSO_4.2aq$ (Awdejeff, *P.* 56, 101). (5) $K_2SO_4.Na_2SO_4$ (Penny, *P. M.* [4] 10, 401; Mitscherlich, *P.* 58, 468; von Hauer, *J. pr.* 83, 356).

The *acid salt* $KHSO_4$ occurs in some volcanic districts as *misenite*; it is formed by heating 13 parts K_2SO_4 with 8 parts conc. H_2SO_4, or by heating KNO_3 and conc. H_2SO_4 in the ratio KNO_3:H_2SO_4. Crystallises in white rhombic forms, S.G. 2·273; also in monoclinic forms, S.G. 2·245 (*v.* Wyrouboff; abstract in *C. J.* 50, 665). Melts at c. 200°. Easily sol. water; Kremers gives S. 33·9 at 0°, 48 at 20°, 62·9 at 40°, 114 at 100°. An aqueous solution is said to deposit, first K_2SO_4, then $KHSO_4.K_2SO_4$, and then $KHSO_4$; by evaporating $KHSO_4Aq$ at a low temperature until a solid mass formed on removing the flame, arborescent and very deliquescent crystals formed on the surface of the solid, which were $2KHSO_4.11H_2O$ according to Senderens (*Bl.* [3] 2, 728).

Other acid salts. (1) $KHSO_4.K_2SO_4$, obtained by evaporating $KHSO_4Aq$. (2) $2KHSO_4.K_2SO_4$, crystallising from K_2SO_4 in H_2SO_4Aq (Phillips, *J. pr.* [2] 1, 429; Marignac, *Ann. M.* [5] 9, 7). (3) $KHSO_4.H_2SO_4$, formed by heating K_2SO_4 with less than 5 parts conc. H_2SO_4 (Schultz, *P.* 133, 137).

Rhodium sulphates. The *normal rhodic sulphate* $Rh_2(SO_4)_3$ is obtained by dissolving $Rh_2O_3.xaq$ in H_2SO_4Aq, evaporating, and heating to 400° till excess of acid is removed; a red powder, decomposed by hot water to the yellow *basic salt* $Rh_2(SO_4)_3.Rh_2O_3$ (Leidié, *C. R.* 107, 234). Claus (*Beiträge zur Chemie der Platinmetalle* [Dorpat, 1854]) obtained the *hydrate* $Rh_2(SO_4)_3.12aq$, as a pale-yellow crystalline salt, by crystallising a solution of $Rh_2O_3.xaq$ in H_2SO_4Aq, and washing with alcohol. The *double salt* $Rh_2(SO_4)_3.3K_2SO_4$ was obtained by Claus (*l.c.*) by evaporating a solution of the constituent salts in the ratio $Rh_2(SO_4)_3$:$5K_2SO_4$. The *double salt* $Rh_2(SO_4)_3.Na_2SO_4$ was obtained by Bunsen (*A.* 146, 265; *v.* also Seubert a. Kobbé, *B.* 23, 2556) by the action of hot conc. H_2SO_4 on $RhSO_3.6Na_2SO_3.9aq$ (formed by heating $RhCl_3Aq$ for some time with $NaHSO_3$).

Rubidium sulphates. The *normal salt* Rb_2SO_4 is obtained by neutralising H_2SO_4Aq by Rb_2CO_3 and evaporating; it crystallises in transparent, hexagonal forms, unchanged in air. S. 42·4 at 70°. S.G. 3·6438 at 0°; 3·6256 at 50°; 3·6036 at 100° (Spring, *B.* 15, 1940). If excess of H_2SO_4Aq is used, the *acid salt* $RbHSO_4$ separates in rhombic prisms (Kirchoff a. Bunsen, *P.* 115, 584).

Double salts. (1) With Li_2SO_4 to form $RbLiSO_4$ (Wyrouboff, *Bl.* [2] 48, 134, 630). (2) With $CaSO_4$ and $PbSO_4$ to form the compounds $Rb_2SO_4.2MSO_4.xaq$ (Ditte, *C. R.* 89, 641). (3) With $Al_2(SO_4)_3$ to form *rubidium alum* $Al_2(SO_4)_3.Rb_2SO_4.24aq$ (Bunsen, *P.* 119, 1; Godeffroy, *A.* 181, 176; Redtenbacher, *J. pr.* 95, 143).

Ruthenium sulphate. *Normal ruthenic sulphate* $Ru(SO_4)_2$ is obtained by oxidising RuS_2 (formed by prolonged action of H_2S on $RuCl_3Aq$) by conc. HNO_3Aq, and evaporating off excess of acid. An amorphous, brownish-yellow, very hygroscopic solid. Strongly heated gives RuO_2 (Claus, *J. pr.* 42, 364).

Silver sulphates. The *normal salt* Ag_2SO_4 is obtained by heating finely divided Ag with excess of conc. H_2SO_4, by neutralising H_2SO_4Aq by Ag_2O or Ag_2CO_3 and evaporating, by evaporating $AgNO_3$ with H_2SO_4Aq, or by ppg. $AgNO_3Aq$ by Na_2SO_4Aq. Small, white, lustrous, rhombic crystals, isomorphous with Na_2SO_4 (Mitscherlich, *P.* 12, 138; 25, 301). S. 1·15 cold water, 1·45 at 100° (Wenzel, *P.* 82, 136). S.G. 5·322 (Playfair a. Joule, *C. S. Mem.* 2, 401), 5·425 when fused (Schröder, *P.* 106, 226). Decrepitates when heated to 300°; melts at 645° (Carnelley, *C. J.* 33, 279). Decomposed at very high temperature, giving Ag, SO_2, and O. Reduced to Ag by heating in H, with C, or in CO (Stammer, *J. pr.* 11, 70). Absorbs $2NH_3$ (H. Rose, *P.* 20, 153).

Acid salts are obtained by dissolving Ag_2SO_4 in different quantities of H_2SO_4Aq and crystallising; Schultz (*P.* 133, 137) describes (1) $AgHSO_4$, (2) $2Ag_2SO_4.3H_2SO_4.2aq$, (3) $Ag_2SO_4.3H_2SO_4.2aq$. Carey Lea (*Am. S.* [3] 44, 322) describes a *hemisulphate* $Ag_2SO_4.Ag_4SO_4.aq$, but this salt was not obtained free from Ag_3PO_4.

Forms a *double salt* $Ag_2SO_4.Al_2(SO_4)_3.24aq$; this salt is *an alum* (*v.* Church a. Northcote, *C. N.* 9, 155). Also combines with Ag_2S and with K_2SO_4 (Berzelius; H. Rose, *P.* 53, 463).

Sodium sulphates. The *normal salt* Na_2SO_4 occurs native as *thenardite*, in combination with $CaSO_4$ as *glauberite*, and with $MgSO_4$ as *löweite*; the salt also occurs in sea water and in many mineral springs. It is prepared by adding H_2SO_4 to NaCl in the ratio $NaCl:H_2SO_4$, and strongly heating the $NaHSO_4$ thus produced; also by the reaction between NaCl, SO_2, steam and O at 400°-450°; $2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl$ (for the application of these processes on the large scale *v.* Dictionary of Applied Chemistry, vol. iii. p. 439). Na_2SO_4 is also obtained in the decomposition of NH_4Cl, or $NaNO_3$, by H_2SO_4; it is formed by neutralising H_2SO_4Aq by NaOHAq or Na_2CO_3, evaporating, and heating to redness the crystals of $Na_2SO_4.x$aq that separate. Na_2SO_4 is a white amorphous powder; S.G. 2·597 (Playfair a. Joule, *C. S. Mem.* 2, 401); 2·631 (Karsten, *S.* 65, 394). Obtained in rhombic crystals, isomorphous with Ag_2SO_4 (Mitscherlich, *P.* 12, 138; 25, 301), by heating to 40° a solution saturated at 33°; S.G. 2·6618, or 2·6637 crystallised at 110° (Nicol, *P. M.* [5] 15, 94). Dissolves in water with production of heat; according to Berthelot (*C. R.* 78, 1722) $[Na^2SO^4,Aq] = 780$ at 21·2°, but -100 at 3°; Pickering (*C. J.* 45, 686) thinks that two modifications of Na_2SO_4 exist; the salt dried at 100° or 150° gave $[Na^2SO^4,Aq] = 57$ at 20·4°, but after heating to temperatures varying from 250° to the melting-point the heat of solution was $[Na^2SO^4,Aq] = 760$. Thomsen (*Th.* 3, 516) gives H.F. $[Na^2,S,O^4] = 328,600$. Tilden (*Pr.* 35, 345) gives solubilities as follows: 5 at 0°, 78·8 at 34°, 42·7 at 100°, 41·95 at 120°, 42 at 140°, 42·9 at 160°, 44·25 at 180°, 46·4 at 230°. Étard (*C. R.* 113, 854) says that S. increases from 33° to 80°, remains constant to 230°, and then decreases to 320° (*v.* also Löwel, *A. Ch.* [3] 33, 334; 49, 32; Gernez, *C. R.* 60, 833; de Coppet, *Bl.* [2] 17, 146). For S.H. and expansion of Na_2SO_4Aq *v.* Thomsen (*P.* 142, 337) and Marignac (*A. Ch.* [4] 22, 415). Na_2SO_4 melts at 861° (Carnelley, *C. J.* 33, 280); at 843° (V. Meyer a. Riddle, *B.* 26, 2443). S.G. at melting-point = 2·104 (Braun, *B.* 7, 958).

Heated with *charcoal* out of air Na_2SO_4 is reduced to Na_2S; Gay-Lussac (*A. Ch.* [2] 11, 312) says polysulphides are also formed; CO_2 is evolved, but no CO (Unger, *A.* 63, 240; Scheurer-Kestner, *A. Ch.* [4] 1, 412; Stromeyer, *A.* 107, 361); heated to bright redness with C in a vessel containing air, Na_2S is formed and CO evolved (Berthelot, *C. R.* 110, 1106). Reduced to sulphide by heating to bright redness in *carbon monoxide* (B., *l.c.*); reduction by *hydrogen* begins at c. 500°, the products are Na_2S, NaSH, NaOH, H_2O, and H_2S (B., *l.c.*). Heated with *hydrogen chloride*, NaCl is formed (Boussingault, *C. R.* 78, 593); boiling HClAq produces NaCl and $NaHSO_4$ (Thomas, *C. J.* 33, 373). A little NaCl is formed by heating with *ammonium chloride* (Nicholson, *C. N.* 26, 47). Boiled with *barium carbonate* some Na_2CO_3 and $BaSO_4$ are formed; after a time a condition of equilibrium is attained. A very little NaOHAq is produced by boiling for some time with *milk of lime*; under increased pressure NaOHAq is formed (*v.* Scheurer-Kestner, *A. Ch.* [4] 1, 412). Not decomposed by heating strongly with *calcium carbonate* (S.-K., *l.c.*). When a mixture of Na_2SO_4 and *alumina* is heated in *steam*, SO_2 is given off and sodium aluminate remains; presence of charcoal hastens the reaction (Wagner). According to Stromeyer (*A.* 107, 361) fusion with *iron* produces Fe_2O_3, Na_2O, and $Na_2S.2FeS$. The final products of heating with *silica and carbon* in a closed crucible are $Na_2O.2SiO_2$, S, CO_2 and CO (S.-K., *C. R.* 114, 117).

Hydrates of Na_2SO_4. (1) The heptahydrate $Na_2SO_4.7$aq is obtained by melting *Glauber's salt* $Na_2SO_4.10$aq in its water of crystallisation, heating to boiling, at once closing the vessel, and shaking repeatedly as the liquid cools till 18° is reached; Na_2SO_4 separates at first but dissolves again, and below 18° $Na_2SO_4.7$aq separates (Löwel, *A. Ch.* [3] 33, 334; 49, 32). The following method gives better results (L., *l.c.*): 22 parts $Na_2SO_4.10$aq are dissolved in 10 parts water, the solution is heated to boiling, and the flask is then closed with a cork carrying two narrow tubes bent at right angles; when the liquid is cold the outer end of one of the tubes is dipped into 30 p.c. alcohol at 40°, and the alcohol is caused to run into and fill the flask by sucking at the outer end of the other tube. As the alcohol withdraws water, large, translucent, rhombic or tetragonal crystals of $Na_2SO_4.7$aq gradually separate. The crystals must be quickly pressed between filter paper. They rapidly absorb water from the air, changing to $Na_2SO_4.10$aq; exposed to air, even under dilute alcohol, they soon change to the decahydrate. According to Löwel (*l.c.*) the heptahydrate is much more soluble in water between 0° and 26° than the decahydrate. The temperature of maximum solubility is 27°; the solution then contains 56 p.c. Na_2SO_4, which is the same quantity as is present in solution of $Na_2SO_4.10$aq saturated at 34°-36°. If a crystal of $Na_2SO_4.7$aq is added to the saturated solution of this salt at 27° it does not dissolve, but crystals of Na_2SO_4 separate until a concentration is reached corresponding with a saturated solution of Na_2SO_4 at the temperature. The heptahydrate is able to form supersaturated solutions, but less readily than the decahydrate; addition of a crystal of $Na_2SO_4.7$aq causes separation of the heptahydrate. These results were confirmed by de Coppet (*Bl.* [2] 17, 146).

(2) The *decahydrate* $Na_2SO_4.10$aq crystallises from a hot saturated solution of Na_2SO_4 cooled to at least 32°; a supersaturated solution may be cooled in a closed vessel to 0°. If a crystal of $Na_2SO_4.10$aq is dropped in, a mass of crystals of the decahydrate is formed, and the temperature rises to c. 18°. Large, white, striated, monoclinic prisms; isomorphous with $Na_2CrO_4.10$aq and $Na_2SeO_4.10$aq. S.G. 1·469 (Playfair a. Joule, *C. S. Mem.* 2, 401); 1·485 at 19°, 1·492 at 20° (Pettersson, *Upsala, Nova Acta*, 1874). $[Na^2,S,O^4,10H^2O] = 347,800$ (*Th.* 3, 516). Melts at 34° (Tilden, *C. J.* 45, 267). Effloresces in air. When melted in the water of crystallisation, boiled, and allowed to cool in a closed vessel, Na_2SO_4 separates, but on shaking, this salt dissolves till 18° is reached, after which crystals of $Na_2SO_4.7$aq separate (*v. supra*). $Na_2SO_4.10$aq is insol. absolute alcohol; alcohol of S.G. ·976 dis-

solves 14·35 p.c., of S.G. ·972 dissolves 5·6 p.c., and of S.G. ·939 dissolves 1·3 p.c. Solubility in water increases with temperature to 33°–34°, whereat the solution contains 55 parts Na_2SO_4 in 100 of water; a crystal of $Na_2SO_4.10aq$ dropped into the solution dissolves, and Na_2SO_4 separates till 49·53 parts Na_2SO_4 are in solution in 100 parts water, which is the same quantity of Na_2SO_4 as is present in a solution made by saturating water with Na_2SO_4 at 34° (Löwel, *A. Ch.* [3] 33, 334; 49, 32). As temperature is increased above 34° Na_2SO_4 seems to be formed, and the solubility of this salt decreases as temperature rises to the b.p. of saturated Na_2SO_4Aq. There appear to be three temperatures of maximum solubility for Na_2SO_4 and its hydrates: (1) at 34°, which is the maximum for $Na_2SO_4.10aq$, (2) at 26°–27° for $Na_2SO_4.7aq$, (3) at 17°–18° for Na_2SO_4. The quantity of salt in solution, calculated as Na_2SO_4, is about the same at these temperatures. Löwel (*l.c.*) gives the following table:—

100 *parts water contain, when solution is saturated,*

Temp.	Na_2SO_4	$Na_2SO_4.10aq$	Na_2SO_4	$Na_2SO_4.10aq$	Na_2SO_4	$Na_2SO_4.7aq$	$Na_2SO_4.10aq$
	Sol. made with Na_2SO_4		Sol. made with $Na_2SO_4.10aq$		Sol. made with $Na_2SO_4.7aq$		
0°	—		5·02	12·16	19·62	44·84	59·23
10	—		9·00	23·04	30·49	78·90	112·73
15	—		13·20	35·96	37·43	105·79	161·57
18	53·25	371·97	16·80	48·41	41·63	124·59	200
20	52·76	361·51	19·40	58·35	44·73	140·01	234·4
25	51·53	337·16	28	98·48	52·94	188·46	365·28
26	51·31	333·06	30	109·81	54·97	202·61	411·45
30	50·37	316·19	40	184·09			
33	49·71	305·06	50·76	323·13			
34	49·53	302·07	55	412·22			
40·15	48·78	290·00					
45·04	47·81	275·34					
50·4	46·82	261·36					
59·79	45·42	242·89					
70·61	44·35	229·87					
84·42	42·96	213·98					
103·17	42·65	210·67					

The following table gives S.G. of Na_2SO_4Aq at 19°:—

S.G.	P.c. Na_2SO_4	P.c. $Na_2SO_4.10aq$
1·0040	1·441	1
1·0079	1·881	2
1·0118	1·323	3
1·0158	1·764	4
1·0198	2·205	5
1·0238	2·646	6
1·0278	3·087	7
1·0318	3·528	8
1·0358	3·969	9
1·0398	4·410	10
1·0439	4·851	11
1·0479	5·292	12
1·0520	5·373	13
1·0560	6·174	14
1·0601	6·615	15
1·0642	7·056	16
1·0683	7·497	17
1·0725	7·938	18
1·0766	8·379	19
1·0807	8·820	20
1·0849	9·261	21
1·0890	9·702	22
1·0931	10·143	23
1·0973	10·584	24
1·1015	11·025	25
1·1057	11·466	26
1·1100	11·907	27
1·1142	12·348	28
1·1184	12·789	29
1·1226	13·230	30

Acid salts. (1) $NaHSO_4$; by adding 7 parts H_2SO_4Aq S.G. 1·85, to 10 parts Na_2SO_4, and heating gently till the mass melts and water-vapour ceases to be given off. By dissolving in water, or by evaporating Na_2SO_4 in H_2SO_4Aq at 50°, crystals of $NaHSO_4.aq$ are obtained (Mitscherlich, *P.* 12, 138; H. Rose, *P.* 82, 545). (2) $Na_2SO_4.NaHSO_4$ ($=Na_3H(SO_4)_2$); by crystallising Na_2SO_4 from half as much H_2SO_4 in water as is required to form $NaHSO_4$ (M., *l.c.*; R., *l.c.*). (3) $NaHSO_4.H_2SO_4$ ($NaH_3(SO_4)_2$); by crystallising Na_2SO_4 from solution in almost 7 parts H_2SO_4 (Schultz-Sellack, *J. pr.* [2] 2, 459; Lescœur, *C. R.* 78, 1044).

Double salts. (1) $Na_2SO_4.K_2SO_4$ (Penny, *P. M.* [4] 10, 401; Mitscherlich, *P.* 58, 468; von Hauer, *J. pr.* 83, 356). (2) $Na_2SO_4.(NH_4)_2SO_4$; by the interaction of $(NH_4)_2SO_4$ and NaCl with a little water (Schiff). (3) Various double salts with Li_2SO_4 (Rammelsberg, *P.* 128, 311; Wyrouboff, *Bl.* [2] 9, 35. (4) With sulphates of Cd, Ca, Cu, Di, In, Fe, La, Mn, and Mg; references under CADMIUM SULPHATES, CALCIUM SULPHATES, &c. (5) The compounds $Na_2SO_4.M_2(SO_4)_3.24aq$, where M = Al or Cr, are *alums* (references under ALUMINIUM SULPHATES and CHROMIUM SULPHATES).

Strontium sulphates. The *normal salt* $SrSO_4$ occurs native as *celestine*. It is obtained by adding H_2SO_4Aq or solution of an alkali sulphate to solution of a strontium salt; large crystals are formed by dissolving ppd. $SrSO_4$ in conc. H_2SO_4, adding dilute HClAq, heating to 150°, allowing to cool, again heating to 150° with HClAq, and repeating this treatment three or four times (Bourgeois, *C. R.* 105, 1072). $SrSO_4$ is also obtained crystalline by fusing K_2SO_4 with excess of $SrCl_2$ (Manross, *A.* 82, 350). A white solid; S.G. 3·927 to 3·955 crystalline (M., *l.c.*; Neumann, *P.* 23, 1); 3·7 ppd. (Schröder, *P.* 106, 226; *v.* also Clarke's *Table of Spec. Gravs.* [New Ed.] 82). H.F. [Sr,S,O⁴] = 330,900 (*Th.* 3, 516). Almost insol. water; S. ·0145

ordinary temperature, ·0104 at 100° (Fresenius); insol. dilute H_2SO_4Aq; S. conc. H_2SO_4 at 70° = 14 (Garside, *C. N.* 81, 245); for S. in solutions of NaCl, KCl, $MgCl_2$, and $CaCl_2$ *v.* Virck (*C. C.* 1862. 402). Melts when strongly heated; is decomposed to SrO, SO_2, and O at full white heat (Bousingault, *J.* 1867. 161). Reduced by heating strongly with C, Fe, or Zn (d'Heureuse, *P.* 75, 277), or in a steam of H or moist CO (Jacquemin, *C. R.* 46, 1164). Loses SO_3 when heated with As_2O_5 (Moretti, *S.* 9, 169), or when heated continuously to redness in HCl (Bousingault, *C. R.* 78, 593). Decomposed by heating with solutions of alkali carbonates. Forms *double salts*, $SrSO_4.M_2SO_4$, with alkali sulphates (H. Rose, *P.* 93, 604; 110, 296). An *acid salt* $SrH_2(SO_4)_2$ (= $SrSO_4.H_2SO_4$) is formed by digesting $SrSO_4$ in conc. H_2SO_4 with excess of $SrSO_4$ (Schultz, *P.* 113, 147).

Thallium sulphates. The *normal thallous salt* Tl_2SO_4 is obtained by dissolving Tl in hot H_2SO_4, or by neutralising H_2SO_4Aq by TlOH or Tl_2CO_3, and evaporating (Crookes, *C. N.* 24, 38). Forms white rhombic prisms, isomorphous with K_2SO_4 (von Lang, *P. M.* [4] 25, 348); S.G. 6·77 (Lamy, *Bl.* [2] 11, 210; *v.* also Clarke's *Table of Spec. Gravs.* [new ed.] 79). H.F. $[Tl^2,S,O^4]$ = 221,000 (*Th.* 3, 516). S. 4·74 at 15°, 18·5 at 100° (Lamy, *l.c.*). Not decomposed by heating to full redness in absence of air; heated more strongly in air gives Tl_2O_3, SO_2, and O (Carstanjen, *J.* 1867. 279). Reduced to Tl_2S by heating with KCN. The *acid thallous salt* $TlHSO_4.3aq$ separates from a solution of the normal salt in H_2SO_4Aq after some months. When strongly heated yields Tl_2SO_4 and H_2SO_4 (Carstanjen, *l.c.*). *Double salts*, $Tl_2SO_4.MSO_4.6aq$, are formed when M = Cu, Fe, Mg, Ni, or Zn (Willm, *A. Ch.* [4] 9, 5; Werther, *Bl.* [2] 2, 272). The salt $Tl_2SO_4.Al_2(SO_4)_3.24aq$ is an *alum* (*v.* Lamy, *Bl.* [2] 11, 210). *Normal thallic sulphate* $Tl_2(SO_4)_3.7aq$ is obtained as thin, white leaflets by dissolving $Tl_2O_3.H_2O$ in fairly conc. H_2SO_4Aq and evaporating. Loses 6aq when heated to 200°, at higher temperatures SO_2 and O are given off and Tl_2SO_4 remains (Strecker, *A.* 135, 207; Crookes, *C. N.* 8, 243). The *double salts* $Tl_2(SO_4)_3.M_2SO_4$ [= $TlM(SO_4)_2$], where M = K or Na, are described by Strecker (*l.c.*).

Thorium sulphates. The *hydrated normal sulphate* $Th(SO_4)_2.xaq$ is obtained by dissolving ThO_2 in slight excess of H_2SO_4Aq, and crystallising at 10°–15°. The *anhydrous salt* is obtained by heating the hydrated salt to c. 400° (*v.* Chydenius, *P.* 119, 43; Delafontaine, *A.* 131, 100; Cleve, *Bl.* [2] 21, 115; Demarçay, *C. R.* 96, 1860). For a full discussien of the conditions of formation, relations, and solubilities of the various hydrates of $Th(SO_4)_2$ *v.* Roozeboom (*Z. P. C.* 5, 198). $Th(SO_4)_2$ has S.G. 4·053 at 22·8° (Clarke, *Am.* 2, 175); 4·2252 at 17° (Krüss a. Nilson, *B.* 20, 1675). The S.G. of $Th(SO_4)_2.9aq$ is 2·767 according to Topsöe (*Bl.* [2] 21, 120). The hydrate $Th(SO_4)_2.9aq$ is isomorphous (monoclinic) with $U(SO_4)_2.9aq$ (Rammelsberg, *B. B.* 1886. 603). *Double salts* $Th(SO_4)_2.M_2SO_4.xaq$ are known, where M = an alkali metal (Cleve, *l.c.*; Chydenius, *l.c.*).

Tin sulphates. The *normal stannous salt* $SnSO_4$ is obtained, in very small white crystals, by dissolving Sn in warm fairly conc. H_2SO_4Aq, taking care that Sn is in excess, dissolving the white solid so formed in water, and allowing to crystallise out of contact with air (Marignac, *Ann. M.* [5] 15, 221). $SnSO_4$ is very sol. water; the solution soon deposits basic salts. The *normal stannic salt* $Sn(SO_4)_2.2aq$ was obtained by Ditte (*C. R.* 104, 178) by dissolving $SnO_2.xaq$ (ppd. from $SnCl_4Aq$ by alkali) in dilute H_2SO_4Aq and evaporating (*v.* also Kraskowitz, *P.* 35, 518). It forms white rhombic leaflets; very sol. water; decomposed by much water with separation of SnO_2. A *basic salt* $SnO(SO_4).aq$ is said to be formed (Ditte, *l.c.*) by dissolving the normal salt in H_2SO_4Aq, warming, adding excess of Sn, and then ether.

Titanium sulphates. *Normal titanous sulphate* $Ti_2(SO_4)_3.8aq$ is obtained, as violet crystals, by evaporating a solution of Ti in H_2SO_4Aq; sol. water, solution gives a black pp. when warmed (Glatzel, *B.* 9, 1833; Ebelmen, *J. pr.* 42, 76). *Normal titanic sulphate* $Ti(SO_4)_2.3aq$ was obtained by Glatzel (*l.c.*) by oxidising the titanous salt by HNO_3, adding a drop or two H_2SO_4Aq, and evaporating; a white, translucent mass. A *double salt* $Ti(SO_4)_2.K_2SO_4.3aq$ was obtained by Warren (*P.* 102, 449), by fusing TiO_2 with $KHSO_4$, treating with conc. H_2SO_4, evaporating, and washing the residue with cold water (*v.* also Glatzel, *l.c.*). By dissolving TiO_2 in hot H_2SO_4Aq, evaporating, drying the residue on a porous tile at 180°, and then heating to c. 350°, Merz (*J. pr.* 99, 157) obtained the *acid salt* $TiO.SO_4$ as a hard white solid.

Uranium sulphates. *Normal uranic sulphate* $U(SO_4)_2.9aq$ is obtained, as green monoclinic crystals isomorphous with $Th(SO_4)_2.9aq$ (Rammelsberg, *B. B.* 1886. 603), by evaporating a solution of UO_2 in excess of H_2SO_4Aq (R., *l.c.*; Ebelmen, *J. pr.* 27, 385). Unchanged in air; slowly loses water of crystallisation when heated; at higher temperatures gives yellow $(UO_2)SO_4$, and when strongly heated leaves U_3O_8. Heated in H gives UO_2. Easily sol. dilute H_2SO_4Aq or HClAq. Decomposed by water, giving *basic salts* (*v.* R., *l.c.*; Athanasesco, *C. R.* 103, 271). Forms *double salts* with alkali sulphates (R., *l.c.*). The *uranyl salt* $(UO_2)SO_4.xaq$ is obtained, in citron-yellow crystals, by dissolving U_3O_8 in H_2SO_4Aq with a little HNO_3; or by decomposing $UO_2(NO_3)_2$ by conc. H_2SO_4, evaporating nearly to dryness, dissolving in water, evaporating to a syrup, and allowing to crystallise slowly (Ebelmen, *A.* 56, 230). By evaporating a solution of the hydrated salt in conc. H_2SO_4, Schultz-Sellack obtained the anhydrous salt $(UO_2)SO_4$ (*B.* 4, 13). Forms *double salts* with alkali sulphates $(UO_2)SO_4.M_2SO_4.2aq$ (Rammelsberg, *B.* 5, 1005).

Vanadium sulphates. *Vanadyl sulphate* $(VO)SO_4.xaq$ is obtained by heating a solution of V_2O_4 in conc. H_2SO_4. Gerlach (*B.* 11, 98) prepared several compounds of V_2O_5 and SO_3 by dissolving V_2O_5 in H_2SO_4. For more details and descriptions of various salts *v.* VANADIUM TETROXIDE and PENTOXIDE (*infra*).

Zinc sulphates. The *normal salt* $ZnSO_4$ is obtained by dissolving Zn, ZnO, or $ZnCO_3$ in dilute H_2SO_4Aq, evaporating, drying the crystals of $ZnSO_4.7aq$, and gradually heating to c. 280° till water ceases to be given off; it is difficult to drive off every trace of water without decomposing some of the $ZnSO_4$ and forming

basic sulphates. Klobb (*C. R.* 114, 836) obtained $ZnSO_4$ in crystals by heating $ZnSO_4.7aq$ mixed with excess of $(NH_4)_2SO_4$ in a partly-closed crucible, protected from the gases of the flame, till all $(NH_4)_2SO_4$ was volatilised. A white solid; S.G. 3·435 at 16° (Pape, *P.* 120, 367); 3·6235 at 15° (Thorpe a. Watts, *C. J.* 37, 108). H.F. $[Zn,S,O^4]=230,100$ (*Th.* 3, 516). Decomposed to ZnO, SO_2, and O at c. 400° (Bailey, *C. J.* 51, 681). Heated with charcoal, SO_2 and CO_2 are evolved and ZnO remains; if the temperature is rapidly raised to a white heat, SO_2 and CO are given off and ZnS is formed. Heating in H produces an oxysulphide of Zn. For solubility in water *v. infra.* $[ZnSO_4,Aq]=9,950$ (*Th.* 3, 516). For compounds of $ZnSO_4$ with NH_3 *v.* Schindler (*Mag. Pharm.* 31, 167; 36, 43), Kane (*A. Ch.* [2] 72, 290), Müller (*Z.* [2] 5, 250; 6, 96).

Hydrated zinc sulphate. Several hydrates are known. The *heptahydrate* $ZnSO_4.7aq$ crystallises, at ordinary temperatures, in white, right rhombic, prisms, isomorphous with $MgSO_4.7aq$. S.G. 1·964 (Thorpe a. Watts, *C. J.* 37, 110). H.F. $[Zn,S,O^4,7H^2O]=252,700$ (*Th.* 3, 516). Melts at 50° (Tilden, *C. J.* 45, 267). At 100° loses $6H_2O$. Poggiale (*A. Ch.* [3] 8, 467) gives solubility in water as follows:—

Temp.	S.	
	$ZnSO_4.7aq$	$ZnSO_4$
0°	115·22	43·02
10	138·21	48·36
20	161·49	53·13
30	190·90	58·40
40	224·05	63·52
50	263·84	68·75
60	313·48	74·20
70	369·36	79·25
80	442·62	84·60
90	532·02	89·78
100	653·59	95·03

Gerlach (*Fr.* 8, 260) and Schiff (*A.* 110, 72) give the following data for $ZnSO_4Aq$:—

S.G.		
Gerlach, at 15°	Schiff, at 20·5°	Pctge. $ZnSO_4.7aq$
1·0288	1·0289	5
1·0593	1·0588	10
1·0905	1·0899	15
1·1236	1·1222	20
1·1574	1·1560	25
1·1933	1·1914	30
1·2315	1·2285	35
1·2709	1·2674	40
1·3100	1·3083	45
1·3532	1·3511	50
1·3986	1·3964	55
1·4451	1·4439	60

Almost insol. absolute alcohol; 100 parts of a saturated solution in alcohol of 40 p.c. contain 3·48 parts $ZnSO_4.7aq$ (Schiff, *J.* 1861. 87).

Hexahydrate, $ZnSO_4.6aq$; obtained by crystallising $ZnSO_4Aq$ at 40°; S.G. 2·07 (T. a. W., *l.c.*; *v.* also Marignac, *J.* 1855. 389). *Pentahydrate*, $ZnSO_4.5aq$; obtained by boiling the finely-powdered heptahydrate with alcohol of S.G. ·825; S.G. 2·206 (T. a. W., *l.c.*; *v.* also Kühn, *J.* 1830. 300; Schindler, *Mag. Pharm.* 31, 167; 36, 43; Pierre, *A. Ch.* [3] 16, 242). *Dihydrate*, $ZnSO_4.2aq$; formed by pouring cold saturated $ZnSO_4Aq$ into conc. H_2SO_4, and washing the pp. with absolute alcohol; S.G. 2·958 (T. a. W., *l.c.*). *Monohydrate*, $ZnSO_4.aq$; obtained by heating $ZnSO_4.7aq$ to 100°–110° till it ceases to lose weight; S.G. 3·28 (T. a. W., *l.c.*; *v.* also Graham, *P. M.* [3] 6, 327, 417).

An *acid salt* $ZnSO_4.H_2SO_4.8aq$ is described by von Kobell (*J. pr.* 28, 492). Several *basic salts* are formed by boiling solutions of $ZnSO_4.7aq$ with ZnO or ZnO_2H_2 (*v.* Schindler, *l.c.*; Kühn, *l.c.*; Kane, *A. Ch.* [2] 72, 290; Reindel, *Z.* [2] 5, 508; Habermann, *M.* 5, 432; Athanasesco, *C. R.* 103, 271).

Double salts are numerous: (1) With alkali sulphates, $ZnSO_4.M_2SO_4.xaq$ (*v.* Pierre, *Ph. C.* 1846. 410; Tobler, *A.* 95, 193; Graham, *P. M.* [3] 6, 327, 417; Karsten, *B. B.* 1841). (2) With $CoSO_4$, $FeSO_4$, $MgSO_4$, $NiSO_4$, &c., to form $ZnSO_4.MSO_4.xaq$ (*v.* Rammelsberg, *P.* 91, 321; Pierre, *l.c.*; Étard, *C. R.* 86, 1399; 87, 602).

Zirconium sulphates. The *normal salt* $Zr(SO_4)_2$ is obtained by dissolving ZrO_2 in slightly diluted H_2SO_4, evaporating, and driving off excess of acid at a temperature below red heat. $Zr(SO_4)_2$ is decomposed by heating to redness, giving ZrO_2. By concentrating a solution of $Zr(SO_4)_2$ containing some free H_2SO_4, Paykull (*B.* 6, 1467) obtained crystals of the *tetrahydrate* $Zr(SO_4)_2.4aq$ (confirmed by Weibull, *B.* 20, 1394).

Basic salts are obtained by digesting a solution of a salt of Zr with saturated K_2SO_4Aq (*v.* Berzelius, *P.* 4, 117; Warren, *J. pr.* 75, 361).

Double salts with K_2SO_4 are formed by fusing $KHSO_4$ and ZrO_2 (B., *l.c.*; W., *l.c.*).

DITHIOPERSULPHATES. Under the name of *sodium dithiopersulphate*, Villiers (*C. R.* 106, 851, 1354) described a salt $Na_2S_4O_8.5aq$. This salt was said to be obtained by adding to sodium thiosulphate insufficient water to dissolve all the salt, saturating with SO_2, adding a little more water, again saturating with SO_2, keeping the yellow solution at the ordinary temperature for two or three days, passing in SO_2 as long as it was absorbed, and, after standing a day or two, evaporating *in vacuo* over H_2SO_4. A mixture of $Na_2S_4O_8$ and $Na_2S_3O_6$ was thus obtained; on exposure to air the crystals of $Na_2S_3O_6$ effloresced, and the $Na_2S_4O_6$ was then picked out. The salt $Na_2S_4O_8$ was described as white, lustrous, rhombic prisms; unchanged in air; melting at c. 125°, and giving off SO_2 at c. 140°, leaving Na_2SO_4 mixed with S. In a later paper (*C. R.* 108, 402) V. announced that the salt supposed by him to be $Na_2S_4O_8$ was only hydrated sodium tetrathionate $Na_2S_4O_6.H_2O$.

NITROSOSULPHATES. In 1800 Davy (*Researches, chiefly concerning Nitrous Oxyde*) noticed that NO was absorbed by a mixture of Na_2SO_3Aq and NaOHAq, a compound being formed which, on addition of an acid, gave off N_2O while Na_2SO_4 remained in solution; he supposed that the NO was reduced to N_2O, the Na_2SO_3 being oxidised to Na_2SO_4, and that the N_2O combined with the NaOH. Pelouze (*A. Ch.* [2] 60, 151) found that a salt containing N, S, and O was formed in the reaction examined by Davy; to this salt he gave the composition $Na_2SO_2(NO)_2$.

A mixture of 1 vol. SO_2 and 2 vols. NO is gradually absorbed by conc. KOHAq or NaOHAq, forming $K_2(NO)_2SO_3$ or $Na_2(NO)_2SO_3$.

Ammonium nitrososulphate $(NH_4)_2(NO)_2SO_3$ is best prepared by passing NO for some hours into cold conc. $(NH_4)_2SO_3Aq$ mixed with 5 to 6 times its volume of NH_3Aq. White crystals of the salt gradually form; they are washed with ice-cold NH_3Aq, dried *in vacuo*, and kept in a well-stoppered bottle (Pelouze, *l.c.*). *Potassium nitrososulphate* and *sodium nitrososulphate*, $M_2(NO)_2SO_3$, are prepared similarly to the ammonium salt. *Barium* and *lead nitrososulphates* are obtained by ppg. aqueous solutions of the K salt by conc. BaOAq and solution of basic acetate of lead, respectively (Divers a. Haga, *C. J.* 47, 364). The nitrososulphates readily decompose; they are stable in solution only in presence of excess of alkali. Heated moist they give off N_2O, leaving pure sulphate; heated dry they give NO and sulphite (*v.* D. a. H., *C. J.* 47, 203). With acids, and also with most metallic salts in solution, also in contact with spongy Pt, charcoal, Ag_2O, MnO_2, &c., they give N_2O and sulphates. Solution of an alkali nitrososulphate has no reaction with $KMnO_4Aq$ (D. a. H., *l.c.* p. 205). An alkaline solution of the K or Na salt is slowly reduced by Na amalgam, giving K_2SO_3Aq and $K_2N_2O_2Aq$, or the corresponding Na salts (D. a. H., *l.c.* p. 203).

PERSULPHATES. Persulphuric anhydride S_2O_7 is formed at the anode during the electrolysis of fairly conc. H_2SO_4Aq (*v. Sulphuric peroxide*, under SULPHUR OXIDES, p. 616). The acid corresponding with this oxide would be $H_2S_2O_8$ or HSO_4; this acid has not been isolated, but some of its salts have been prepared by Marshall (*C. J.* 59, 771 [1891]).

Potassium persulphate $K_2S_2O_8$ is obtained by passing a current of 3 to 3½ ampères, for some days, through saturated $KHSO_4Aq$ contained in a Pt dish, wherein is suspended a porous cell containing dilute H_2SO_4Aq; the Pt dish stands in a vessel of copper, through which runs a stream of cold water, and which is connected with the battery so that the Pt dish becomes the anode; the cathode consists of a stout wire of Pt dipping into the dilute H_2SO_4Aq in the porous cell (for description, and diagram, of the apparatus *v.* Marshall, *C. J.* 59, 765-6). The granular salt that slowly separates during electrolysis is collected by filtering through Pt foil, dried on a porous plate, treated with hot water so as to obtain a nearly saturated solution, which is at once rapidly cooled (the mother-liquor yields more $K_2S_2O_8$ when again electrolysed). $K_2S_2O_8$ forms small, white, prismatic crystals; by spontaneous evaporation of a solution, large, flat tables are obtained, probably asymmetric. Slightly sol. cold water; S. at $0° = 1·77$; insol. absolute alcohol, hot or cold. Measurements of the electrical conductivities of solutions of the salt indicated the formula KSO_4, and not $K_2S_2O_8$; but Bredig (*Z. P. C.* 12, 230) showed that Marshall's results were based on data, given by Ostwald, which were not quite accurate (the data were afterwards corrected in Ostwald's *Lehrbuch* [2nd ed.] 2, 730). Bredig's measurements established the formula $K_2S_2O_8$; and this was confirmed by Löwenberg's determinations of the freezing-points and conductivities of solutions of the salt (*Chem. Zeitung*, 1892. 838). $K_2S_2O_8Aq$ very slowly decomposes at the ordinary temperature, giving $KHSO_4Aq$ and O; in contact with zinc, decomposition is still very slow; with a Cu-Zn couple the rate of change is hastened; heating also hastens the reaction. After keeping for some time in a closed bottle a peculiar smell is noticed on opening the bottle, perhaps due to $H_2S_2O_8$ or S_2O_7; ozone is sometimes also given off. Heat decomposes $K_2S_2O_8$; K_2SO_4 remains and SO_3 and O are given off; decomposition is marked at a little above 100°, but is not complete at 250°. When gently warmed with conc. HNO_3Aq or H_2SO_4, much ozone is given off; Cl is evolved when conc. HClAq is used. $K_2S_2O_8Aq$ does not yield pps. of persulphates with solutions of metallic salts; when pps. are formed they are due to reactions with K_2SO_4Aq formed by the decomposition of the $K_2S_2O_8Aq$. Solution of a salt of Ba slowly throws down $BaSO_4$; the reaction is very slow, even when the solution is boiled. Solution of a salt of Pb also slowly forms $PbSO_4$ when heated with $K_2S_2O_8Aq$; if alkali is added, PbO_2 is ppd. $AgNO_3Aq$ produces no pp. at once, but after a time black AgO, the solution becoming acid; several other metallic salts in presence of alkali yield pps. of peroxides with $K_2S_2O_8Aq$, *e.g.* salts of Co, Cu, Mn, and Ni. KIAq is slowly decomposed by $K_2S_2O_8Aq$, with separation of I; litmus and turmeric solutions are gradually bleached; paper and cloth become rotten when dipped in $K_2S_2O_8Aq$. K_4FeCy_6Aq is oxidised to K_3FeCy_6Aq, and alcohol yields aldehyde, by warming with $K_2S_2O_8Aq$.

Ammonium persulphate $(NH_4)_2S_2O_8$. Prepared, similarly to $K_2S_2O_8$, by electrolysing dilute H_2SO_4Aq (c. 1 to 6 by volume) with $(NH_4)_2SO_4$; the salt is purified by cooling by ice a solution saturated at a little above the ordinary temperature. Crystallises in transparent lozenge-shaped, apparently mono-symmetric tables. Very sol. water; S. at $0° = 58·2$. Reacts similarly to $K_2S_2O_8$ (*cf.* Elbs, *J. pr.* [2] 48, 185).

Barium persulphate $Ba_2(SO_4)_4.8aq$. Prepared by rubbing in a mortar saturated $(NH_4)_2S_2O_8Aq$ with excess of pure BaO_2H_2—$Ba_2(SO_4)_4$ goes into solution, and $BaSO_4$ also forms—passing a rapid stream of air till most of the NH_3 set free in the reaction is removed, placing *in vacuo* over H_2SO_4 till no free NH_3 remains, passing in CO_2 to remove excess of BaO_2H_2, keeping *in vacuo* for a short time (to decompose Ba bicarbonate to $BaCO_3$), filtering from $BaSO_4$ and $BaSO_3$, evaporating *in vacuo* till crystallisation begins (with addition from time to time of a little BaOAq to neutralise $H_2S_2O_8$ that is set free during evaporation), dissolving the crystals that first separate in as little water as possible, filtering, cooling by ice, and drying the small prismatic crystals that form on a porous plate. The crystals of $Ba_2(SO_4)_4.8aq$ gradually become milky from formation of $BaSO_4$, the change soon spreads, and the crystals crumble to a moist, powdery mass of $BaSO_4$. $Ba_2(SO_4)_4.8aq$ is very sol. cold water; S. at $0° = 52·2$. Sol. absolute alcohol; on standing white crystals are deposited, probably $Ba_2(SO_4)_4.2aq$.

Lead persulphate $Pb_2(SO_4)_4.xaq$; $x = 4$ or 6, probably 6. Obtained by adding a slight excess of H_2SO_4Aq to conc. $Ba_2(SO_4)_4Aq$, neutralising with $PbCO_3$, filtering after some time, evaporating *in vacuo* over H_2SO_4 (removing $PbSO_4$ from time to time by filtration) till a solid mass is obtained, which is at once dried between filter paper and placed *in vacuo*. $Pb_2(SO_4)_4$ was not obtained quite free from $PbSO_4$; it decomposes very readily, giving off pungent fumes, that separate I from KIAq on paper.

Zinc persulphate was obtained, but not pure, by adding $ZnSO_4$Aq to $Ba_2(SO_4)_4$Aq in the proper proportions, filtering, and evaporating *in vacuo* over H_2SO_4. The *copper salt* was also obtained, but not free from $CuSO_4$. For thermal data concerning the formation and solution of the persulphates of NH_4, Ba, K, and Na *v.* Berthelot (*C. R.* 114, 875; abstract in *C. J.* 62, 931).

PYROSULPHATES. (*Disulphates. Anhydrosulphates.*) Salts of the acid $H_2S_2O_7$ (*v. Pyrosulphuric acid*, under SULPHURIC ACID, p. 620). These salts bear to the sulphates a relation similar to that of the dichromates to the chromates. The sulphates may be written $SO_2(OM)_2$, and the pyrosulphates $OM.SO_2.O.SO_2.OM$. The sulphates and pyrosulphates may also be regarded as compounds of the acidic radicle SO_3 with basic radicles MO; thus sulphates $MO.SO_3$, pyrosulphates $MO.2SO_3$. Inasmuch as $H_2S_2O_7$ may be regarded as a partial anhydride of $H_2SO_4(2H_2SO_4 - H_2O = H_2S_2O_7)$, the acid $H_2S_2O_7$ is sometimes called anhydrosulphuric (*cf.* ACIDS, vol. i. p. 50).

Potassium pyrosulphate $K_2S_2O_7$ is formed by heating K_2SO_4 with half its weight of H_2SO_4 till acid ceases to come off at an incipient red heat. Prismatic needles; S.G. 2·277 (Jacquelain, *A. Ch.* [2] 70, 311). Melts at 300°, according to Schultz-Sellack (*B.* 4, 109). Cannot be crystallised from water. Solution in fuming H_2SO_4 gives crystals of the *acid salt* KHS_2O_7, melting at 168° (S.-S., *l.c.*). Heated with alcoholic solution of KSH gives K_2SO_4, $K_2S_2O_3$, and H_2S; boiled with C_2H_5ONa in alcohol gives $KNaSO_4$ and $KEtSO_4$ (Drechsel, *J. pr.* [2] 5, 367). The pyrosulphates of NH_4, Ba, Ag, and Na are prepared similarly to $K_2S_2O_7$ (*v.* Schulze, *B.* 17, 2707; J., *l.c.*; S.-S., *l.c.*). M. M. P. M.

SULPHAZIDES $X.NH.NH.SO_2.Y$.

Formation.—1. By the action of alcoholic SO_2 upon diazo-compounds.—2. By the action of hydrazines upon sulphonic chlorides $Y.SO_2Cl$. 3. By the action of hydrazine hydrochlorides upon sulphinic acids $Y.SO_2H$.—4. By reduction of the compounds $X.N_2.SO_2.Y$.

Reaction.—By heating with aqueous alkalis (*e.g.* baryta-water) they are decomposed into a sulphinic acid, a hydrocarbon, and nitrogen: $X.N_2H_2.SO_2.Y = XH + Y.SO_2H + N_2$.

References: Koenigs, *B.* 10, 1531; Wiesinger, *B.* 10, 1715; Fischer, *A.* 190, 132; Escales, *B.* 18, 893; Limpricht, *B.* 20, 1238.

SULPHAZOTISED ACIDS *v.* SULPHUR OXYACIDS, NITROGEN DERIVATIVES OF (p. 619).

SULPHIDES. Binary compounds of sulphur. The name is generally applied only to binary compounds of S with elements less negative than itself—that is, to compounds with elements other than Br, Cl, F, I, or O; thus SO_2 and SO_3 are called oxides of sulphur rather than sulphides of oxygen. Compounds of S with organic radicles, which compounds react similarly to sulphides of metals, must be regarded as binary compounds if the definition of the term sulphide is to be made as wide as possible. In the present article, however, only binary compounds of S with less negative elements are included. Sulphides of all the metals, and also of the non-metals H, B, C, N, Si, P, Se, and Te, are known.

Many sulphides of metals occur native. Sulphides are frequently prepared by the direct union of the elements; sometimes by heating metallic oxides with excess of S, *e.g.* As_2S_3—in many cases a mixture of sulphide and oxide is formed in this way; addition of alkali carbonate to the mixture of metallic oxide and S sometimes brings about formation of sulphides, *e.g.* formation of sulphides of Cr and U; polysulphides mixed with sulphates are produced by heating the hydroxides or carbonates of alkali metals with S. Most heavy metals give sulphides when their oxides are heated in H_2S gas, also when H_2S is passed into solutions of their salts. Heating metals in H_2S gas often produces sulphides. Sulphides are also formed by heating one metal with the sulphide of another, more negative, metal. Reduction of sulphates, generally by heating in H or with C, frequently yields sulphides. Some metallic oxides yield sulphides when strongly heated in vapour of CS_2. Sulphides of many heavy metals are formed by immersing the metals in $(NH_4)_2S$Aq containing excess of S (*v.* Priwoznik, *A.* 164, 46). Many metallic oxides yield sulphides by heating with dry $Na_2S_2O_3$ (*v.* Landauer, *Fr.* 1872. 427).

The sulphides of the alkali and alkaline earth metals are soluble in water; other sulphides are insoluble, or only very slightly soluble, in water.

Very dilute aqueous solutions of several metallic sulphides, in the colloidal form, were obtained by Winssinger (*Bl.* [2] 49, 452) by the following methods: (1) ppg. the sulphide by H_2S from an extremely dilute solution, and dialysing; (2) washing the ppd. sulphide for a long time with cold water, or with dilute H_2SAq; (3) forming the sulphide in a solution free from all substances capable of causing coagulation. In these ways W. obtained colloidal soluble sulphides of Bi, Co, Au, Fe, In, Pb, Hg, Mo, Ni, Pd, Pt, Ag, Tl, W, and Zn. For preparation of colloidal soluble CdS *v.* Prost (*C. C.* 1888. 32), and of colloidal soluble CuS *v.* Spring a. de Boeck (*Bl.* [2] 48, 165).

Metallic sulphides are decomposed by strong acids, giving salts and H_2S; secondary reactions frequently occur, S almost invariably separating. Several sulphides, *e.g.* As_2S_3 and HgS, are sublimable out of contact with air; all sulphides are oxidised by heating to redness in air. The sulphides of the very positive metals yield sulphates, and the sulphides of the heavy metals generally form oxides (the sulphides of Au, Hg, Pt, and Ag form metal) and give off SO_2. All sulphides of metals yield metallic chlorides and S_2Cl_2 when heated in a stream of Cl. Many metallic sulphides are decomposed by water, at different temperatures, giving oxides or hydroxides and H_2S (*cf.* de Clermont a. Frommel, *C. R.* 87, 330). Sulphides of non-metals are decomposed by water, generally to oxyacids and H_2S; NS gives NH_4 salts of $H_2S_2O_3$ and $H_2S_3O_6$. Many sulphides of heavy metals are decomposed by heating with water and I, giving iodides, S, and a little sulphate (*v.* Filhol a. Mellies, *A. Ch.* [4] 22, 58).

The *double sulphides*, formed by the union of sulphides of more positive elements with sulphides of less positive elements, are comparable with the double oxides or oxysalts; most of these double sulphides are probably best regarded as salts of thio-acids corresponding with salts of oxyacids, but it is customary to apply this conception generally only to those compounds which contain sulphides of non-metals or of Sb, As, or Sn. The double sulphides, or thio- salts, are generally decomposed by water, forming oxides and H_2S. Many double sulphides, containing K_2S or Na_2S as one constituent, are formed by fusing metals or metallic sulphates with K_2CO_3, or Na_2CO_3, and S (*v.* Schneider, *J. pr.* [2] 7, 214; 9, 209; 10, 55). The sulphides may be classified, like the oxides, as monosulphides, disulphides, &c. It is better, however, to divide them into *basic*, *acidic*, *indifferent*, and *persulphides*; but this classification has been less developed and applied than in the case of the oxides. Basic sulphides react with acids to form salts and H_2S, just as basic oxides react with acids to form salts and H_2O. Acidic sulphides react with the basic sulphides to form thio- salts, as acidic oxides react with basic oxides to form oxy- salts; but few compounds have been isolated of acidic sulphides with H_2S, corresponding with the compounds of acidic oxides with water which are oxyacids. The more strongly acidic sulphides—that is, the sulphides of non-metals—are decomposed by water, generally giving H_2S and oxyacids. The persulphides have not been much studied; any sulphide of an element containing more S than the basic or acidic sulphide of the same element may be placed provisionally among the persulphides. A sulphide which does not react as basic or acidic, and which from its composition cannot well be called a persulphide, may be classed as an indifferent sulphide. The sulphides of C and P combine with several metallic sulphides to form thio- salts; double sulphides (or thio- salts) have not been isolated containing sulphides of B, N, Si, Se, or Te; the sulphides of Sb, As, and Sn combine with the sulphides of the alkali metals, and with some other sulphides of positive metals, to form thio- salts. The greater number of the double sulphides are formed by the union of two sulphides, both of which are metallic. The sulphide of that metal which, on the whole, is the more positive is regarded as the basic radicle; and the sulphide of the metal which, on the whole, is the less positive is regarded as the acidic radicle of the double sulphide. Some metallic sulphides must be classed both as basic and acidic; Cu_2S, for example, combines with As_2S_3, and is therefore basic towards the distinctly acidic sulphide of As, but it also combines with K_2S, and is therefore acidic towards the distinctly basic sulphide of K. It is impossible to divide the metallic sulphides into two distinctly-marked classes; the relativity of the terms 'basic' and 'acidic' becomes even more apparent in dealing with sulphides than in dealing with oxides. The sulphides BaS_3, BaS_4, CaS_4, and CaS_5 may be taken as examples of those which are loosely put together under the name persulphides. As examples of indifferent sulphides NS and Cr_3S_4 may be mentioned. Many metallic sulphides which have been little studied—and which must, therefore, for a time be called indifferent—are very probably basic in their reactions; such are Al_2S_3 and CdS. M. M. P. M.

SULPHIDO-DIACETIC ACID $C_4H_6SO_4$ *i.e.* $S(CH_2.CO_2.H)_2$. *Thiodiglycollic acid.* [129°]. S. 42 at 18°. Formed from chloro-acetic acid and alcoholic ammonium sulphide, aqueous $Ca(SH)_2$, or Na_2S (Schulze, *Z.* 1865, 73; 1866, 184; Schreiber, *J. pr.* [2] 13, 472; Lovén, *B.* 17, 2818). Formed also by heating bromo-acetic acid with benzyl sulphide, allyl sulphide, or ethylene sulphide (Letts, *Tr. E.* 28, 612). Trimetric tables, v. sol. alcohol. Oxidised by $KMnO_4$ to $SO_2(CH_2.SO_3H)_2$. The Na salt is converted by treatment with sodium chloro-acetate into $CO_2H.CH_2SMe\Big\langle\begin{matrix}O\\CH_2\end{matrix}\Big\rangle CO$ [150°] (Delisle, *B.* 25, 2450). The analogous compound $(CO_2H.CH_2)_2S\Big\langle\begin{matrix}O\\CH_2\end{matrix}\Big\rangle CO$ [158°] is formed from chloro-acetic acid, Na_2CO_3, and Na_2S (Delisle), and yields Na_2A'' 3aq.

Salts.—K_2A'' aq: deliquescent prisms.—KHA''.—CaA''. S. 2 at 21°.—BaA''.—BaA'' 5aq. — ZnA'' 4aq. — PbA''. — $Pb_2A''O$. — CuA'' aq.—Ag_2A''.

Methyl ether Me_2A''. (135° at 11 mm.).

Ethyl ether Et_2A''. (268° cor.). Formed from chloroacetic ether and alcoholic KSH (Wislicenus, *A.* 146, 153).

Amide $S(CH_2.CO.NH_2)_2$. Formed from chloro-acetic acid and alcoholic $(NH_4)_2S$.

Amic acid $S(CH_2.CO_2H).CH_2.CO.NH_2$. [125°]. Prisms, m. sol. cold water.—BaA'_2 aq.—CaA'_2 aq.—AgA': needles (from hot water).

Imide $S\Big\langle\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}\Big\rangle NH$. [128°]. Formed by heating the ammonium salt at 200°. Crystals.

Anhydride $S\Big\langle\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}\Big\rangle O$. [102°]. (158° at 10 mm.). Formed by boiling the acid with AcCl (Anschütz, *A.* 273, 68). Needles (from $CHCl_3$).

Chloride $S(CH_2.COCl)_2$.

Mono-anilide $S(CH_2.CO_2H).CH_2.CONHPh$. [103°].

Di-anilide $S(CH_2.CO.NHPh)_2$. [168°].

p-Toluide $S(CH_2.CO_2H).CH_2.CO.NHC_7H_7$. [95°]. Needles.

Di-sulphido-di-acetic acid (*di-thio-di-glycollic acid*) $S_2(CH_2.CO_2H)_2$ [100° uncor.]. Formed from thio-glycollic acid $CH_2(SH).CO_2H$ by Fe_2Cl_6 or by atmospheric oxidation of the alkaline solution (Claesson, *B.* 14, 410; Ginsburg a. Bondzynski, *B.* 19, 114). White plates or prisms. V. sol. water, alcohol, and ether, sl. sol. benzene. Gives with $AgNO_3$ a white pp. $AgHA''$. By tin and HCl it is reduced to thio-glycollic acid.—K_2A'' $1\frac{1}{2}$aq: easily soluble crystals.—KHA'' aq.—BaA'' 4aq: amorphous pp.

Ethyl ether Et_2A''. (c. 280°).

Amide [155°]. Crystalline.

SULPHIDO-DI-ACETOACETIC ETHER $C_{12}H_{18}SO_6$ *i.e.* $S(CHAc.CO_2Et)_2$. [90°] (S.); [84°] (D.); [76°] (B.). Formed by the action of S_2Cl_2 (2 mols.) or of SCl_2 on sodium acetoacetic ether (1 mol.) suspended in benzene (Buchka, *B.* 18, 2092; 22, 2545, 2555; Delisle, *B.* 22, 306). Formed also from cupric acetoacetic ether and S in benzene (Schönbrodt, *A.* 253, 197). Needles, v. e. sol. benzene. Converted by KOH into sulphido-diacetic acid. Yields a crystalline phenyl-hydrazide $C_{20}H_{22}N_4SO_4$, converted by warming with an alcoholic solution of phenyl-hydrazine into oxy-phenyl-methyl-pyrazole-azobenzene $\begin{matrix}NPh.CO\\ N{=\!=}CMe\end{matrix}>C:N.NHPh$ (Michaelis a. Phillips, *B.* 23, 560). Phenyl-hydrazine (2 mols.) added to sulphido-di-acetoacetic ether dissolved in cooled HOAc forms $C_{20}H_{18}N_4SO_2$, which yields B′HOAc [161°] and B′HOEt (Michaelis, *B.* 23, 2476; Sprague, *C. J.* 59, 332).

SULPHIDO-ANILINE *v.* DI-AMIDO-DI-PHENYL SULPHIDE.

DISULPHIDO-DI-BENZOIC ACID $S_2(C_6H_4.CO_2H)_2$. [244°]. Formed by oxidation of $C_6H_4(SH).CO_2H$ by moist air or by bromine water (Frerichs, *B.* 7, 794; Hübner a. Upmann, *Z.* 1870, 294). Formed also from *m*-diazo-benzoic acid and H_2S (Griess, *J. pr.* [2] 1, 102) and, in small quantity, by fusing sodium sulphobenzoate with sodium formate (Ador, *B.* 4, 622; Meyer, *B.* 6, 1150). Needles, nearly insol. hot water, sl. sol. alcohol. –$(NH_4)_2A''$ 2aq.—CaA″ 3aq.—BaA″ 3aq. — PbA″ aq. — $Cu_2(OH)_2A''$ 5aq. — Ag_2A'' 1½aq: yellowish-white pp.

γ-SULPHIDO-DIBUTYRIC ACID $S(CH_2.CH_2.CH_2.CO_2H)_2$. [99°]. Formed by warming its nitrile with fuming HClAq (Gabriel, *B.* 23, 2492). Flat crystals.

Nitrile $S(CH_2.CH_2.CH_2.CN)_2$. (above 300°). Formed by boiling γ-chloro-butyronitrile with alcoholic K_2S. Thick liquid.

α-Sulphido-dibutyric acid $S(CHEt.CO_2H)_2$. [105°]. Formed by heating α-bromo-butyric ether (2 mols.) with an alcoholic solution of KSH (1 mol.) and KOH (1 mol.), and saponifying the product (Lovén, *J. pr.* [2] 33, 102). Tufts of needles (from water).—BaA″.

α-Sulphido-di-isobutyric acid $S(CMe_2.CO_2H)_2$. Formed from α-bromo-isobutyric ether and alcoholic K_2S, the product being saponified. Tablets (from water), insol. dilute H_2SO_4.—BaA″ 2aq.

Di-γ-sulphido-dibutyric acid $S_2(CH_2.CH_2.CH_2.CO_2H)_2$. [109°]. Formed by boiling the amide with conc. HClAq (Gabriel). Flat plates, v. sol. alkalis.

Amide $S_2(C_3H_6.CO.NH_2)_2$. [167°]. Formed by dissolving $Cy.C_3H_6.S.Cy$ in cold conc. H_2SO_4.

SULPHIDO-DICINNAMIC ACID $C_{18}H_{14}SO_4$ *i.e.* $(PhCH:C(CO_2H))_2S$. Formed by boiling sulphido-diacetic acid with Ac_2O and NaOAc (Lovén, *B.* 18, 3242). Small needles (from alcohol), insol. water. Yields $C_{18}H_{14}Br_2SO_4$.—Na_2A'' $2\frac{1}{3}$aq: silvery plates.

Di-α-sulphido-di-cinnamic acid $C_{22}H_{22}S_2O_4$ *i.e.* $(Ph.CH:C.CO_2H)_2S_2$ [179°]. Formed by the oxidation of sulphydro-cinnamic acid $Ph.CH:C(SH).CO_2H$ by iodine in alcoholic solution. Long yellowish needles, v. sol. alcohol, less in benzene (Ginsburg a. Bondzynski, *B.* 19, 123).

DI-SULPHIDO-DI-METHENYL-DI-AMIDO-DI-NAPHTHYL MERCAPTAN $S_2(C\ll^{N}_{S}>C_{10}H_6)_2$. Formed by oxidation of $C_{10}H_6<^{N}_{S}\gg C.SH$ with alkaline K_3FeCy_6 (Jacobson a. Frankenbacher, *B.* 24, 1408). The (α)-compound melts at 194°, the (β)-isomeride at 180°.

DISULPHIDO-DI-METHENYL-DI-AMIDO-DI-PHENYL MERCAPTAN $S_2(C\ll^{N}_{S}>C_6H_4)_2$. [186°]. Formed by oxidising sulphydro-methenyl-amido-phenyl mercaptan with $K_2Cr_2O_7$ and HOAc (Jacobson a. Frankenbacher, *B.* 24, 1404; *cf.* Hofmann, *B.* 20, 1780). Plates (from benzene).

DI-SULPHIDO-DI-METHENYL-DI-BENZENYL-DI-AMIDOSULPHIM $S_2(C\ll^{N}_{S.N}\gg CPh)_2$. [120°]. Formed by oxidation of $C_6H_5.C\ll^{N}_{N.S}\gg C.SH$ (Crayen, *B.* 24, 389). Stellate groups of needles, insol. water, sl. sol. alcohol. Reduced by sodium-amalgam to the parent substance.

DI-SULPHIDO-DI-METHENYL-DI-*p*-TOLENYL-DI-AMIDOSULPHIM $S_2(C\ll^{N}_{S.N}\gg C.C_6H_4Me)_2$. [169°]. Formed by oxidation of $C_7H_7.C\ll^{N}_{N.S}\gg C.SH$ with HNO_3 free from nitrous acid (Crayen, *B.* 24, 392). Needles, insol. alcohol and ether, sol. hot C_6H_6.

DI-SULPHIDO-DI-METHYL-ANILINE *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL-DI-SULPHIDE.

DI-SULPHIDO-DI-NAPHTHALENE-DI-(β)-SULPHONIC ACID $S_2(C_{10}H_6.SO_3H)_2$. Formed from the product of the action of potassium xanthate on diazotised (β)-naphthylamine (β)-sulphonic acid by treatment with alcoholic potash (Leuckart, *J. pr.* [2] 41, 223). Colourless plates, v. sol. water and alcohol. Reduced by zinc-dust and dilute H_2SO_4 to $C_{10}H_6(SH).SO_3H$.—K_2A''.—PbA″: amorphous pp., sl. sol. water.

SULPHIDO-DI-(β)-NAPHTHYL-CARBAMIC ACID. *Phenyl ether* $S<^{C_{10}H_6}_{C_{10}H_6}>N.CO.OPh$. [215°]. S. (96 p.c. alcohol) ·20 at 16°; S. (benzene) 1·20 at 16°. Formed from the chloride and alcoholic NaOPh (Paschkowezky, *B.* 24, 2916). Needles.

Chloride $S:(C_{10}H_6)_2:N.COCl$. [255°]. Formed by heating β-imido-di-naphthyl sulphide with $COCl_2$ in toluene at 170°. Needles (from benzene-alcohol), v. sl. sol. ether. Converted by aniline into $S:(C_{10}H_6)_2:N.CO.NHPh$, which is crystalline, S. (96 p.c. alcohol) ·04; S. (benzene) ·18 at 17·5°, converted by boiling aniline into $S(C_{10}H_6NH_2)_2$ and $CO(NHPh)_2$. The chloride is converted by alcoholic NH_3 at 145° into $S<^{C_{10}H_6}_{C_{10}H_6}>N.CO.NH_2$, crystallising in needles, S (96 p.c. alcohol) ·06; S. (benzene) ·10 at 17·5°. The chloride $S<^{C_{10}H_6}_{C_{10}H_6}>N.COCl$ is converted by β-imido-di-naphthyl sulphide in xylene at 280° into $\left(S<^{C_{10}H_6}_{C_{10}H_6}>N\right)_2CO$, crystallising in yellowish plates and tables [over 350°].

SULPHIDO-DI-PHENYL-AMINE *v.* IMIDO-DI-PHENYL SULPHIDE.

SULPHIDO-DI-PHENYL-CARBAMIC ACID. *Ethyl ether* $S<^{C_6H_4}_{C_6H_4}>N.CO_2Et$. [110°]. Formed from imido-di-phenyl-sulphide and $ClCO_2Et$ (Fränckel, *B.* 13, 1845). Silky plates.

Phenyl ether $S:(C_6H_4)_2:N.CO_2Ph$. [164°]. S. (96 p.c. alcohol) ·24 at 16°; S. (benzene) 1·9 at 16°. Formed by heating the chloride with NaOPh in alcohol on the water-bath (Paschkowezky, *B.* 24, 2908). Needles.

Chloride $S:(C_6H_4)_2:N.COCl$. [172°]. Formed from $S:(C_6H_4)_2:NH$ and $COCl_2$ at 100°. Colourless prisms, sol. chloroform, and hot HOAc.

p-SULPHIDO-DI-PHENYL-DI-HYDRAZINE $S(C_6H_4.NH.NH_2)_2$. [115°]. Formed from $S(C_6H_4.NH_2)_2$ by diazotisation, treatment with $NaHSO_3$, and reduction with zinc-dust (Ruhl, *B.* 28, 3482; *A.* 270, 149). Yellowish leaflets, decomposing at 130°, sl. sol. cold water and ether, v. sol. alcohol. Reduces Fehling's solution in the cold. Benzoic aldehyde yields $S(C_6H_4.N_2H{:}CHPh)_2$. — $B''2HCl$. [209°]. — $B''H_2SO_4$. [219°].—$B''H_2C_2O_4$.

SULPHIDO-PHENYL-NAPHTHYLAMINE $S<\substack{C_{10}H_6\\C_6H_4}>NH$. *Imido-phenyl-naphthylamine.* Formed by heating phenyl-naphthyl-amine with S at 240° (Kym, *B.* 23, 2464). The (α)-compound melts at 138°, the (β)-isomeride at 178°. Both form yellow crystals, m. sol. hot alcohol, and give a deep blue solution in conc. H_2SO_4.

SULPHIDO-DI-PHENYL-DI-(β)-NAPHTHYL-UREA $N(C_{10}H_7)_2.CO.N<\substack{C_6H_4\\C_6H_4}>S$. [225°]. S. (96 p.c. alcohol) ·12; S. (benzene) ·55 at 16°. Formed from $S{:}(C_6H_4)_2{:}N.COCl$ and $(C_{10}H_7)_2NH$ at 260° (Paschkowezky, *B.* 24, 2914). White nodules, sl. sol. hot alcohol, sol. hot benzene.

Sulphido-tri-phenyl-(β)-naphthyl-urea $NPh(C_{10}H_7).CO.N{:}(C_6H_4)_2{:}S$. [170°]. S. (96 p.c. alcohol) ·52; S. (benzene) 3·38 at 15°. Formed by heating sulphido-di-phenyl-carbamic chloride with phenyl-(β)-naphthylamine at 250° (P.).

SULPHIDO-DI-PHENYL-DI-TOLYL-DI-GUANIDINE $(NHPh.C(NH).NH.C_7H_6)_2S$. [153°]. Formed from the corresponding thio-urea, HgO, and alcoholic NH_3 (Truhlar, *B.* 20, 675). Needles (from ether ligroïn).—$C_{28}H_{28}SN_6H_2PtCl_6$.

Sulphido-tetra-phenyl-di-tolyl-di-guanidine $(NHPh.C(NPh).NH.C_7H_6)_2S$. [106°]. Formed by warming an alcoholic solution of $(NHPh.CS.NHC_7H_6)_2S$ with aniline and HgO. Grey amorphous powder, v. e. sol. alcohol.

Disulphido-di-phenyl-tetra-tolyl-di-guanidine $NPh{:}C<\substack{NH.C_7H_6.S.C_7H_6.NH\\NH.C_7H_6.S.C_7H_6.NH}>C.NPh$. [119°]. Formed by heating the corresponding thio-urea with excess of aniline and HgO. Resinous mass, v. e. sol. alcohol.

SULPHIDO-DI-PHENYL-DI-TOLYL-DI-THIO-DI-UREA $(NHPh.CS.NH.C_7H_6)_2S$. [134°]. Formed from $S(C_7H_6.NH_2)_2$ and phenyl-thio-carbimide (Truhlar, *B.* 20, 670). Needles.

SULPHIDO-DI-PHENYL-UREA $C_{13}H_{10}N_2SO$ *i.e.* $S<\substack{C_6H_4\\C_6H_4}>N.CO.NH_2$. [202°]. S. (96 p.c. alcohol at 17·5°) ·3; S. (benzene) 2·7 at 17·5°. Formed from $S{:}(C_6H_4)_2{:}N.COCl$ and alcoholic NH_3 (Paschkowezky, *B.* 24, 2908). Plates.

Sulphido-tri-phenyl-urea $S<\substack{C_6H_4\\C_6H_4}>N.CO.NHPh$. [169°]. S. (96 p.c. alcohol) ·26 at 17·5°; S. (benzene) 3·74 at 17·5°. Formed from $S(C_6H_4)_2NCOCl$ and aniline. Bluish needles, sol. alcohol.

Sulphido-tetra-phenyl-urea $S(C_6H_4)_2N.CO.NPh_2$. Formed in like manner, using NPh_2H. Hexagonal plates.

Di-sulphido-tetra-phenyl-urea $CO\left(N<\substack{C_6H_4\\C_6H_4}>S\right)_2$. [225°] (F.); [231°] (P.). S. (96 p.c. alcohol) ·043 at 17°; 4·16 at 78°. Formed by heating $NH{:}(C_6H_4)_2{:}S$ with $S{:}(C_6H_4)_2{:}N.COCl$ (Fränckel, *B.* 18, 1848). Plates (from HOAc), v. sl. sol. ether and hot alcohol.

DI-SULPHIDO-DI-PROPYL-DI-PHTHALAMIC ACID $C_{22}H_{24}N_2S_2O_6$ *i.e.* $S_2(C_3H_6.NH.CO.C_6H_4.CO_2H)_2$. [136°]. Formed by boiling (γ)-phthalimido-propyl sulphocyanide with a 10 p.c. solution of KOH (Gabriel a. Lauer, *B.* 23, 89). Plates (from HOAc), v. sol. alkalis.—K_2A'': crystalline pp.

(α)-SULPHIDO-DIPROPIONIC ACID $S(CHMe.CO_2H)_2$. *Thiodilactylic acid.* [125°]. Formed, together with $CH_3.CH(SH).CO_2H$, by boiling potassium α-chloro-propionate with KSH (Schacht, *A.* 129, 4; Böttinger, *A.* 196, 106). Formed also by passing H_2S into a solution of potassium pyruvate (Böttinger, *B.* 12, 1425) and by the action of $CH_3.CH(SK).CO_2K$ on $CH_3.CHCl.CO_2K$ (Lovén, *J. pr.* [2] 29, 373). Monoclinic prisms, v. e. sol. water, alcohol, and ether. Not affected by nascent hydrogen. Oxidised by dilute HNO_3 to $SO_2(CHMe.CO_2H)_2$. —K_2A'': deliquescent.—BaA'': amorphous, v. sol. water (S.). Its solution on boiling deposits a crystalline salt, S. ·1 (L.).—Ag_2A'': amorphous pp.

Di-(α)-sulphido-dipropionic acid $S_2(CHMe.CO_2H)_2$. [142°]. Formed by oxidation of $CH_3.CH(SH).CO_2H$ by I or $FeCl_3$ (S.; Böttinger, *A.* 196, 103; *B.* 16, 1047; Lovén, *J. pr.* [2] 29, 372). Needles, sl. sol. cold water, v. sol. alcohol and ether. Reduced by zinc and HClAq to $CH_3.CH(SH).CO_2H$. — $(NH_4)_2A''$. — K_2A'' 2aq. — Ag_2A'': amorphous pp.

Di-β-sulphido-dipropionic acid $S_2(CH_2.CH_2.CO_2H)_2$. Formed by oxidation of $CH_2(SH).CH_2.CO_2H$ (L.). Thin silvery plates.

Tri-sulphido-di-propionic acid $S_3(CHMe.CO_2H)_2$. [95°]. Formed from $CH_3.CO.CO_2H$ and H_2S (Lovén, *J. pr.* [2] 47, 173). Plates, v. sol. hot water. Yields α-sulpho-propionic acid on oxidation.

SULPHIDO-TOLUIDINE *v.* DI-AMIDO-DI-TOLYL SULPHIDE.

SULPHIDO-DI-TOLYL-DI-CARBAMIC ETHER $S(C_6H_3Me.NH.CO_2Et)_2$. [113°]. Formed from imido-di-tolyl sulphide and $ClCO_2Et$ (Truhlar, *B.* 20, 668). Needles, v. sol. alcohol.

DI-SULPHIDO-TETRA-TOLYL-DI-GUANIDINE $C(NH)<\substack{NH.C_7H_6.S.C_7H_6.NH\\NH.C_7H_6.S.C_7H_6.NH}>C(NH)$. [196°]. Formed by boiling the corresponding thio-urea with alcoholic NH_3 and HgO (Truhlar, *B.* 20, 673). White amorphous powder, v. sol. benzene and hot alcohol.—$B'_2H_2PtCl_6$: brown amorphous powder.

SULPHIDO-DI-TOLYL-THIO-UREA $S<\substack{C_7H_6.NH\\C_7H_6.NH}>CS$. [235°]. Formed from $S(C_7H_6.NH_2)_2$ and alcoholic CS_2.

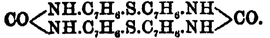
Sulphido-di-tolyl-di-thio-di-urea $S(C_7H_6.NH.CS.NH_2)_2$. [121°]. Formed by evaporating the hydrochloride of di-amido-di-tolyl-sulphide with ammonium sulphocyanide (Truhlar, *B.* 20, 669). Amorphous powder, sl. sol. ether.

Di-sulphido-tetra-tolyl-di-thio-di-urea $CS<\substack{NH.C_7H_6.S.C_7H_6.NH\\NH.C_7H_6.S.C_7H_6.NH}>CS$. [231°]. Formed by boiling an alcoholic solution of di-p-amido-di-tolyl sulphide with CS_2 (Truhlar, *B.* 20, 672).

White amorphous powder, nearly insol. ordinary solvents.

SULPHIDO-DI-TOLYL-DI-UREA $S(C_6H_3Me.NH.CO.NH_2)_2$. Formed from di-amido-di-tolyl sulphide, hydrochloride and potassium cyanate (Truhlar, *B.* 20, 669). Crystallises from benzene in needles [151°] containing C_6H_6.

Di-sulphido-tetra-tolyl-di-urea



$CO\left<\begin{matrix}NH.C_7H_6.S.C_7H_6.NH\\NH.C_7H_6.S.C_7H_6.NH\end{matrix}\right>CO$. Formed from $S(C_7H_6.NH_2)_2$ and $COCl_2$ (Truhlar, *B.* 20, 671). White amorphous powder, sol. hot alcohol.

SULPHIDO-DI-ISOVALERIC ACID $S(C_4H_8.CO_2H)_2$. Formed from bromo-isovaleric acid and K_2S (Lovén, *J. pr.* [2] 33, 102). Crystals. —BaA″: in soluble powder.

SULPHIMIDE $SO_2.NHAq$. Obtained only in aqueous solution, which is prepared by decomposing the Ag derivative, $SO_2.NAg$, with the proper quantity of dilute HClAq, and filtering. The compound $SO_2.NAg$ is prepared by saturating well-cooled SO_2Cl_2 in 15-20 vols. $CHCl_3$, with dry NH_3, dissolving the pp. in water, acidifying with HNO_3, ppg. all Cl by $AgNO_3Aq$, filtering, neutralising with KOHAq, and adding more $AgNO_3Aq$; the pp. thus obtained is purified by recrystallisation from water. The compound $SO_2.NAg$ is also obtained by heating $SO_2(NH_2)_2$ (*v.* Sulphamide, p. 567) to 200°-210°, dissolving in water, ppg. by $AgNO_3Aq$, and recrystallising the pp. from water. The solution in water of $SO_2.NH$ is strongly acid; when dilute it may be boiled for a short time without decomposition; $NH_4.HSO_4$ is formed on evaporation, even below 40°; the solution is decomposed by warming with acids, giving H_2SO_4Aq and NH_3Aq; excess of alkali reacts slowly even on boiling (W. Traube, *B.* 25, 2472; 26, 607). Metallic derivatives of $SO_2.NH$ wherein H is replaced by NH_4, Ba, Ca, Pb, K, Ag, and Na are described by T. (*cf. Imido-sulphonic acid and salts*, under Sulphonic acids and derivatives, p. 600). M. M. P. M.

SULPHIMIDO-AMIDE $SO_2NH_2.NH.NH_2SO_2$. (*Imido-sulphamide. Imido-sulphonamide. Imido-sulphurylamide*). Prepared by adding ammonium carbamate *very slowly* to $S_2O_5Cl_2$ well cooled in a small closed flask, allowing to stand for some time with a $CaCl_2$ tube fitted through the cork, then heating to 60° for some hours, washing out NH_4Cl by repeated treatment with dry alcohol saturated with NH_3, dissolving the residue in a little NH_3Aq, and placing the solution in ice. Forms white lustrous crystals; boiling NH_3Aq transforms it wholly to ammonium imidosulphonate; with boiling conc. HClAq is completely changed to $(NH_4)_2SO_4$; when boiled with NaOHAq gives off two-thirds of its N as NH_3 and forms sodium imidosulphonate (Mente, *A.* 248, 263). M. M. P. M.

SULPHINDIGOTIC ACID *v.* Indigo di-sulphonic acid.

SULPHINES. Alkyl iodides combine with di-alkyl sulphides forming compounds $R_2SR'I$, from which moist Ag_2O produces strong bases $R_2SR'.OH$. In these bases the group (SR_2R') may be looked upon as a monovalent basylous radicle derived from the hypothetical sulphine (SH_3). Thus Me_2SEtI may be called di-methyl-ethyl-sulphine iodide, but in this dictionary it is described as the ethylo-iodide of Di-methyl sulphide. In the same manner Me_3SCl may be called tri-methyl-sulphine chloride, but in this dictionary it is described as the methylo-chloride of Di-methyl-sulphide.

SULPHINIC ACIDS. Organic acids containing the group SO(OH) where S is united to carbon. They may be obtained by reducing the chlorides of the sulphonic acids, in alcoholic or ethereal solution, with zinc-dust (Otto, *B.* 9, 1584). Fatty sulphinic acids are formed by the action of SO_2 or of SO_3 on zinc alkyls (Hofmann, *A.* 102, 72; 106, 287). They are readily oxidised to sulphonic acids. The aromatic sulphinic ethers are readily oxidised by $KMnO_4$ and HOAc to sulphonic ethers (Otto a. Rossing, *B.* 19, 1224). By zinc and dilute H_2SO_4 sulphinic acids are reduced to mercaptans. The aromatic sulphinic acids yield K_2SO_3 and hydrocarbons when fused with potash. The alkyl ethers of sulphinic acids X.SO.OR are formed by passing HCl into a solution of the acid in the corresponding alcohol, and also by the action of chloro-carbonic ethers $Cl.CO_2R$ upon the sodium sulphinate X.SO.ONa in cold alcohol, CO_2 being evolved. The ethers are not formed by the action of alkyl halogenides upon sulphinates, for by this reaction the isomeric sulphones $X.SO_2.R$ are produced instead (Otto a. Rossing, *B.* 18, 2493). H_2S passing through benzene sulphinic ether at 50° forms mercaptan, benzene sulphinic acid, benzene sulphonic acid, and other products (Otto a. Rossing, *B.* 20, 2275). $COCl_2$ converts sodium benzene sulphinate into the anhydride $(Ph.SO)_2O$, which is v. sol. ether and benzene, and decomposed by water and alcohol into benzene sulphinic acid and ether respectively (Otto, *B.* 20, 3337).

SULPHITES AND HYPOSULPHITES. Sulphites are *salts of sulphurous acid formed by replacing* H *in* H_2SO_3 *by metals.* All sulphites may be represented by the formula $xMO.ySO_2$, where MO stands for an equivalent of a metallic oxide; the normal sulphites belong to the forms $M^{I}_2SO_3$, $M^{II}SO_3$, $M^{III}_2(SO_3)_3$, and $M^{IV}(SO_3)_2$; the greater number of the acidic sulphites are of the forms $M^{I}HSO_3$ and $M^{II}(HSO_3)_2$, a few which contain more than one equivalent of acidic radicle to one of basic radicle may be represented as $M^{I}_2SO_3.xSO_2$. Double sulphites are fairly numerous.

Many sulphites are prepared by passing SO_2 into water wherein metallic hydroxides or carbonates are dissolved or suspended; some are formed by double decomposition from the alkali sulphites. Several metallic sulphites that are insoluble in water can be prepared by the reaction between solutions of the sulphates and solution of Na_2SO_3; two main reactions occur, approximately in accordance with the equations (1) $M^{II}SO_4Aq + Na_2SO_3Aq = M^{II}SO_3 + Na_2SO_4Aq$, (2) $M^{II}SO_4Aq + 2H_2O = MO_2H_2 + H_2SO_4Aq$, so that normal sulphites are formed in some cases and basic sulphites in other cases. This method of forming sulphites has been examined by Seubert a. Elten (*Zeit. f. anorg. Chem.* 4, 44): they find that normal sulphites are always formed when M = Ba, Cd, Ca, Fe^{II}, Pb, Ag, Sr, or Tl (with Hg^{II} a double sulphite $HgSO_3.Na_2SO_3.H_2O$ was formed); that normal sulphites are formed at low temperatures, using the salts in the ratio of equal molecules, when $M = Mg$, Mn, Sn^{II}, $U(UO_2)$, or Zn, but that at higher temperatures, or with more dilute solutions, basic sulphites of these metals are produced; and that basic sulphites are always obtained when $M = Al$, Be, Bi, Cr, Co, Cu, Fe^{III}, or Ni.

The sulphites of the alkali metals, and the acid sulphites of the alkaline earths, are soluble in water; most other sulphites are insoluble. Sulphites in aqueous solution, and many in moist air, readily oxidise to sulphates; salts of other S oxyacids are sometimes formed, and S is frequently separated (*cf.* Pierre, *C. R.* 62, 460; 73, 749). Oxidisers, such as ClAq, HNO_3Aq, &c., quickly convert sulphites into sulphates; sulphite solutions are, therefore, energetic reducers. Solutions of sulphites are readily reduced, giving H_2S or metallic sulphides, by $SnCl_2Aq$, Zn and HClAq, &c. Heated with C, they are reduced to sulphides, sometimes to oxides. Sulphites decompose at a red heat to sulphides and sulphates, or to oxides and SO_2. Sulphites are decomposed by almost all acids, not by CO_2Aq or boric acid, giving off SO_2. Solutions of sulphites generally form thiosulphates by reacting with S, H_2S, or alkali hydrosulphides. Sulphites give sulphates and thiosulphates when heated in SO_2 (Divers, *C. J.* 47, 205). Sulphites scarcely react with $POCl_3$, according to Divers (*l.c.*); a little metallic chloride and phosphate are formed, but no $SOCl_2$. Divers (*l.c.*; also *C. J.* 49, 577) contends that the normal sulphites have the constitution $SO_2OM.M$—that is, that they contain the sulphonic group SO_2OM—and that they are not thionyl compounds, $SO(OM)_2$.

Aluminium sulphites. The only salt that has been definitely isolated is the *basic sulphite* $Al_2O_3.SO_2.4aq$; obtained by dissolving freshly ppd. AlO_3H_3 in SO_2Aq, and heating to 74°, when the salt separates as a white powder. Heated in air gives off H_2O and SO_2, and leaves sulphate (Gougginsberg, *A.* 45, 132; confirmed by Röhrig, *J. pr.* [2] 37, 217).

Ammonium sulphites. The *normal salt* $(NH_4)_2SO_3.aq$ was found in the fumes from the residues from gas-works used in the preparation of $(NH_4)_2SO_4$ (Scheitz, *Ar. Ph.* [3] 5, 332); it is prepared by adding absolute alcohol to SO_2Aq made alkaline by NH_3Aq, or by passing moist SO_2 and moist NH_3 into absolute alcohol (Muspratt, *P. M.* [3] 30, 414). White monoclinic leaflets; sol. in 1 part water at 12° with disappearance of heat. Does not deliquesce in air, but oxidises gradually to sulphate (Marignac, *Ann. M.* [5] 12, 25). The *acid salt* $NH_4.HSO_3$ is obtained, as very deliquescent rhombic crystals, by saturating a solution of the normal salt with SO_2 and allowing to crystallise *in vacuo*; loses SO_2 at the ordinary temperature; S separates on exposure to light; a saturated solution heated to 150° in a sealed tube decomposes to S, H_2SO_4Aq, and $(NH_4)_2SO_4Aq$ (Barbaglia a. Gucci, *B.* 13, 2325). The *basic salt* $3(NH_4)_2O.2SO_2.2aq$ described by Muspratt could not be obtained by Marignac. *Double salts* are described under the various sulphites.

Barium sulphites. The *normal salt* $BaSO_3$ is prepared by double decomposition from $BaCl_2Aq$ and Na_2SO_3Aq; a white powder, insol. water; may be crystallised in hexagonal forms from warm saturated SO_2Aq; heated in a closed tube decomposes to $BaSO_4$ and BaS (Rammelsberg, *P.* 67, 391). Easily sol. HClAq (Johnson, *C. N.* 58, 155; *cf.* Hodges, *ibid.* 128).

Beryllium sulphites. No salt has been isolated; a solution of a sulphite (? $BeSO_3$) is obtained by dissolving BeO_2H_2 in SO_2Aq, but crystals do not form on evaporation alone or over H_4SO_4; addition of alcohol causes formation of a thick syrup (Atterberg, *Bl.* [2] 24, 358; *cf.* Berthier, *A. Ch.* [3] 7, 77).

Bismuth sulphites. A *basic salt* $2Bi_2O_3.3SO_2.5aq$ is formed by the action of conc. SO_2Aq on BiO_3H_3 (Röhrig, *J. pr.* [2] 37, 217; *cf.* Muspratt, *P. M.* [3] 30, 414).

Cadmium sulphites. The *normal salt* $CdSO_3$ is obtained by dissolving $CdCO_3$ in SO_2Aq, and crystallising; white, indistinctly crystalline salt; scarcely sol. water; heated gives SO_2, CdO, CdS, and $CdSO_4$ (Rammelsberg, *P.* 67, 256). By treating Cd with SO_2Aq, filtering from CdS, and concentrating carefully, Fordos a. Gélis obtained the *dihydrate* $CdSO_3.2aq$; the same salt was obtained by Muspratt (*l.c.*); confirmed by Röhrig (*l.c.*). Denigès (*Bl.* [3] 7, 569) failed to obtain this hydrate, but states that a *trihydrate* is produced by mixing equal vols. of 10 p.c. solutions of $CdSO_4$ acidified with acetic acid and Na_2SO_3. A *double ammonium-cadmium sulphite* $CdSO_3.(NH_4)_2SO_3$ was obtained by Rammelsberg (*l.c.*).

Calcium sulphites. The *normal salt* $CaSO_3.2aq$ is prepared by ppg. $CaCl_2Aq$ by Na_2SO_3Aq, dissolving in SO_2Aq, and crystallising; it forms small lustrous crystals (Muspratt, *l.c.*). Also obtained by passing SO_2 into water with $CaCO_3$ in suspension (Röhrig, *l.c.*). Heated to 80° gives $2CaSO_3.aq$, and loses all water at 100° (R., *l.c.*). R. failed to isolate any acid salt.

Chromium sulphites. A *basic chromic salt* $2Cr_2O_3.3SO_2.16aq$ was obtained by Muspratt (*P. M.* [3] 30, 414), as a pale-green pp., by adding alcohol to solution of CrO_3H_3 in SO_2Aq; composition confirmed by Röhrig (*J. pr.* [2] 37, 217). Alkali sulphite solutions do not ppt. solutions of chromic salts even after long boiling (Berthier, *A. Ch.* [3] 7, 77). By adding K_2SO_3Aq to $CrCl_2Aq$, Moberg (*J.* 1847–8. 413) obtained a reddish pp. which was perhaps a *chromous sulphite*.

Cobalt sulphites. The *normal cobaltous salt* $CoSO_3.5aq$ was obtained by Muspratt (*l.c.*), as a red granular pp., by passing SO_2 into water with $CoCO_3$ in suspension, boiling out air from the solution, and letting cool in a closed vessel. By evaporating in H, Rammelsberg (*P.* 67, 391) obtained the *trihydrate*; the existence of both hydrates has been confirmed by Röhrig (*l.c.*). *Double salts* $CoSO_3.K_2SO_3$ and $2CoSO_3.Na_2SO_3.CoO$ were obtained by Schultze (*J.* 1865. 270) by heating $CoSO_3$ or $CoCl_2$ with alkali sulphite solutions. *Double salts of cobaltic sulphite* $Co_2(SO_3)_3.M_2SO_3$, where $M = K$ or Na, were obtained by Geuther (*A.* 128, 157) by continued heating of CoO_2H_2 with fresh quantities of conc. M_2SO_3Aq.

Copper sulphites. Neither cuprous nor cupric sulphite has been isolated, but several double salts of cuprous sulphite are known. The green liquid obtained by dissolving $CuCO_3$ (Berthier, *A. Ch.* [3] 7, 86) or CuO_2H_2 (Böttger, *A.* 39, 178) in SO_2Aq probably contains Cu_2SO_3; but this solution rapidly decomposes with separation of a red pp. and formation of $CuSO_4Aq$. The red solution formed by passing SO_2 into water with freshly prepared $Cu_2SO_3(NH_4)_2SO_3$ (*v. infra*) in solution was supposed to contain Cu_2SO_3 by Rogojski (*J. pr.* 53, 403); but Péan de Saint-Gilles obtained only $Cu_2SO_3.CuSO_3.2aq$ from this solution (*A. Ch.* [3] 42, 23), and this was confirmed by Svensson (*B.* 4, 713).

According to Newbury (*Am.* 14, 232), a *basic cupric sulphite* $6CuO.4SO_2.3aq$ is formed by passing SO_2 into cold water with CuO_2H_2 in suspension, and sending a stream of air into the green solution so formed until a bright-yellow pp. is produced. When this basic salt is boiled with water for a few minutes $CuSO_4Aq$ is formed, and a brown pp. is thrown down. The brown pp. is thought by N. to be Cu_2SO_3; on continued boiling with water it gives off SO_2, and Cu_2O remains.

Double cupro-cupric sulphites. The *dihydrated salt* $Cu_2SO_3.CuSO_3.2aq$ was obtained by Chevreul (*A. Ch.* 83, 183) by heating CuO or $CuCO_3$ with SO_2Aq; it is also prepared by boiling $CuSO_4Aq$ with solution of an alkali sulphite or thiosulphate, by boiling the green double salt $Cu_2SO_3.(NH_4)_2SO_3$ (*infra*) with water (P. de St.-G., *l.c.*), by passing SO_2 into conc. $Cu(C_2H_3O_2)_2Aq$ at 65° till the yellow pp. that forms is dissolved, and then letting stand in air (Étard, *C. R.* 93, 725), and by passing a slow stream of SO_2 into 10 p.c. $CuSO_4Aq$ containing a roll of thin sheet Cu till the liquid is almost colourless (the salt deposits on the Cu) (Newbury, *Am.* 14, 232). Translucent, garnet-red octahedra; S.G. 3·57; gives up $2H_2O$, and also SO_2, above 150°, and at a higher temperature leaves Cu_2O with some $CuSO_4$ (Rammelsberg, *P.* 67, 391). Soluble SO_2Aq, HClAq, and NH_3Aq; KOHAq ppts. hydrates of CuO and Cu_2O; heated with water to 200° gives $CuSO_4Aq$ and Cu in crystalline leaflets (Geitner, *A.* 129, 350). The *pentahydrate* $Cu_2SO_3.CuSO_3.5aq$ separates, as a greenish-yellow pp., from conc. $Cu(C_2H_3O_2)_2Aq$, into which a slow stream of SO_2 has been passed till the liquid has become emerald-green (P. de St.-G., *l.c.*). Easily sol. SO_2Aq or acetic acid, also in solutions of cupric salts and in NH_3Aq; when boiled with water the red dihydrate is formed.

Double salts of cuprous sulphite with alkali sulphites are readily produced by the reaction of conc. solutions of alkali sulphites with solutions of cupric salts. These double salts are colourless and crystalline; their composition is $xCu_2SO_3.yM_2SO_3.zaq$ (x generally $=1$), where $M = NH_4$, K, or Na (for details of preparation, composition, and properties *v.* Rogojski, *J. pr.* 53, 403; Péan de Saint-Gilles, *A. Ch.* [3] 42, 23; Vohl, *J. pr.* 95, 218; and Svensson, *B.* 4, 713). Some *acid salts* of the form $Cu_2SO_3.xM_2SO_3.ySO_2.zaq$ have also been prepared (S., *l.c.*), and some salts of alkali sulphites with both Cu_2SO_3 and $CuSO_3$ (P. de St.-G., *l.c.*; R., *l.c.*).

Didymium sulphites. The *normal salt* $Di_2(SO_3)_3$ was obtained, as a reddish-white powder, by passing SO_2 into water with Di_2O_3 in suspension, and boiling off excess of SO_2 (Marignac, *A. Ch.* [3] 58, 148; Cleve, *Bl.* [2] 39, 151).

Gold sulphites. No gold sulphite has been isolated. *Double salts* of Au_2SO_3 with Am_2SO_3 and Na_2SO_3 of the form $Au_2SO_3.3M_2SO_3.3aq$ are known; also a Ba salt $Au_2SO_3.3BaSO_3.aq$. The Na salt is obtained by adding Na_2SO_3Aq to a boiling alkaline solution of $NaAuO_2$, or by saturating $NaAuO_2Aq$ at 50° with SO_2, then carefully adding $BaCl_2Aq$ to the solution till free H_2SO_3 and H_2SO_4 are ppd., filtering, adding more $BaCl_2Aq$, quickly filtering off the purple-red $Au_2SO_3.3BaSO_3.aq$ that separates, washing the pp. rapidly out of contact with air, decomposing it by the proper quantity of Na_2CO_3Aq, adding some alcohol to the solution, filtering off any Ba salt that ppts., and adding more alcohol, when the Na salt separates as an orange-red, very easily decomposed, pp. (*v.* Himly, *A.* 56, 252; 59, 95). When $AuCl_3Aq$ is added, drop by drop, to a warm solution of $(NH_4)_2SO_3$ in conc. NH_3Aq, white, lustrous, six-sided plates separate of the salt $(NH_4)_2SO_3.3(NH_3Au)_2SO_3.3aq$; the mother-liquor from this salt yields the salt $Au_2SO_3.3(NH_4)_2SO_3.3aq$, very similar to the corresponding Na salt (Haase, *Z.* 1869. 535).

Indium sulphites. The only salt that has been isolated is a *basic salt* $2In_2O_3.3SO_2.8aq$. Obtained by boiling a solution of a salt of In with excess of $NaHSO_3Aq$; insol. water, sol. in dilute acids; loses $3H_2O$ at 100°, and all water at 260°; decomposed at 280°, giving off SO_2 and leaving In_2O_3 (Bayer, *A.* 158, 372).

Iridium sulphites. The *normal iridic salt* $Ir_2(SO_3)_3.6aq$ is obtained, in yellow crystals, by passing SO_2 into water with IrO_3H_3 in suspension, filtering and evaporating. The salt loses all water at 160°-180°; at a higher temperature Ir_2O_3 remains; sl. sol. water, easily sol. acids; decomposed by boiling with KOHAq with separation of Ir_2O_3 (Birnbaum, *A.* 136, 179). The insoluble matter that remains on treating IrO_3H_3 in water with SO_2 is a *basic salt* $Ir_2O_3.SO_2.4aq$ (Birnbaum, *l.c.*). *Double salts of iridous sulphite* were obtained by Seubert (*B.* 11, 1761) in separating Ir from Rh by means of Na_2SO_3 (by Bunsen's method, *A.* 146, 274). Seubert gave the formulæ $IrSO_3.3Na_2SO_3.10aq$ and $IrH_2(SO_3)_2.3Na_2SO_3.xaq$, x being $=4$ and 10, to the salts he prepared.

Iron sulphites. The *normal ferrous salt* $FeSO_3.3aq$ is formed, along with FeS_2O_3, by dissolving iron wire in SO_2Aq out of contact with air; on evaporating (out of air) the sulphite crystallises out, leaving the thiosulphate in solution (Fordos a. Gélis, *J. Ph.* [3] 4, 333; *cf.* Koene, *P.* 63, 245, 631; also Muspratt, *P. M.* [3] 30, 414). Sl. sol. water, easily sol. SO_2Aq; loses H_2O, and then (at 250°) SO_2, on heating. *Basic ferric salts* are formed by reacting on ferric salt solutions with alkali sulphites; on adding alcohol to the red liquids thus formed, Koene (*P.* 63, 245, 431) obtained the salts $Fe_2O_3.SO_2.6aq$ and $2Fe_2O_3.3SO_2$ (*cf.* Muspratt, *l.c.*). By passing SO_2 into water with FeO_3H_3 in suspension, and adding KOHAq, Muspratt (*l.c.*) obtained the *double salt* $Fe_2O_3.SO_2.2K_2SO_3.5aq$.

Lead sulphites. Only the *normal salt* $PbSO_3$ has been obtained; a white powder, insol. water, formed by adding Na_2SO_3Aq to solution of a salt of Pb (confirmed by Röhrig, *J. pr.* [2] 37, 217).

Lithium sulphites. The *normal salt* Li_2SO_3. aq is prepared by passing SO_2 into water with Li_2CO_3 in suspension, till CO_2 ceases to be given off, and evaporating on a water-bath or over H_2SO_4 (Röhrig, *J. pr.* [2] 37, 217). Danson (*C. J.* 2, 205) represented the salt as a *hexahydrate*. By adding ether to the solution obtained from Li_2CO_3, as described, R. got the *dihydrate* Li_2SO_3. 2aq. Easily sol. water, somewhat sol. alcohol, very sl. sol. ether; oxidised in moist air. Röhrig failed to obtain an acid salt. By adding the proper quantity of K_2CO_3 to the acid solution of Li_2CO_3 in SO_2Aq, evaporating to a syrup, and placing in a freezing mixture of snow and salt, R. obtained the *double salt* $2LiKSO_3$. aq; by a similar process he got monoclinic crystals of $6Li_2SO_3.Na_2SO_3$. 8aq (*J. pr.* [2] 37, 217).

Magnesium sulphites. The *normal salt* $MgSO_3$. *x*aq is formed by suspending *magnesia alba* in water, passing in SO_2, and concentrating the solution (Rammelsberg, *P.* 52, 89); if evaporation is carried on over H_2SO_4 (Röhrig, *l.c.*), or *in vacuo* below 100° (Hartog, *C. R.* 104, 1793), the *hexahydrate* separates; if evaporation proceeds above 100° the *trihydrate* is obtained (Muspratt, *l.c.*; R., *l.c.*; H., *l.c.*). Slowly oxidises in air to sulphate; loses all water at 200°; when more strongly heated the salt loses SO_2 and leaves MgO.

Double salts with $(NH_4)_2SO_3$ are formed by mixing the constituents and evaporating; also by dissolving MgO_2H_2 in cold $(NH_4)_2SO_3$Aq (Rammelsberg, *P.* 94, 507; Hartog, *l.c.*).

Manganese sulphites. Several hydrates of the *normal manganous salt* $MnSO_3$ have been described. By adding alkali sulphite solution to dilute $MnCl_2$Aq so long as the pp. that forms dissolves again, and then letting stand, monoclinic crystals of the *trihydrate* $MnSO_3$. 3aq are obtained; this hydrate is also formed by mixing 10 p.c. of $MnSO_4$Aq, acidified with acetic acid, and Na_2SO_3 (Denigès, *Bl.* [3] 7, 569); if Na_2SO_3Aq is added to hot dilute $MnCl_2$Aq the *monohydrate* is said to be produced. (Rammelsberg (*P.* 67, 245, 391) gives the formula $2MnSO_3$. 5aq to the salt obtained by reacting on Mn acetate solution with Na_2SO_3Aq, and this is confirmed by Röhrig (*J. pr.* [2] 37, 217; *cf.* also Muspratt, *P. M.* [3] 30, 414). *Double salts* $MnSO_3.K_2SO_3$ and $2MnSO_3.K_2SO_3$ were prepared by Gorgeu (*C. R.* 96, 376) by saturating 20 p.c. K_2SO_3Aq with SO_2, adding 4 p.c. $MnSO_3$. 3aq, and evaporating over an absorbent of SO_2; double Mn-Na salts are also described by G. (*l.c.*).

Mercury sulphites. According to Péan de Saint-Gilles (*C. R.* 34, 905) the *normal mercuric salt* $HgSO_3$ is formed by adding dilute Na_2SO_3Aq to a very conc. solution of $Hg(NO_3)_2$ free from excess of acid; it is, however, difficult to obtain the salt free from basic sulphites. The *basic mercuric sulphite* $2HgO.SO_2$ was obtained pure by P. de St.-G. by using solution of basic mercuric nitrate. The normal salt is easily decomposed; boiling water produces Hg_2SO_4 and Hg. Boiling water is said (P. de St.-G., *l.c.*) to convert the basic salt into the isomeric compound Hg_2SO_4 ($2HgO.SO_2 = Hg_2O.SO_3$). Divers a. Shimidzu (*C. J.* 49, 533) say that normal mercuric sulphite cannot be isolated; the reaction of Na_2SO_3Aq with $Hg(NO_3)_2$Aq produces at first the basic salt $2[2HgO.SO_2]$. aq, and then a salt which is most simply represented as $HgSO_3.Hg_2SO_3$. 4aq, and which is called *mercurosic* (or *mercuro-mercuric*) *sulphite* by D. a. S., and represented by them as $Hg\Big\langle\begin{matrix}SO_2.O\\ SO_2.O\end{matrix}\Big\rangle Hg_2$. 4aq. D. a. S. represent the basic salt as $Hg\Big\langle\begin{matrix}SO_2.OHgO\\ SO_2.OHgO\end{matrix}\Big\rangle Hg$. aq, and call it *mercuric oxysulphite*.

For the best conditions of preparation of $2HgO.SO_2$ *v.* D. a. S., *l.c.*, p. 550, and for the reactions of this salt *v. ibid.* pp. 546–50; for preparation of mercurosic sulphite *v. ibid.* p. 564, and for the reactions of this salt, pp. 559–63.

By adding dilute Na_2SO_3Aq to moist Hg_2SO_4 or to $HgNO_3$Aq, D. a. S. (*l.c.*, p. 572) obtained a greyish-black amorphous solid to which they gave the formula $Hg_4(SO_3)_2$. aq, the constitution $Hg\Big\langle\begin{matrix}SO_2.O\\ SO_2.O\end{matrix}\Big\rangle Hg_3$. aq, and the name *mercuric hypomercurous sulphite* or *hypomercurosic sulphite*. For the best method of preparing this salt (action of SO_2Aq on Hg_2SO_4 or $HgNO_3$) *v.* D. a. S., *l.c.*, p. 571; for the reactions of the salt *v.* pp. 567–70. It is evident that the formula given to this salt is the same as that of *normal mercurous sulphite* ($Hg_4(SO_3)_2 = 2Hg_2SO_3$); the salt is produced from mercurous compounds, and in many of its reactions yields mercurous compounds; D. a. S. insist that the salt belongs to a new class of Hg compounds that contain what they call the 'hypomercurous radicle.'

By treating solid $HgCl_2$ with $NaHSO_3$Aq, Wicke (*A.* 95, 176) obtained a solution that deposited a white crystalline powder to which he gave the composition $Hg(HSO_3)_2$—*i.e. acid mercuric sulphite.* According to D. a. S. (*l.c.*, p. 554) the pp. is $HgSO_3.Na_2SO_3$. aq. By reacting on HgO with SO_2Aq a white solid is formed, together with a solution containing a compound of Hg. Rammelsberg thought that the white solid was a basic mercurous sulphite of varying composition, and that the solution contained Hg_2SO_4 (*P.* 67, 405; the reaction was also examined by P. de St.-G. and by Vogel). D. a. S. say that the white residue is $HgSO_3.Hg_2SO_3$. 4aq (mercurosic sulphite, according to D. a. S.); by using freshly ppd. HgO suspended in water, and adding a little of this to SO_2Aq (nearly free from H_2SO_4), D. a. S. obtained a clear solution which reacted as a solution of $HgSO_3$ in H_2SO_3, and which they regarded as a *solution of acid mercuric sulphite*, $Hg(HSO_3)_2$ (*v. l.c.*, pp. 554–8). Several *double salts of mercuric sulphite with alkali sulphites* have been isolated. The chief are $HgSO_3.M_2SO_3$. *x*aq, where M = NH_4, K, or Na, and $2HgSO_3.Na_2SO_3$. aq (*v.* P. de St.-G., *C. R.* 34, 905; Hirzel, *A.* 84, 258; D. a. S., *l.c.*, pp. 538–46). D. a. S. regard these double salts as alkali derivatives of the hypothetical acid $Hg\Big\langle\begin{matrix}SO_2.OH\\ SO_2.OH\end{matrix}$ (they greatly doubt the existence of the salt $2HgSO_3.Na_2SO_3$ described by P. de St.-G.); this view is confirmed by Barth's measurements of the electrolytic conductivities, and the freezing-points, of solutions of these salts (*Z. P. C.* 9, 176); Barth's results point to the dissociation in dilute aqueous solution of these salts into three ions, HgS_2O_6, R, and R'.

Nickel sulphites. The *normal salt* $NiSO_3$. 6aq separates, in green tetrahedric crys.

tals, on slowly evaporating a solution formed by passing SO_2 into water with NiO. *x*aq in suspension (Rammelsberg, *P.* 67, 391). By boiling the solution of NiO. *x*aq in SO_2Aq, Muspratt (*P. M.* [3] 30, 414) obtained a *tetrahydrate* $NiSO_3$. 4aq; this hydrate was also obtained by Röhrig (*J. pr.* [2] 37, 217) by quickly evaporating the solution at c. 150°. The *compound with ammonia*, $NiSO_3.3NH_3$. 3aq, separates, as a blue crystalline pp., on adding alcohol to an ammoniacal solution of $NiSO_3$ (Rammelsberg, *l.c.*).

Osmium sulphites. The *normal salt* $OsSO_3$ was obtained by Claus (*J. pr.* 90, 65) by treating OsO_4Aq with excess of SO_2, and evaporating or adding Na_2CO_3 or Na_2SO_4; after drying the salt is a blackish-blue powder, insol. water, sol. HClAq without giving off SO_2, reppd. from this solution by KOH or K_2CO_3, decomposed to K_2SO_3 and OsO. *x*aq by long boiling with conc. KOHAq. When moist the salt oxidises in air to $OsSO_4$. The *double salt* $OsSO_3.2K_2SO_3.2KHSO_3$. 4aq was obtained by Claus (*A.* 63, 355) as a pale rose-red crystalline powder, by heating K_2OsCl_6 with K_2SO_3Aq.

Palladium sulphites. Only the *double pallado-sodium salt* $PdSO_3.3Na_2SO_3$. 2aq has been isolated; a white pp. obtained by dropping NaOHAq into $PdCl_2$Aq, after adding SO_2 (Wöhler, *A.* 174, 199).

Platinum sulphites. Neither platinosulphite $PtSO_3$ nor platinisulphite $Pt(SO_3)_2$ has been isolated. Several salts which may be regarded as double compounds of $PtSO_3$, but are better classed as platinosulphonates or platinosulphites, have been obtained; they are shortly described under PLATINO-SULPHONATES (this vol., p. 285). By passing SO_2 into water with PtO_4H_4 in suspension, and adding alkali sulphites to the dark-red liquid so formed, Birnbaum (*A.* 139, 172) obtained *double salts* of the form $PtO.SO_2.xM_2SO_3.y$aq, where M = K or Na, *x* varied from 1 to 2, and *y* also from 1 to 2. These salts gave no pp. of $BaSO_4$ with $BaCl_2$Aq, with HClAq SO_2 was given off and $PtCl_4$ formed; hence they are better classed as *double salts of platinyl sulphite*, $PtO.SO_2$, than of platinous sulphate $PtSO_4$.

Potassium sulphites. The *normal salt* K_2SO_3. 2aq is obtained, in large, deliquescent, monoclinic prisms, by passing SO_2 into K_2CO_3Aq as long as CO_2 is given off, and evaporating over H_2SO_4 at the ordinary temperature (Muspratt, *P. M.* [3] 30, 414). More soluble cold than hot water; decomposed by heat to K_2S and K_2SO_4 (Rammelsberg, *A.* 50, 259; results of M. and R. confirmed by Röhrig, *J. pr.* [2] 37, 217; *v.* also Hartog, *C. R.* 109, 179, 221, 436). The *acid salt* $KHSO_3$ separates in white needles on adding alcohol to a solution of the normal salt saturated with SO_2 (M., *l.c.*; confirmed by Röhrig, *l.c.*). By passing SO_2 into hot saturated K_2CO_3 till CO_2 ceased to come off and the solution was greenish, and then allowing to cool, Muspratt (*l.c.*) obtained hard monoclinic crystals of the *acid salt* $K_2SO_3.SO_2$ ($= K_2S_2O_5$), sometimes called *pyrosulphite*; only sl. sol. water; decomposed by heat to K_2SO_4, SO_2, and S (confirmed by Röhrig, *l.c.*). Dilute K_2SO_3Aq heated in a closed tube to 100° and then let stand is very slowly decomposed to K_2SO_4, $H_2S_2O_6$, and S (Saint-Pierre, *C. R.* 62, 460; 73, 749). K_2SO_3Aq with KNO_2Aq gives K salts of various acids; *v.* SULPHUR OXY-ACIDS, NITROGEN DERIVATIVES OF (p. 619).

Double sulphites of potassium and sodium. Schwicker (*B.* 22, 1728) obtained two distinct salts $KNaSO_3$. *x*aq; one by neutralising conc. $KHSO_3$Aq by the proper quantity of Na_2CO_3 and evaporating over H_2SO_4, the other by adding K_2CO_3 to $NaHSO_3$Aq. Röhrig (*J. pr.* [2] 37, 217) ppts. the salts by adding alcohol, or better ether. The first salt, heated with EtI to 140°, gives $4(SO_2Et.OK).NaI$, the second gives $4(SO_2Et.ONa).KI$; hence the first salt seems to be $NaSO_2.OK$ and the other $KSO_2.ONa$. Schwicker assigns different quantities of crystalline water to the salts, viz. $NaSO_2.OK.2$aq and $KSO_2.ONa$.aq; Röhrig (*l.c.*) gives 2aq to both salts. The two salts seem to be isomeric. Aqueous solutions of these salts have identical electrolytic conductivities, as would be expected (Barth, *Z. P. C.* 9, 176). Schwicker (*l.c.*) also describes the salts $KNa_2H(SO_3)_2$. 4aq and $K_2NaH(SO_3)_2$. 3aq. Hartog (*C. R.* 109, 179, 221, 436) describes the salts $K_2SO_3.2Na_2SO_3.SO_2$. 9aq ($= K_2O.2Na_2O.4SO_2$. 9aq) and $2K_2SO_3.(NH_4)_2SO_3.SO_2$. 9aq ($= 2K_2O.(NH_4)_2O.4SO_2$. 9aq).

For other double salts of potassium sulphite *v. supra*, *cobalt sulphites*, *copper sulphites*, *iron sulphites*, *lithium sulphites*, *manganese sulphites*, *mercury sulphites*, *osmium sulphites*, and *platinum sulphites*; and *infra*, *ruthenium sulphites* and *silver sulphites*.

Rhodium sulphites. The *normal rhodic salt* $Rh_2(SO_3)_3$. 6aq is prepared, as a yellowish crystalline mass, by dissolving RhO_3H_3. aq in SO_2Aq and evaporating; fairly sol. water, insol. alcohol (Bunsen, *A.* 146, 265). The *double rhodous salt* $4RhSO_3.6Na_2SO_3$. 9aq is obtained by treating Na_3RhCl_6. 12aq with excess of $NaHSO_3$Aq (Bunsen, *l.c.*); it has been examined by Seubert a. Kobbé (*B.* 23, 2556), who prepared it by heating a solution of $RhCl_3$. 4aq with excess of $NaHSO_3$Aq for some time, washing the pp. with cold water, and drying over P_2O_5. Pale-yellow solid; very sl. sol. hot water; dissolves in dilute HNO_3Aq, giving off SO_2; warmed with conc. H_2SO_4 forms $Rh_2(SO_4)_3.Na_2SO_4$ (B., *l.c.*; S. a. K., *l.c.*).

Ruthenium sulphites. Only the *double rutheno-potassium salt* $RuSO_3.K_2SO_3$ has been isolated; prepared by heating K_2RuCl_5Aq with K_2SO_3Aq till a dark-red solution is formed, evaporating to dryness, dissolving, again evaporating to dryness, and repeating these processes till a pure white residue is obtained (Claus, *J. pr.* 42, 351).

Silver sulphites. The *normal salt* Ag_2SO_3 forms small, white lustrous crystals; obtained by treating $AgNO_3$Aq with alkali sulphite solution or with SO_2Aq; if excess of SO_2Aq is allowed to remain in contact with the salt for some time Ag is formed (H. Rose, *P.* 88, 240). Darkens in air (Muspratt, *P. M.* [3] 30, 414; Sodeau, *C. N.* 65, 102); products depend on method of preparation of the salt (*v.* Stas, *Stas Nouv. R.*). Heated alone, or with water, to 100° gives Ag_2SO_4, Ag, and SO_2 (Berthier, *A. Ch.* [3] 7, 82; *cf.* Geitner, *J.* 1864. 142, who says that decomposition begins at 200°). Scarcely sol. water or SO_2Aq; sol. NH_3Aq (Berthier, *l.c.*), also in alkali sulphite solutions.

Double salts. $AgNaSO_3.2aq$; small lustrous needles, formed by dissolving Ag_2SO_3 in hot saturated Na_2SO_3Aq, letting cool, and pressing salt that separates (cannot be washed with water) (Svensson, *B.* 4, 714). $AgKSO_3.xaq$, prepared like the Na salt. Svensson (*l.c.*) describes three double salts with $(NH_4)_2SO_3$, obtained by dissolving Ag_2SO_3, or AgCl, in $(NH_4)_2SO_3Aq$; he gives the formulæ $Ag(NH_4)SO_3$, $Ag_2SO_3.6(NH_4)_2SO_3.19aq$, and $Ag_2SO_3.3(NH_4)_2SO_3.4(NH_4)HSO_3.18aq$.

Sodium sulphites. The *normal salt* Na_2SO_3 is prepared by completely saturating Na_2CO_3Aq with SO_2, warming, adding an equal quantity of the same Na_2CO_3Aq, evaporating, and crystallising above 33° (Rammelsberg, *P.* 56, 298; Schultz-Sellack, *J. pr.* [2] 2, 459). Also obtained by heating the hydrate $Na_2SO_3.7aq$ to 150°. Na_2SO_3 also crystallises from solution of $NaHSO_3$ that has been made strongly alkaline. Heated above 150° melts to a yellowish-red mass containing sulphide and sulphate in the ratio $Na_2S{:}3Na_2SO_4$ (R., *P.* 67, 246; 94, 507). The *heptahydrate* $Na_2SO_3.7aq$ is obtained by crystallising at the ordinary temperature a solution of Na_2CO_3 saturated with SO_2, warmed, and mixed with an equal quantity of the same Na_2CO_3Aq; monoclinic prisms; S.G. 1·561 (Buignet, *J.* 14, 15). Effloresces and partially oxidises in air. Very sol. water; maximum solubility at 33°. Another hydrate, $Na_2SO_3.10aq$, was described by Muspratt (*P. M.* [3] 30, 414) as formed by evaporating Na_2SO_3Aq over H_2SO_4; according to Röhrig (*J. pr.* [2] 37, 217) only the heptahydrate exists.

The *acid salt* $NaHSO_3$ is formed by saturating Na_2CO_3Aq with SO_2 and cooling; better crystals are obtained by treating $Na_2CO_3.10aq$ with SO_2 and evaporating the liquid so produced in SO_2. Easily sol. water, but less sol. than $Na_2SO_3.7aq$. (For heat of solution *v.* De Forcrand, *C. R.* 98, 738.) Gives off SO_2 on exposure to air; SO_2 is also removed from $NaHSO_3Aq$ by passage of an indifferent gas (Gernez, *C. R.* 64, 606). When heated gives off H_2O, SO_2, and S, leaving Na_2SO_4; heated in a closed tube forms Na_2SO_4, H_2SO_4, S, and H_2O (Barbaglia a. Gucci, *B.* 13, 2325). Reacts with I to give $NaHSO_4$ and NaI (Spring a. Bourgeois, *Ar. Ph.* 229, 707, where references are given to other experiments). Another *acid salt* $Na_2SO_3.SO_2$ ($= Na_2S_2O_5$), sometimes called *pyrosulphite*, is said to separate, in lustrous prisms, from conc. hot NaOHAq saturated with SO_2 (*v.* Röhrig, *l.c.*).

Double salts with ammonium sulphite. Marignac (*Ann. M.* [5] 12, 30) described a double salt obtained by passing NH_3 into conc. $NaHSO_3Aq$; the salt is probably identical with that described by Schwicker (*B.* 22, 1728), to which he gives the formula $Na_2SO_3.(NH_4)HSO_3.4aq$. By partially saturating conc. $(NH_4)HSO_3$ with Na_2CO_3Aq, Trauber (*J. C. T.* 1888. 44) obtained the salt $2Na_2SO_3.(NH_4)_2S_2O_5.10aq$; Hartog writes the formula of this salt $2Na_2O.(NH_4)_2O.4SO_2$, and says it crystallises with 9aq (*C. R.* 109, 179, 221, 436). For other double salts of Na_2SO_3 *v. supra*, *cobalt sulphites*, *copper sulphites*, *gold sulphites*, *iridium sulphites*, *lithium sulphites*, *manganese sulphites*, *mercury sulphites*, *palladium sulphites*, *platinum sulphites*, *potassium sulphites*, *rhodium sulphites*, and *silver sulphites*.

Strontium sulphites. The *normal salt* $SrSO_3$ is formed by passing SO_2 over SrO at 290° (Birnbaum a. Wittich, *B.* 13, 651); also by decomposing $SrCl_2Aq$ by alkali sulphite solution. Small white crystals; slowly oxidises in air to sulphate (Muspratt, *P. M.* [3] 30, 414); gives SrS and $SrSO_4$ on heating (Forster, *P.* 133, 106).

Thallium sulphites. The *normal thallous salt* Tl_2SO_3 is prepared by adding Na_2SO_3Aq to Tl_2SO_4Aq, and crystallising the pp. from warm water. White crystals; S. 3·34 at 15°; insol. alcohol; S.G. 6·427 at 20° (Seubert a. Elten, *Zeit. f. anorg. Chem.* 2, 434). The same salt was obtained by Röhrig (*J. pr.* [2] 37, 217) by passing SO_2 into solution of a thallous salt, evaporating at 100° or over H_2SO_4, or adding alcohol.

Tin sulphites. *Basic stannous salts*, $xSnO.2SO_2.20aq$, x being probably 5, 8, and 11, were obtained by Röhrig (*J. pr.* [2] 37, 217) by treating freshly ppd. $SnO.xaq$ with SO_2Aq.

Titanium sulphites. Berthier (*A. Ch.* [3] 7, 77) made some observations, but described no definite salts.

Uranium sulphites. *A basic uranous salt* $UO_2.SO_2.2aq = U(OH)_2SO_3.aq$ is obtained, as a greyish-green pp., by adding Na_2SO_3Aq to UCl_4Aq (Rammelsberg, *P.* 56, 125; confirmed by Röhrig, *J. pr.* [2] 37, 217). The *uranyl salt* $UO_2.SO_3.xaq$ was obtained, in yellow prisms, by Muspratt (*P. M.* [3] 30, 414), by passing SO_2 into water with UO_3 in suspension, and allowing the solution so formed to evaporate at the ordinary temperature; Muspratt gave $x = 3$, according to Röhrig (*l.c.*) $x = 4$ (*cf.* Girard, *C. R.* 34, 22; and Reinele, *P.* 125, 238).

Zinc sulphites. The *normal salt* $2ZnSO_3.5aq$ is prepared by evaporating, or by adding alcohol to, a solution of $ZnCO_3$ in SO_2Aq (Rammelsberg, *P.* 52, 90); also by mixing cold 25 p.c. $ZnSO_4Aq$ acidified with acetic acid with cold 25 p.c. Na_2SO_3Aq, and letting stand (Denigès, *Bl.* [3] 7, 569). Muspratt (*l.c.*), Fordos a. Gélis (*J. Ph.* [3] 4, 333), and Koene (*P.* 63, 245, 431) give the formula $ZnSO_3.2aq$; but Röhrig (*J. pr.* [2] 37, 217) confirms Rammelsberg's formula.

Zirconium sulphites. Compositions of salts obtained by ppg. Zr salt solutions by alkali sulphites are doubtful (*v.* Berthier, *A. Ch.* [3] 7, 77; Hermann, *J. pr.* 31, 77).

HYPOSULPHITES. (*Hydrosulphites.*) *Salts of the acid* $H_2S_2O_4$. Hyposulphurous acid is known only in aqueous solution. Schützenberger (*A. Ch.* [4] 70, 351) obtained the Na salt, and an aqueous solution of the acid, in 1869; he gave the formula H_2SO_2 to the acid; but Bernthsen (*A.* 208, 142; 209, 285; 211, 285) in 1881 showed that the acid has the composition $H_2S_2O_4$. This acid corresponds with the oxide S_2O_3 ($S_2O_3 + H_2O = H_2S_2O_4$). Schützenberger prepared the Na salt by digesting conc. $NaHSO_3Aq$ with zinc shavings in a closed flask for c. half an hour, pouring the liquid from the crystals of the double Na-Zn sulphite which formed (this is a basic Zn-Na sulphite, according to Bernthsen, *A.* 211, 297) into a flask about three-fourths filled with conc. alcohol, allowing to stand for some time in the closed flask, and then pouring off into flasks, each flask being quite filled with the liquid and then sealed; after a time crystals of the hyposulphite were formed, to which S. gave the composition $NaHSO_2$. Bernthsen (*l.c.*) after reducing $NaHSO_3Aq$ by Zn, pouring off from the double sulphite formed, &c., removed sulphite and sulphate by adding $BaCl_2Aq$; he then filtered and titrated the solution by ammoniacal $CuSO_4Aq$, which is decolourised by $Na_2S_2O_4Aq$ to a cuprous salt (and eventually to Cu_2H_2 and Cu_2S). For details of the method of analysis *v.* Bernthsen (*B.* 13, 2277; *A.* 211, 292 *note*). B. failed to obtain $Na_2S_2O_4$ free from Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$ and Zn salts.

B. expresses the first part of the reduction of $NaHSO_3$ by the equation $4NaHSO_3Aq + Zn = Na_2S_2O_4Aq + ZnSO_3 + Na_2SO_3Aq + 2H_2O$, and the complete change by the equation

$$10NaHSO_3Aq + 3Zn =$$
$$3Na_2S_2O_4Aq + Na_2SO_3Aq + Zn_3Na_2S_4O_{10} + 5H_2O.$$

Moist sodium hyposulphite is rapidly oxidised in air to Na_2SO_3; when dry it is unchanged in O; it is easily sol. water, less sol. dilute alcohol, and insol. conc. alcohol; but according to B. even approximately pure $Na_2S_2O_4$ has not been isolated. $Na_2S_2O_4Aq$ is oxidised by iodine solution to Na_2SO_4Aq.

By heating $Na_2S_2O_4Aq$ with an equivalent quantity of H_2SO_4Aq or $H_2C_2O_4Aq$, an *aqueous solution of hyposulphurous acid* $H_2S_2O_4Aq$ is obtained; this solution is an energetic reducer, decolourising indigo, and reducing salts of Cu, Hg, Ag, &c.; the solution rapidly decomposes in air with separation of S. M. M. P. M.

SULPHO-.—*Use of this prefix applied to inorganic compounds*: for *sulpho- compounds* and *sulpho- salts v.* the compounds or salts to the names of which *sulpho-* is prefixed; thus *sulpho-molybdates* are described under MOLYBDATES; but the prefix *thio-* is used in almost every case in preference to *sulpho-* to denote the replacement of O by S. *Sulphocyanides* and similar compounds are described under CYANIDES; *sulphocyanic anhydride* is described as CYANOGEN SULPHIDE.

SULPHO-ACETIC ACID $C_2H_4SO_5$ *i.e.* $SO_3H.CH_2.CO_2H$. [75°].

Formation.—1. By adding SO_3 to cooled HOAc (Melsens, *A. Ch.* [3] 5, 392; 10, 370; *A.* 52, 276).—2. By the action of fuming H_2SO_4 on acetamide or acetonitrile (Buckton a. Hofmann, *C. J.* 9, 247).—3. By boiling chloro-acetic acid with aqueous K_2SO_3 (Strecker, *Z.* [2] 4, 214; Collmann, *A.* 148, 109).—4. By heating Ag_2SO_4 with AcCl at 120° (Kämmerer a. Carius, *A.* 131, 165).—5. By boiling chloro-acetic acid with ammonium sulphite solution (Hemilian, *A.* 168, 145).—6. By heating Ac_2O with H_2SO_4 at 130° (Franchimont, *C. R.* 92, 1054; *cf.* Baumstark, *A.* 140, 83).—7. By heating $ClSO_3H$ with HOAc at 140° (Baumstark).—8. By oxidation of isethionic acid by CrO_3 (Carl, *B.* 14, 63).

Properties.—Deliquescent crystals (containing 1½aq) giving off water of crystallisation at about 160° and decomposed at 230° into CO_2, SO_2, acetic acid, and other products (Franchimont, *R. T. C.* 7, 25). V. sol. water. Its salts are sol. water, insol. alcohol. PCl_5 acting on the Na salt forms $CHCl(SO_2Cl).COCl$ (R. Siemens, *B.* 6, 659).

Salts.—K_2A''aq: hard crystals.—KHA'': six-sided tables.—BaA''aq. S. ·267 at 20°.—$BaA''Et_2SO_4$ (Laube, *A.* 218, 258).—CaA''aq.—PbA'': radiating needles.—Ag_2A''aq: flat prisms.

Mono-ethyl ether $EtHA''$. Formed by passing HCl into the Ag salt suspended in alcohol. Syrup, v. sol. water.—$AgEtA''$: plates.

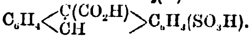
Ethyl ether Et_2A''. Oil. Formed, together with $C_6H_{11}Ag_2S_4O_{16}$ by the action of Ag_2A'' on EtI (F.). May be distilled (Mauzelius, *B.* 21, 1550).

Sulpho-diacetic acid *v.* DI-METHYL SULPHONE DICARBOXYLIC ACID.

Di-sulpho-acetic aldehyde $C_2H_4S_2O_7$ *i.e.* $CH(SO_3H)_2.CHO$. By adding chloral hydrate to conc. $KHSO_3Aq$ at 80° there are formed crystals of $C_2H_2K_2S_2O_7KHSO_3$, and these when boiled with HClAq yields $C_2H_2K_2S_2O_7$aq, from which $C_2H_2BaS_2O_7$2aq may be prepared (Rathke, *A.* 161, 154). Boiling K_2CO_3 yields $CH_2(SO_3K)_2$, potassium formiate, and K_2SO_3.

SULPHO-AMIDO-BENZOIC ACID *v.* AMIDO-SULPHO-BENZOIC ACID.

DI-SULPHO-ANILINE *v.* DI-AMIDO-DI-PHENYL DISULPHIDE.



(*B.*)-SULPHO-ANTHRACENE-(*A*)-CARBOXYLIC ACID $C_6H_4\left\langle\begin{matrix}C(CO_2H)\\CH\end{matrix}\right\rangle C_6H_3(SO_3H)$. [above 360°]. Obtained by dissolving anthracene-(*A.*)-carboxylic acid in cold conc. H_2SO_4 and allowing to stand for 12 hours on ice (Behla, *B.* 20, 706). Minute yellowish prisms (from alcohol). V. sol. water and alcohol, insol. benzene and ether. The aqueous solutions of the acid and its salts have a strong blue fluorescence.—BaA'': very soluble yellowish minute prisms.

Di-sulpho-anthracene-(*A*.)-carboxylic acid $C_{14}H_7(SO_3H)_2.CO_2H$. [above 360°]. Formed by dissolving anthracene-(*A.*)-carboxylic acid in cold fuming H_2SO_4 (Behla). Yellow prisms (from alcohol). V. sol. water and alcohol, insol. benzene. Its aqueous solution scarcely fluoresces, but the conc. H_2SO_4 solution has a strong yellowish-green fluorescence. -A'''_2Ba: very sparingly soluble crystalline powder.

SULPHOBENZIDE *v.* DI-PHENYL SULPHONE.

***o*-SULPHO-BENZOIC ACID** $C_7H_6SO_5$ *i.e.* $C_6H_4(SO_3H).CO_2H$. S. 50 in the cold.

Formation.—1. Together with its imide, by oxidation of toluene *o*-sulphonic amide with $KMnO_4$ (Remsen a. Fahlberg, *Am.* 1, 433).—2. By heating the imide with HClAq at 100° (Fahlberg a. Remsen, *B.* 12, 472; Fahlberg a. Barge, *B.* 22, 754; Brackett a. Hayes, *Am.* 9, 399). By this means the acid ammonium salt is first obtained (F.; Remsen a. Dohme, *Am.* 11, 332).—3. By boiling *o*-diazo-benzoic acid with alcoholic SO_2 (Wiesinger, *B.* 12, 1349).—4. By oxidation of toluene *o*-sulphonic acid by $KMnO_4$.

Properties.—Trimetric crystals (containing 3aq or 4aq); *a*:*b*:*c* = ·551:1:·812, v. e. sol. water, sol. alcohol, insol. ether. According to Fahlberg (*B.* 22, 754), it crystallises with 3aq, and is decomposed at 105°. According to Remsen (*Am.* 11, 332), it crystallises with 4aq, melts at 69° in its water of crystallisation, melts at 130° when anhydrous, and gives a sublimate of long needles (containing 2aq). Resorcin (1·2 pts.) at 195° forms 'sulphofluoresceïn' $C_{19}H_{12}SO_6$2aq, which fluoresces in aqueous and alkaline solutions (Remsen a. Hayes, *Am.* 9, 372). By condensation of resorcin (4 mols.) with *o*-sulpho-benzoic acid there is likewise formed a similar body $C_{31}H_{20}SO_8 4aq$ (Fahlberg a. Barge, *B.* 22, 765). Potash-fusion gives salicylic acid.

Salts.—KHA'': transparent plates, sol. water.—$K_2A'' 2aq$.—$Ba(HA'')_2 2\frac{1}{2}aq$: needles, sol. water. — $Ba(HA'')_2 2aq$. — $BaH_2A''_2 4\frac{1}{2}aq$. — $BaA'' 2aq$. — $Ca(HA'')_2 6aq$. — $CaA'' 5aq$. — $CuA'' 3\frac{1}{2}aq$. — Ag_2A''. — $C_6H_4(SO_3NH_4).CO_2H$. Formed by heating the imide with HClAq at 100°.

Anhydride $C_6H_4<\substack{CO\\SO_2}>O$. [119°] (F.). [128°] (Remsen a. Dohme, *Am.* 11, 332). Formed by heating the K salt with PCl_5 at 180° or the acid with P_2O_5 at 130°. Monoclinic tables, insol. cold water. NH_3 passed into its solution in benzene forms $C_6H_4(CONH_2)SO_2ONH_4$ [256°], which crystallises from alcohol in needles.

Chloride $C_6H_4(SO_2Cl).COCl$. [73°]. Prisms (from ether). When reduced by zinc-dust and H_2SO_4 it yields $C_6H_4(SH).CO_2H$ (Delisle, *B.* 22, 2205).

Amic acid $C_6H_4(CO.NH_2)SO_3H$. Crystals (containing aq), v. sol. alcohol and water. Got by the action of H_2S on $C_6H_4(CONH_2).SO_3Ag$ aq, which is obtained by adding silver nitrate to $C_6H_4(CONH_2).SO_3NH_4$ prepared as above (Fahlberg a. Barge, *B.* 22, 760).

Amic acid $C_6H_4(SO_2NH_2).CO_2H$. *Sulphamine-benzoic acid.* Formed by boiling toluene *o*-sulphonic amide with K_3FeCy_6 and aqueous potash (Noyes, *Am.* 8, 178; *cf.* Fahlberg, *Am.* 1, 170). Slender needles or prisms, v. sol. water, alcohol, and ether. Melts at 155° when slowly heated, and at 167° when quickly heated. At 180° it is completely converted into imide. Gives rise to the salts $MgA'_2 6\frac{1}{2}aq$, $BaA'_2 4\frac{1}{2}aq$, $BaA'_2 9aq$, AgA', and $Ag_2C_7H_5NSO_4$. By passing HCl into an alcoholic solution of the imide, the ether $C_6H_4(SO_2NH_2).CO_2Et$ [83°] is formed. The methyl and propyl ethers have also been obtained and may be converted by aniline into $C_6H_4(SO_2NH_2).CONHPh$ [189°], by *o*-toluidine into $C_6H_4(SO_2NH_2).CONHC_7H_7$ [193°], and by means of *p*-toluidine into the isomeric *p*-toluide $C_6H_4(SO_2NH_2).CONHC_7H_7$ [202°].

Imide $C_6H_4<\substack{SO_2\\CO}>NH$. *Saccharin.* [220°] (Remsen a. Fahlberg, *Am.* 1, 432). Formed by oxidising $CH_3.C_6H_4.SO_2NH_2$ with $KMnO_4$ in neutral solution (Remsen a. Fahlberg, *B.* 12, 469; Remsen a. Palmer, *Am.* 8, 223; Fahlberg a. List, *B.* 20, 1597; 21, 242; Remsen a. Linn, *Am.* 11, 73). Elongated triangular plates (by sublimation), sl. sol. cold water, v. sol. alcohol and ether. Has a very sweet taste (500 times that of cane sugar). The solubility of commercial saccharin is given by Gravill (*Ph.* [3] 18, 337) as S. (water) ·2 at 15°; ·6 at 100°; S. (alcohol) 5·4 at 15°; S. (ether) 1·3 at 15°. According to Stift (*B. C.* 18, 458) and Aducco and Mosso (*C. C.* 1887, 1148) it retards digestion, and is antiseptic. The imide is converted into $C_6H_4(SO_2NH_2).CO_2H$ on evaporation with KOHAq. Conc. hydrochloric acid at 150° forms $C_6H_4(SO_3NH_4).CO_2H$. The imide gives rise to salts of the form $C_6H_4<\substack{SO_2\\CO}>NAg$, of which the following have been described.—KA' aq: prisms, v. sol. water.—$NaA' 2aq$: tables.—$BaA'_2 1\frac{1}{2}aq$.—$BaA'_2 4aq$ (Noyes, *Am.* 8, 180).—AgA': needles (from hot water). To detect 'saccharin,' a suspected liquid may be acidified, extracted with ether, the ether evaporated, the residue fused with NaOH, and the product tested for salicylic acid and for sulphate (C. Schmitt, *Fr.* 27, 396; Allen, *An.* 13, 105; Börnstein, *Fr.* 27, 165). 'Saccharin' evaporated to dryness on a water-bath leaves a residue which, when warmed with alcoholic potash, exhibits yellow, blue, and red colours (Lindo, *C. N.* 58, 51, 155).

Methylimide $C_6H_4<\substack{SO_2\\CO}>NMe$. [132°]. Formed by heating $C_6H_4<\substack{SO_2\\CO}>NAg$ with MeI at 100° (Brackett, *Am.* 9, 406). Long flat needles, sol. ether, alcohol, and hot water.

Ethylimide $C_6H_4<\substack{SO_2\\CO}>NEt$. [97°]. Needles (from water). Converted by boiling alcoholic potash into $C_6H_4(SO_2NHEt).CO_2H$ [116°], which yields $C_6H_4(SO_2NKEt).CO_2K$ crystallising in nacreous scales, $Na_2C_9H_9NSO_4$, $CuA'_2 2aq$, and AgA' (Fahlberg a. List, *B.* 20, 1596).

Propylimide $C_6H_4<\substack{SO_2\\CO}>NPr$. [60°–70°].

***m*-Sulpho-benzoic acid** [1:3]$C_6H_4(SO_3H).CO_2H$.

Formation.—1. By mixing benzoic acid (2 pts.) with SO_3 (1 pt.) (Mitscherlich, *P.* 31, 287; 32, 227; Barth, *A.* 148, 33).—2. By heating BzCl with Ag_2SO_4 at 150° (Kämmerer a. Carius, *A.* 131, 153; *B.* 4, 219).—3. By heating BzCl with H_2SO_4 (Oppenheim, *B.* 3, 735).—4. By the action of an alcoholic solution of SO_2 on *m*-diazobenzoic acid (Wiesinger a. Vollbrecht, *B.* 10, 1715).—5. By oxidation of *m*-sulpho-benzoic aldehyde with air at 95° (Kafka, *B.* 24, 796).

Properties.—Deliquescent crystalline mass. Yields *m*-oxy-benzoic acid when fused with potash.

Salts.—$NaHA'' 2aq$: triclinic crystals.—$Na_2A''Me_2SO_4$ (Stengel, *A.* 218, 260). Crystals.—$Na_2A''Et_2SO_4$: v. sol. water.—$KHA'' 2\frac{1}{2}aq$.—$KHA'' 5aq$ (Otto, *A.* 122, 155).—$BaA'' 3aq$: v. sol. water (Fehling, *A.* 27, 322).—$BaH_2A''_2 3aq$. White monoclinic prisms. S. 5 at 20° (M.).—$BaA''Me_2SO_4$.—$BaA''Me_2SO_4 3\frac{1}{2}aq$. S. 34 at 21°.—$BaA''Et_2SO_4 3\frac{1}{2}aq$. S. 31 at 21°. Formed from the acid, $NaHSO_4$, and alcohol (Stengel). Long needles.—$BaA''Pr_2SO_4 7aq$. S. 11 at 19°.—$PbA'' 2aq$: stellate groups of white needles.—$PbA''Et_2SO_4 2\frac{1}{2}aq$.—$CuA''Me_2SO_4 2\frac{1}{2}aq$. Crystals.—$CuA''Et_2SO_4 2\frac{1}{2}aq$.—$AgHA''$: nodules (Limpricht a. Uslar, *A.* 106, 50).—Ag_2A'' aq: small yellowish prisms.

Mono-ethyl ether $EtHA''$. Formed by the action of alcoholic NH_3 on Et_2A'' or on the chloride (Limpricht a. Uslar, *A.* 102, 252). The free acid is unstable.—$EtNH_4A''$: four-sided triclinic tables (Keferstein, *A.* 106, 385).—$NaEtA'' x aq$. — $Ba(EtA'')_2 x aq$: efflorescent tables.

Ethyl ether Et_2A''. Formed from the chloride and alcohol. Syrup, miscible with water. Saponified by heating with water.

Semi-chloride $C_7H_5SO_4Cl$. Formed by heating the acid (1 mol.) with PCl_5 (1 mol.) (L. a. S.). Formed also by leaving the chloride $C_6H_4(SO_2Cl)(COCl)$ in contact with water for

several weeks. Crystalline powder, sol. ether. Converted by hot water into the acid.

Chloride $C_6H_4(SO_2Cl).COCl$. Formed by heating the acid (1 mol.) with PCl_5 (2 mols.) at 100°. Thick oil, slowly decomposed by water. Yields $C_6H_4Cl.COCl$ on distillation and on heating with PCl_5 at 150° (Kämmerer a. Carius, *A.* 131, 159).

Benzoyl derivative $C_{11}H_{10}SO_6$. The first product of the action of BzCl (2 mols.) on Ag_2SO_4 (1 mol.) (K. a. C.). Amorphous, sol. ether. Resolved by water into benzoic and sulphobenzoic acids.

Amic acid $C_6H_4(SO_2NH_2).CO_2H$. *m-Sulphamine-benzoic acid.* [235° uncor.] (R. a. P.); [247°] (N. a. W.). Formed by the action of conc. KOHAq at 100° on the amide (Limpricht a. Uslar, *A.* 106, 27). Prepared by oxidation of [1:3] $C_6H_4Me.SO_2NH_2$ with alkaline $KMnO_4$, with chromic acid mixture (Remsen a. Palmer, *Am.* 4, 143), or with alkaline K_3FeCy_6 (Noyes a. Walker, *Am.* 8, 188). Scales (from water), sl. sol. cold water, v. sol. alcohol. Converted by PCl_5 at 150°-200° into the oily chloride $C_6H_4(SO_2NH_2)COCl$. — BaA'_2 4aq. — AgA' aq. — $Ag_2C_7H_5NSO_4$: amorphous pp., sol. hot water.— EtA'. Monoclinic crystals, sl. sol. hot water.

Amide $C_6H_4(SO_2NH_2)(CONH_2)$. [170°]. Formed from the chloride and conc. NH_3Aq. Small anhydrous crystals (from alcohol) or needles (containing aq). V. sol. hot water and alcohol. PCl_5 at 100° forms $C_6H_4(SO_2NH_2)CCl:NH$, which is decomposed by distillation into *m*-chloro-benzonitrile, SO_2, and NH_3; and by treatment with NH_4Aq into $C_6H_4(SO_2NH_2).CN$ [152°] (Wallach a. Huth, *B.* 9, 428).

Anilide $C_6H_4(SO_2NHPh).CONHPh$. Formed from the chloride and aniline. Small crystals (from alcohol).

Isomeride of the amic acid $C_6H_5C(NH_2):N.SO_3H$. *Benzamidine v-sulphonic acid.* [247°]. Mol. w. 200 (obs.). Formed by passing SO_3 into cold benzonitrile (Engelhardt, *J. pr.* 75, 363; Eitner, *B.* 25, 471). Prisms and rhombohedra. Converted by HClAq into benzamidine sulphate.—CaA'_2.—BaA'_2 4aq.

Amorphous isomeride of the amic acid. A product of the action of PCl_5 on the amic acid (L. a. U.). Insol. water, alcohol, and ether. Forms amorphous salts. Water at 180° reconverts it into the ordinary amic acid.— BaA'_2 4aq: brittle mass.

***p*-Sulpho-benzoic acid** [1:4] $C_6H_4(SO_3H).CO_2H$. [c. 200°]. Formed, in small quantity, together with the *m*- isomeride, by the action of SO_3 on benzoic acid (Remsen, *A.* 178, 275; *Z.* [2] 7, 81, 199). Formed also by oxidation of toluene *p*-sulphonic acid with $KMnO_4$ (Hart, *Am.* 1, 342), and by the action of an alcoholic solution of SO_2 on diazotised *p*-amido-benzoic acid (Wiesinger, *B.* 10, 1715). Needles, not deliquescent, decomposed by heat. Potash-fusion converts it into *p*-oxy-benzoic acid. The K salt heated with potassium formate yields terephthalic acid.

Salts.—$NaHA''$ 2½aq. Stellate groups of prisms, m. sol. cold water.—BaA'' 2aq: groups of needles, m. sol. cold water.—$BaH_2A''_2$ 3aq: flat needles, v. sl. sol. cold water.

Amic acid $C_6H_4(SO_2NH_2).CO_2H$. [c. 280°]. Formed by oxidation of $C_6H_4Me.SO_2NH_2$ and of *p*-sulpho-cinnamic amide (Remsen, *A.* 178, 299; Fahlberg, *Am.* 1, 170; Palmer, *Am.* 4, 164; Noyes, *Am.* 7, 145; 8, 182). Flat prisms (from water), sl. sol. hot water, v. sol. alcohol. Decomposed on fusion.—NH_4A': needles or long laminæ, v. sol. water.—BaA'_2 5aq.—AgA': v. sl. sol. hot water.—$C_6H_4(SO_2NHAg).CO_2Ag$: v. sol. hot water.—EtA'. [111°].

Di-sulpho-benzoic acid $C_7H_6S_2O_8$ *i.e.* $C_6H_3(SO_3H)_2CO_2H$ [4:2:1]. [above 285°]. Formed by oxidation of toluene disulphonic acid with chromic acid mixture (Blomstrand a. Hakansson, *B.* 5, 1088; Brunner, *Sitz. W.* [2] 78, 665) and by digesting $C_6H_3(SO_2NH_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH$ with HClAq at 160° (Fahlberg, *Am.* 2, 190). Large crystals (from HClAq), sol. cold water, insol. alcohol and ether. Yields (4,2,1)-di-oxy-benzoic acid on fusion with potash.

Salts.—K_3A''' 2aq: prisms, v. e. sol. water. —K_2HA'''aq: large crystals, sl. sol. water.— $Ba_3A'''_2$ 7aq.—$Cu_3A'''_2$ 7aq: minute crystals.

Amic acid $C_6H_3(SO_3H)(SO_2NH_2).CO_2H$ [2:4:1]. [165°]. Formed by boiling the imide of the amic acid with dilute HClAq for five hours. Large crystals, v. e. sol. water, sl. sol. HClAq, insol. ether.—HKA'': crystals (from dilute HClAq), v. e. sol. water.

Di-amic acid $C_6H_3(SO_2NH_2)_2CO_2H$. [183°]. Formed by heating $C_6H_3Me(SO_2NH_2)_2$ with aqueous potassium permanganate and by evaporating $C_6H_3(SO_2NH_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH$ with KOHAq (Fahlberg, *Am.* 2, 186; *B.* 21, 246). Minute satiny needles, v. e. sol. water and alcohol, sl. sol. ether. Tastes acid. Decomposes completely at 250°-260°. Its salts are crystalline. Those of alkalis and alkaline earths are v. sol. water.—BaA'_2 5aq: monoclinic prisms.—CuA'_2 2aq: pale-blue silky needles.—AgA': white needles.—EtA'. [200°]. Silky needles (from water).

Imide of the amic acid $C_6H_3(SO_2NH_2)\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH$. [285°]. Formed by warming $C_6H_3(SO_2NH_2)_2CO_2Et$ with KOHAq (Fahlberg a. List, *B.* 20, 1603; 21, 242). Tables, sl. sol. cold water, v. e. sol. alcohol and ether.— $K_2C_7H_4N_2S_2O_5$: deliquescent crystalline mass.— $(C_6H_3(SO_2NH_2):SCO_2:N)_2Ba$ 3½aq: crystals. — $Cu(C_7H_5N_2S_2O_5)_2$ 4aq: minute blue needles.— $AgC_7H_5N_2S_2O_5$.

***s*-Di-sulpho-benzoic acid** $C_6H_3(SO_3H)_2.CO_2H$. Formed by heating benzoic acid with H_2SO_4, SO_3, and P_2O_5 (Barth a. Senhofer, *A.* 159, 217). Hygroscopic prisms (containing *x*aq). Turns brown at 140°. Yields *s*-di-oxy-benzoic acid on fusion with potash. The K salt forms isophthalic acid when fused with potassium formate.—K_3A''' 1½aq: needles.—$BaHA''$ 2aq: minute needles.—$Ba_3A'''_2$ 7aq: white prisms.— $Cu_3A'''_2$ 8½aq.—Ag_3A''' 2aq: crystalline pp.

References.—BROMO-, NITRO-, OXY-AMIDO, and OXY-, SULPHOBENZOIC ACIDS.

***m*-SULPHO-BENZOIC ALDEHYDE** $C_6H_4(SO_3H).CHO$. *Sulphonic acid of benzoic aldehyde.* Formed from benzoic aldehyde and fuming H_2SO_4 below 50° (Wallach a. Wüsten, *B.* 16, 150; *cf.* Engelhardt, *J.* 1864, 350). The Na salt reacts with (α)-naphthylamine forming $C_6H_4(SO_3Na).CH:NC_{10}H_7$, and forms with sodium naphthionate $C_6H_4(SO_3Na).CH:NC_{10}H_6.SO_3Na$.

Yields *m*-sulpho-benzoic acid on oxidation.—MgA'_2 (dried at 170°).—BaA'_2 (dried at 170°). Nodules.

Oxim. The salt $C_6H_4(SO_3Na).CH:NOH$ crystallises in plates, v. e. sol. water, m. sol. alcohol (Kafka, *B.* 24, 791).

Phenyl-hydrazide. The salt $C_6H_4(SO_3Na).CH:N.NHPh$ crystallises in needles, sl. sol. cold water, v. sol. alcohol.

Di-phenyl-hydrazide. The salt $C_6H_4(SO_3Na).CH:N.NPh_2$ crystallises from water in plates.

SULPHOBENZOLIC ACID *v.* BENZENE SULPHONIC ACID.

SULPHO - BENZYL - SULPHAMIC ACID $C_6H_5.CH(SO_3H).NHSO_3H$. The salt Na_2A'' 3aq is formed from $C_6H_5.CH:NOH$ and aqueous Na_2SO_3 (Pechmann, *B.* 20, 2541). It crystallises in needles and is decomposed by NaOHAq into benzoic aldehyde, Na_2SO_4, and $H(NH_4)SO_3$.

(*α*)-**SULPHO-BUTYRIC ACID** $C_4H_8SO_5$ *i.e.* $CH_3.CH_2.CH(SO_3H).CO_2H$. Formed from butyric acid and $ClSO_3H$; and also by the action of $(NH_4)_2SO_3$ on *α*-bromo-butyric acid (Hemilian, *B.* 6, 196, 562; *A.* 176, 1; Franchimont, *R. T. C.* 7, 27). Formed also from crotonic acid and $KHSO_3$ at 130° (Beilstein a. Wiegand, *B.* 18, 483). Syrup. The Ba salt is converted by PCl_5 into $CH_3.CH_2.CHCl.COCl$.—CaA'' 2aq: needles (from ether-alcohol), insol. alcohol.—BaA''2aq. S. 7·1 at 16°.—PbA''2aq.—CuA''4aq.—ZnA'' 5aq.—Ag_2A'': prisms, insol. alcohol.

α-Sulpho-isobutyric acid $C_4H_8SO_5$ *i.e.* $CMe_2(SO_3H).CO_2H$. Formed by the action of $Cl.SO_2.OH$ on isobutyric acid and also by oxidation of $C_5H_8N_2SO$, which is prepared by heating thio-urea with *α*-bromo-isobutyric acid (Andreasch, *M.* 8, 412).—Na_2H'' ½aq.—BaA'' 4aq.

Ammonium sulphite appears to convert *α*-bromo-isobutyric acid into an isomeride which yields $BaC_4H_6SO_5$ 2aq, crystallising in needles, v. sol. water.

β-Sulpho-butyric acid $CH_3.CH(SO_3H).CH_2.CO_2H$. Formed from *β*-chloro-butyric ether and $(NH_4)_2SO_3$ (H.). Got also by oxidising barium oxy-butane disulphonate with chlorine-water (Haubner, *M.* 12, 547). Amorphous.—BaA'' aq (H.).—$BaC_4H_8SO_5$. White amorphous mass, v. sol. water, almost insol. alcohol. Yields acetic acid by potash-fusion.

Sulphodibutyric acid *v.* DI-PROPYL SULPHONE DICARBOXYLIC ACID.

SULPHOBUTYRIC ALDEHYDE $C_4H_8SO_4$ *i.e.* $CH_3.CH(SO_3H).CH_2.CHO$. Got by saturating a solution of crotonic aldehyde with SO_2 and distilling *in vacuo*, afterwards distilling with steam. On neutralisation of the residue with baryta the salt BaA'_2 is got (Haubner, *M.* 12, 546). The barium salt is converted by hydroxylamine into $(CH(NOH).CH_2.CHMe.SO_3)_2Ba$, which is reduced by sodium-amalgam to $(CH_2(NH_2).CH_2.CHMe.SO_3)_2Ba$, which on distillation with lime yields butylamine and a little $CH_3.CH:CH.CH_2NH_2$. Sodium-amalgam reduces the sulpho-butyric aldehyde to oxy-butane sulphonic acid $CH_3.CH(SO_3H).CH_2.CH_2OH$, whence NaA', which when distilled with lime gives a mixture of butyl and crotyl alcohols.

SULPHOCAMPHORIC ACID *v.* CAMPHORIC ACID.

SULPHOCAMPHYLIC ACID *v.* CAMPHORIC ACID.

SULPHO-CHLORO-BENZOIC ACID *v.* CHLORO-SULPHO-BENZOIC ACID.

o-**SULPHO-CINNAMIC ACID** $C_9H_8SO_5$ *i.e.* $C_6H_4(SO_3H).CH:CH.CO_2H$. Formed, together with the *p*- isomeride, by the action of SO_3 or fuming H_2SO_4 on cinnamic acid (Marchand, *J. pr.* 16, 60; Herzog, *J. pr.* 29, 51; Rudneff, *A.* 173, 8). Prisms (containing 3aq), v. e. sol. water and alcohol. Yields *m*-oxy-benzoic acid on fusion with potash.—K_2A'': amorphous, v. sol. water.—KHA'': groups of needles.—CaA'' 1½aq.—$BaH_2A''_2$. S. ·45 at 20°.—BaA'' 1½aq. S. 4·2 at 16°.—Ag_2A''.

m-**Sulpho-cinnamic acid** [1:3] $C_6H_4(SO_3H).CH:CH.CO_2H$. Formed from *m*-sulpho-benzoic aldehyde, NaOAc, and Ac_2O (Kafka, *B.* 24, 791).—BaA'': nodules, v. sol. water, sl. sol. alcohol.

p-**Sulpho-cinnamic acid** [1:4] $C_6H_4(SO_3H).CH:CH.CO_2H$. Formed as above. Monoclinic prisms (containing 5aq). Yields *p*-oxy-benzoic acid by potash-fusion.—K_2A'' ½aq. Nodules (from alcohol). Reduces $KMnO_4$ in the cold (Liebermann, *B.* 22, 782).—CaA'' ½aq.—BaA'' 3aq. S. (of BaA'') ·12 at 20°.—BaA'' aq. S. ·4 at 18°.—CuA'' 6aq: greenish-prisms, v. sol. water.

Amide $C_6H_4(SO_2NH_2).CH:CH.CONH_2$. [218°]. Needles, v. sol. hot water (Palmer, *Am.* 4, 163).

Amic acid $C_6H_4(SO_2NH_2).CH:CH.CO_2H$. S. ·058 at 21°. Formed by heating the amide with NaOHAq. Needles (from water), sol. alcohol, sl. sol. ether. Decomposes at 250°. Yields CaA'_2 aq and BaA'_2 2aq, both crystallising in needles.

SULPHO-CUMINIC ACID $C_{10}H_{12}SO_5$ *i.e.* $C_6H_3Pr(SO_3H).CO_2H$ [4:3:1]. [160°]. Formed by sulphonating cuminic acid (Widman, *B.* 22, 2276). Crystalline.—BaA'' aq: sl. sol. water.—$BaH_2A''_2$ 4½aq. Prisms, m. sol. water.

Chloride $C_6H_3Pr(SO_2Cl).COCl$. [56°].

Amide $C_6H_3Pr(SO_2NH_2).CONH_2$. [225°]. Tables, sol. hot water.

Amic acid $C_6H_3Pr(SO_2NH_2).CO_2H$. [246° cor.]. Formed by heating the amide with KOHAq at 100°. Formed also by oxidising (*β*)-cymene sulphonic amide [148°] with chromic acid mixture, an isomeric change taking place (Remsen a. Day, *Am.* 5, 158). Needles, sol. hot water. Yields BaA'_2 3aq, v. e. sol. water.

Sulpho-*n*-cuminic acid $C_6H_3Pr(SO_3H).CO_2H$ [4:3:1]. Formed by sulphonation of *n*-cuminic acid (W.). V. sol. alcohol, ether, and water.—BaA'' aq: needles, sl. sol. Aq.

Chloride $C_6H_3Pr(SO_2Cl).COCl$. [43°].

Amide $C_6H_3Pr(SO_2NH_2).CONH_2$. [203°]. Tables (from water).

Amic acid $C_6H_3Pr(SO_2NH_2).CO_2H$. [216° cor.]. Formed from the amide (W.), and also by oxidation of *p*-di-*n*-propyl-benzene sulphonic amide [103°] (Remsen, *Am.* 5, 158). Long needles (from water).—CaA'_2 6aq.—$CuHA'_3$ 2aq.—AgA': flocculent pp.

Sulpho-cuminic acid. *Amic acid* $C_6HMe_3(SO_2NH_2).CO_2H$ [5:3:2:x:1]. Formed by oxidation of isodurene sulphonic amide by alkaline $KMnO_4$ (Jacobsen, *B.* 15, 1855). The K salt is amorphous.

Sulpho-cuminic acid. *Amic acid* $C_6HMe_3(SO_2NH_2).CO_2H$ [6:4:2:*x*:1]. Formed by oxidation of the corresponding isodurene sulphonic amide (J.). The K salt is crystalline.

Reference.—Oxy-sulpho-cuminic acid.

SULPHO-CYANIC ACID *v.* vol. ii. p. 303.

SULPHOCYANO-ACETIC ACID $C_3H_3NSO_2$ *i.e.* $Cy.S.CH_2.CO_2H$. Formed from potassium sulphocyanide and sodium chloro-acetate (Claesson, *B.* 10, 1347). Thick oil, changing to a solid polymeride when heated.—NaA′ aq: prisms. Converted by $AgNO_3$ into $HS.CH_2.CO_2Na$. $CuSO_4$ forms, after a time, a black pp. of cuprous thioglycollate. — KA′ aq. — BaA'_2 4aq: tables. — BaA'_2 aq: prisms.—CaA'_2 2aq.—MnA'_2 2aq.

Ethyl ether EtA′. (225°). S.G. 1·174. Formed by boiling chloro-acetic ether with potassium sulphocyanide (Heintz, *A.* 136, 223). Liquid. Yields thioglycollic acid and thioglycollic ether on distillation with phosphoric acid. Polymerised by repeated distillation, many other products being formed at the same time. Boiling dilute HClAq forms $NH_2.CO.S.CH_2.CO_2H$ [143°], which is v. sol. alcohol and ether, yields MeA′ [75°–80°] and CaA'_2 2aq, and is resolved by heat into cyanic and thioglycollic acids (Nencki, *J. pr.* [2] 16, 11). EtI at 120° forms ethyl sulphocyanide and iodo-acetic acid.

Isoamyl ether $C_5H_{11}A'$. (255°).

Amide $CH_2(S.CN).CONH_2$. Needles.

Polymeride $(C_3H_3SNO_2)_3$. [200°]. Formed from potassium sulphocyanurate and potassium chloro-acetate (Claesson, *J. pr.* [2] 33, 121; *B.* 14, 732). Needles, sol. alcohol and ether. Decomposed by HClAq at 100° into thioglycollic acid and cyanuric acid.—$Ba_3A'''_2$ 6aq: small prisms, nearly insol. water.—BaHA‴ 2aq: large prisms.—Et_3A'''. [81°]. Formed by distilling sulphocyano-acetic ether. Needles, nearly insol. hot water.

Persulphocyano-diacetic acid $C_2N_2S(S.CH_2.CO_2H)_2$. [177°]. Formed from sodium chloro-acetate, iso-persulphocyanic acid, and KOHAq (Klason, *J. pr.* [2] 38, 381). Plates. —BaA″ 3aq.—CaA″ 3$\frac{1}{2}$aq.—ZnA″ aq.—CdA″.—CuA″ 6aq.—Et_2A''. Oil.

Amide. [125°]. Prisms.

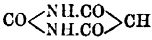
SULPHOCYANO-ACETIC ALDEHYDE $CH_2(SCy).COH$. [below −20°]. S.G. $^{\underline{10}}$ **1·47**. Formed by heating iodo-acetic aldehyde with AgSCy and ether (Chautard, *A. Ch.* [6] 16, 193; *C. R.* 106, 1169). Oil, miscible with alcohol and ether. Decomposed by distillation, by treatment with Cl, and by HClAq. HNO_3 forms acetic acid, sulphocyano-acetic acid, and thiocarbimido-acetic acid [128°]. Resinified by alkalis.

SULPHOCYANO-ACETONE C_4H_5NSO *i.e.* $CH_3.CO.CH_2SCy$. S.G. $^{\underline{0}}$ 1·2; $^{\underline{20}}$ 1·18. S. 7 at 15°. Formed from chloro-acetone and barium sulphocyanide (Tschnerniac, *C. R.* 96, 587; *B.* 16, 349; 25, 2607, 2623). Liquid, v. e. sol. ether, v. sl. sol. ligroïn. Decomposed by heat. Dissolves in aqueous $KHSO_3$. Boiling dilute HClAq converts it into oxy-methyl-thiazole. Ammonium sulphocyanide forms 'propimine sulphocyanide' $CH_3.C(NH).CH_2SCy$ [42°] (231°), which yields $B'_2H_2PtCl_6$, $B'HNO_3$ [183°], $B'H_2SO_4$ 2aq, B′HSCy [115°], B′MeI [160°], and $CH_3.C(NAc).CH_2SCy$ [134°].

Oxim $CH_3.C(NOH).CH_2.SCy$. [135°]. Yellowish prisms (Arapides, *A.* 249, 18). Produces great irritation on the skin.

SULPHOCYANO-ACETOPHENONE *v.* Phenacyl sulphocyanide.

SULPHOCYANO-BARBITURIC ACID $C_5H_3N_3SO_3$ *i.e.*



$CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CH.SCy$. Formed from di-bromo-barbituric acid and alcoholic KSCy in the cold (Trzcinski, *B.* 16, 1058). The free acid splits up into thiodialuric acid and other products. Hot KOHAq also forms thiodialuric acid.—NH_4A'.—KA′: tables (from water). —AgA′: crystalline pp.

γ-SULPHOCYANO-BUTYRIC ACID. *Nitrile.* $CH_2(SCy).CH_2.CH_2.CN$. (c. 195° at 40 mm.). Formed by boiling potassium sulphocyanide (1 pt.) with γ-chloro-butyronitrile (1 pt.) and alcohol (Gabriel, *B.* 23, 2190). Liquid. Partially decomposed by distillation under atmospheric pressure. Converted by conc. H_2SO_4 into $S_2(CH_2.CH_2.CH_2.CO.NH_2)_2$.

α-SULPHOCYANO-ISOBUTYRIC ALDEHYDE $CMe_2(SCy).CHO$. S.G. $^{\underline{12}}$ 1·63. Formed from α-iodo-isobutyric aldehyde and AgSCy (Chautard, *A. Ch.* [6] 16, 198). Liquid with nauseous odour, decomposed by heat, by acids, and by alkalis.

SULPHOCYANO-ETHANE-SULPHONIC ACID $C_3H_5NS_2O_3$ *i.e.* $CH_2(SCy).CH_2.SO_3H$. Formed from $CH_2(SCy).CH_2Cl$ and aqueous Na_2SO_3 in sunlight (James, *J. pr.* [2] 26, 381).

SULPHOCYANO-FORMIC ETHER $CyS.CO_2Et$. The compound $(CyS.CO_2Et)EtOH$ is got by mixing chloro-formic ether with ammonium sulphocyanide and alcohol (Delitsch, *J. pr.* [2] 10, 118; *cf.* Henry, *J. pr.* [2] 9, 464). It crystallises in prisms [41°], insol. water, v. e. sol. alcohol. Alcoholic potash forms $C_6H_{10}KSNO_3$ crystallising from alcohol in plates. KOHAq forms KSCy, alcohol, and K_2CO_3.

SULPHOCYANO-HEPTOÏC ALDEHYDE. Formed from iodo-heptoic aldehyde and AgSCy in ether (Chautard, *A. Ch.* [6] 16, 198). Yellowish liquid with fœtid odour. Decomposed by heat, by acids, and by alkalis.

β-SULPHOCYANO-PROPIONIC ALDEHYDE $CH_2(SCy).CH_2.CHO$. Formed by treating β-iodo-propionic aldehyde dissolved in ether with AgSCy (Chautard, *A. Ch.* [6] 16, 197). Liquid with fœtid odour. Decomposed by heat, and resinified by alkalis and by mineral acids.

ω-SULPHOCYANO-TOLUIC ACID. *Nitrile.* $CH_2(SCy).C_6H_4.CN$. [86°]. Formed from *o*-cyano-benzyl chloride and KSCy in alcohol (Gabriel a. Day, *B.* 23, 2179). Needles. Converted by conc. HClAq at 180° into thiophthalide C_8H_6SO [57°]. Conc. H_2SO_4 at 30°–70° forms cyano-benzyl-mercaptan C_8H_7NS [62°].

SULPHOCYANO-ISOVALERIC ALDEHYDE. Formed from iodo-isovaleric aldehyde and AgSCy in ether (Chautard, *A. Ch.* [6] 16, 198). Liquid, with fœtid odour, easily decomposed by heat, by HClAq, and by alkalis.

SULPHO-DURIDE *v.* Di-duryl sulphone.

SULPHO-ETHYL-BENZOIC ACID. *Amic acid* $C_9H_{11}NSO_4$ *i.e.* $C_6H_3Et(SO_2NH_2).CO_2H$. [262° cor.]. Formed by oxidising the sulphonic amide of *p*-di-ethyl-benzene with CrO_3 (Remsen a. Noyes, *Am.* 4, 202). Needles.—BaA'_2 8aq.

SULPHO-FUMARIC ACID $C_4H_4SO_7$ *i.e.* $CO_2H.CH:C(SO_3H).CO_2H$. Formed by the action of Br or of HNO_3 on the salts of (δ)-bromo-(β)-sulpho-pyromucic acid (Hill a. Palmer, *Am.* 10, 409).—$Ba_3A'''_2$ *x*aq: v. sl. sol. water.—Ag_3A''' *x*aq.

SULPHO-HIPPURIC ACID $C_9H_9NSO_6$ *i.e.* $C_6H_4(SO_3H).CO.NH.CH_2.CO_2H$. Formed from hippuric acid and SO_3 (Schwanert, *A.* 112, 59). Amorphous, deliquescent mass. Converted by nitrous acid into sulpho-benzoic acid.—BaA''aq: needles.—Pb_2OA''.

SULPHO-ISATIC ACID *v.* Isatic acid.

SULPHO-TRIMELLITIC ACID $C_9H_6SO_9$ *i.e.* $C_6H_2(SO_3H)(CO_2H)_3$[5:4:2:1]. Formed, together with the amic acid $C_6H_2(SO_2NH_2)(CO_2H)_3$, by oxidation of $C_6H_2Me(SO_2NH_2)(CO_2H)_2$ [2:5:4:1] by $KMnO_4$ (Jacobsen a. H. Meyer, *B.* 16, 192).—KH_3A^{iv} 3aq: prisms, m. sol. cold water. Potash-fusion yields oxy-trimellitic acid.

SULPHO-TRIMESIC ACID. *Amic acid* $C_9H_7NSO_8$ *i.e.* $C_6H_2(SO_2NH_2)(CO_2H)_3$. [*x*:5:3:1]. Formed by oxidation of the amic acid of *o-* or *p-* sulpho-mesitylenic acid (Jacobsen, *A.* 206, 203).—KH_2A''' 2aq: crystalline mass, m. sol. cold water. Conc. HClAq at 210° forms NH_3, H_2SO_4, and trimesic acid. Potash-fusion gives oxytrimesic acid.

a-**SULPHO-MESITYLENIC ACID** $C_9H_{10}SO_5$ *i.e.* $C_6H_2Me_2(SO_3H).CO_2H$. Formed, together with a (β)-isomeride which yields CaA'' 4aq, by the action of SO_3 on mesitylenic acid (Remsen a. Brown, *Am.* 3, 218). Yields *o*-oxy-mesitylenic acid on fusion with potash. By successive treatment with PCl_5 and NH_3 it is converted into an amide [288°].—CaA'' 4aq. Less sol. water than the salt of the (β)-isomeride.

Sulpho-mesitylenic acid. *Amic acid* $C_9H_{11}NSO_4$ *i.e.* $C_6H_2Me_2(SO_2NH_2).CO_2H$ [5:3:6:1]. [262° cor.]. Formed, together with the (5,3,4,1)-isomeride, by oxidising mesitylene sulphonic amide with chromic acid mixture or alkaline $KMnO_4$ (Hall a. Remsen, *Am.* 2, 131; *B.* 10, 1040; Jacobsen, *B.* 12, 604; *A.* 206, 167). Short prisms (from water), sl. sol. hot water, sol. alcohol and ether. Decomposed by heating with conc. HClAq at 200° into H_2SO_4 and mesitylenic acid. Soda-fusion forms mesitylenic acid and *m*-xylene sulphonic amide [137°].—CaA'_2 6aq: long flat plates.—CaA'_2 5aq.—BaA'_2 3aq. S. 3·3 at 0°; 14 at 21°.—CuA'_2 4aq: blue needles.—CuA'_2 3aq.—AgA': pp.

Sulpho-mesitylenic acid. *Amic acid* $C_8H_2Me_2(SO_2NH_2).CO_2H$ [5:3:4:1]. [276° cor.]. Formed as above (J.). Long needles, v. sol. alcohol and ether, more sol. hot water than its isomeride. Conc. HClAq at 200° forms mesitylenic acid. Soda-fusion gives oxy-mesitylenic acid.—BaA'_2 2aq. S. 2·05 at 0°.—CaA'_2 2aq: prisms.—CuA'_2 aq: blue monoclinic prisms.

SULPHO-DI-METHYL-BENZOIC ACID. *Amic acid* $C_9H_{11}NSO_4$ *i.e.* $C_6H_2Me_2(SO_2NH_2).CO_2H$[4:2:5:1]. [268°]. Formed by oxidation of the sulphonic amide of ψ-cumene (Jacobsen a. Meyer, *B.* 16, 190). Long needles (from water). Yields di-methyl-benzoic acid on heating with conc. HClAq at 210°.—KA'aq.

Sulpho-di-methyl-benzoic acid. [180°–190°]. *Amic acid* $C_8H_2Me_2(SO_2NH_2).CO_2H$ [1:2:5:3]. (α) - *Sulphamine - hemimellitic acid.* [238°]. Formed, together with the more soluble (β)-isomeride, by oxidising the sulphonic amide of hemimellithene with alkaline $KMnO_4$ (Jacobsen, *B.* 19, 2519). Needles, sl. sol. cold water. HClAq at 150° forms sulpho-di-methyl-benzoic acid and, finally, hemimellitic acid [144°]. Potash-fusion yields an oxy-hemimellitic acid.—BaA'_2 5aq: small tables, m. sol. water.

Sulpho-di-methyl-benzoic acid. *Amic acid* $C_8H_2Me_2(SO_2NH_2).CO_2H$[1:3:5:2]. [174°]. Formed as above. Stellate groups of minute needles. Converted by heating with HClAq into a very soluble sulphonic acid, and finally into *m*-xylene. Potash-fusion gives an easily soluble oxy-hemimellitic acid.—BaA'_2 4aq: needles.

Isomeride *v.* Sulpho-mesitylenic acid.

SULPHO-METHYL-TEREPHTHALIC ACID. *Amic acid* $C_6H_2Me(SO_2NH_2)(CO_2H)_2$ [2:5:4:1]. [295°–300°]. Formed by oxidation of ψ-cumene sulphonic amide by alkaline $KMnO_4$ (Jacobsen a. H. Meyer, *B.* 16, 190). Small needles (from water).—BaA'' 2½aq: stellate groups of prisms.

SULPHONAMIDE *v.* Sulphamide, p. 567; and IMIDO-SULPHONAMIDE *v.* Sulphimido-amide, p. 587.

SULPHONAMIDES. Amides of sulphonic acids. They contain the group $SO_2.NH_2$ attached by S to carbon.

SULPHONAMIDO- compounds *v. Amic acids* derived from Sulpho- compounds.

SULPHO-NAPHTHALENE-AZO- compounds *v.* Azo- compounds.

('*a*')-SULPHO-(α)-NAPHTHOIC ACID $C_{11}H_8SO_5$ *i.e.* $C_{10}H_6(SO_3H).CO_2H$. [235°]. Formed, together with the (β)- and (γ)-isomerides, by warming (α)-naphthoic acid with fuming H_2SO_4 at 70° (Battershall, *A.* 168, 119; Stumpf, *A.* 188, 1). Prisms, v. sol. water. Not deliquescent. Yields (α)-oxy-naphthoic acid by potash-fusion. — K_2A'' 2aq. — CaA'' 3aq. — BaA'' 4aq. Monoclinic crystals, sl. sol. water. —$BaH_2A''_2$ 2aq: prisms, more sol. than BaA''.

(β)-Sulpho-(α)-naphthoic acid. [218°–222°]. Crystalline mass, v. e. sol. water.—BaA'' 3½aq: needles, m. sol. water.—$BaH_2A''_2$ 4aq.

(γ)-Sulpho-(α)-naphthoic acid. [182°–185°]. Needles, v. sol. water.—K_2A''.—BaA'' 1½aq: m. sol. water.—$BaH_2A''_2$ aq: almost insol. cold Aq.

Sulpho-(α)-naphthoic acid. *Nitrile* $C_{10}H_6Cy.SO_3H$. Formed by sulphonating (α)-naphthonitrile (Dutt, *B.* 16, 1251; Armstrong a. Williamson, *C. J. Proc.* 3, 43).—BaA'_2 6aq: glistening plates.—KA' 3aq: prisms.

Chloride of the nitrile $C_{10}H_6Cy.SO_2Cl$. Prisms, sol. benzene.

('*a*')-Sulpho-(β)-naphthoic acid. [230°]. Formed, together with the ('β')-isomeride, by sulphonating (β)-naphthoic acid (B.; S.). Crystalline.—BaA'' aq.—BaA'' 6½aq.—$BaH_2A''_2$ 6½aq.

('β')-Sulpho-(β)-naphthoic acid.—BaA'' 2aq. Less sol. water than the acid salt.

Reference.—Oxy-sulpho-naphthoic acid.

SULPHO-NAPHTHYL ETHYL DI-THIO-CARBONATE. The salt $SO_3K.C_{10}H_6.S.CS.OEt$, formed from potassium xanthate and diazotised naphthionic acid, crystallises from water in colourless plates, converted by boiling dilute alcoholic potash into $S_2(C_{10}H_6.SO_3K)_2$ (Leuckart, *J. pr.* [2] 41, 218). The corresponding salt from (β)-naphthylamine (β)-sulphonic acid crystallises in small plates.

SULPHO - (β) - NAPHTHYL - PHOSPHORIC ACID $SO_3H.C_{10}H_6.O.PO(OH)_2$. Formed, together with the anhydride $O(PO(OH).C_{10}H_6.SO_3H)_2$, by heating potassium (β)-naphthol sulphonate (1 mol.) with PCl_5 (2 mols.) at 100° (Claus a. Zimmermann, *B.* 14, 1482). Decomposed by boiling alkalis into phosphate and (β)-naphthol sulphonate. The Ba salt is a white powder, sl. sol. water.

SULPHONES. Compounds of the form $R.SO_2.R'$ where R and R′ are attached by means of C to S. They may be formed from the corresponding sulphides and sulphoxides by oxidation with $KMnO_4$ (Beckmann, *J. pr.* [2] 17, 475). Aromatic sulphones can be prepared by the action of $AlCl_3$ on a mixture of a sulphonic chloride and an aromatic hydrocarbon (Beckurts a. Otto, *B.* 11, 472, 2066), and by heating a sulphonic acid with a hydrocarbon and P_2O_5 at 200° (Michael a. Adair, *B.* 10, 583). Sulphones are often formed by the action of sulphuric acid on aromatic hydrocarbons. The sulphones are volatile, and are not reduced by nascent hydrogen. They are not attacked by PCl_5 or $KMnO_4$. Chlorine in daylight converts di-phenyl-sulphone into chloro-benzene (1 mol.) and $C_6H_5.SO_2Cl$, while in sunlight it yields chloro-benzene (2 mols.) and SO_2Cl_2. Disulphones $CHR(SO_2R')_2$ are not attacked by alcoholic potash at 140°, while disulphones of the form $R'.SO_2.CH_2.CH_2.SO_2.R'$ are converted by alcoholic potash into a sulphinic acid and an oxy-sulphone (Otto a. Rössing, *B.* 20, 185). The disulphones $CMe_2(SO_2.Et)_2$ (sulphonal), $CHMe(SO_2Me)_2$, $CHEt(SO_2Et)_2$, $CEt_2(SO_2Me)_2$, $CMeEt(SO_2Et)_2$ (trional), and $CEt_2(SO_2Et)_2$ (tetronal) are powerful hypnotics (Baumann a. Kast, *H.* 14, 52).

SULPHONIC ACIDS (*organic*). Acids containing the group $SO_2.OH$ united to C by S. Fatty sulphonic acids may be formed by the action of silver sulphite on alkyl iodides, the resulting ether being saponified. Fatty sulphonic acids may also be got by boiling alkyl iodides with K_2SO_3 or $(NH_4)_2SO_3Aq$ for a long time. Both fatty and aromatic sulphonic acids may be got by oxidation of the corresponding mercaptans, sulphides, and sulphocyanides. The sulphonic acids of fatty acids and alcohols are formed by the action of SO_3 or $ClSO_3H$ on fatty acids and of SO_3 on alcohols; SO_3H taking the α- position (Hemilian, *A.* 176, 1). Aromatic compounds readily yield sulphonic acids on treatment with SO_3, with H_2SO_4, or with $ClSO_3H$. As a rule not more than two SO_3H groups enter a benzene nucleus. Aromatic sulphonic acids may also be obtained by the action of SO_2 on diazo- compounds. On adding NaCl to the product of sulphonation of aromatic compounds, the Na salt of the sulphonic acid frequently separates in crystalline form (Gattermann, *B.* 24, 2121). Nitric acid does not attack fatty sulphonic acids, while usually it nitrates aromatic sulphonic acids, although it sometimes displaces SO_3H by NO_2. PCl_5 forms sulphonic chlorides which are reduced by zinc and dilute H_2SO_4 to mercaptans. Aromatic sulphonic acids are partially converted into the corresponding amido- compounds by fusion with $NaNH_2$. In this way benzene sulphonic acid yields 15 p.c. of aniline (Jackson a. Wing, *Am.* 9, 75). Aromatic sulphonic acids are decomposed by superheated steam at 200°–210° into the hydrocarbon and H_2SO_4 (Kelbe, *B.* 19, 92). Hydrolysis may also be effected by passing superheated steam into a solution of the sulphonic acid containing H_2SO_4 or H_3PO_4 (Armstrong; Friedel a. Crafts, *C. R.* 109, 95). Aromatic sulphonic acids when fused with potash yield K_2SO_3 and phenols. Fusion with KCN or K_4FeCy_6 yields the corresponding nitriles. Fusion with sodium formate displaces SO_3H by CO_2H.

SULPHONIC ACIDS AND DERIVATIVES. Several inorganic acids, and derivatives of these acids, will be described here, most of which are regarded as derived from $SO_2.OH.OH$ by replacing one OH by a monovalent radicle—such as Cl, F, or NH_2—or as derived from $SO_2.OH.H$ by replacing H by a monovalent radicle. A few sulphonic acids must be formulated as derived from $2(SO_2.OH.OH)$, or $2(SO_2.OH.H)$, by replacing 2OH, or 2H, by a divalent radicle; and one as derived from $3(SO_2.OH.OH)$, or $3(SO_2.OH.H)$, by replacing 3OH, or 3H, by a trivalent radicle (*v. supra*). The sulphonic acids, therefore, are all looked on as compounds of the monovalent radicle $SO_2.OH$. The term sulphonic is also frequently applied to organic acids containing this radicle; but in this dictionary such acids are described as sulpho- acids, *e.g.* sulpho-benzoic acid $C_6H_4(SO_2.OH)CO_2H$. The compositions of the sulphonic acids are expressed by the formulæ $R^{I}SO_2.OH$, $R^{II}(SO_2.OH)_2$, and $R^{III}(SO_2.OH)_3$, where $R^{I} = NH_2, Cl, F, NO_2, NH.OH,$ or $N(NO.OH)$; $R^{II} = NH$, or $N.OH$; and $R^{III} = N$.

AMIDOSULPHONIC ACID AND SALTS $NH_2(SO_2.OH)$ and $NH_2(SO_2.OM)$. These compounds are described in the article SULPHAMIC ACID AND SULPHAMATES (*q.v.* p. 567).

CHLOROSULPHONIC ACID AND SALTS $Cl(SO_2.OH)$ and $Cl(SO_2.OM)$. The acid has also been called *chlorhydrosulphurous acid*, *monochlorosulphuric acid*, *sulphuric chlorhydrate* or *hydrochloride*, *sulphuric chlorhydrin*, and *sulphuryl hydroxyl chloride*.

Chlorosulphonic acid $Cl(SO_2.OH)$.

Formation.—1. By the direct union of SO_3 and HCl (Williamson, *Pr.* 7, 11; Baumstark, *A.* 140, 75; Williams, *C. J.* [2] 7, 804; Dewar a. Cranston, *C. N.* 20, 174; Michaelis, *J. Z.* 6, 235, 292).—2. By the reaction of PCl_5, $POCl_3$, or PCl_3 with conc. H_2SO_4 (Müller, *B.* 6, 227; Geuther, *B.* 5, 925; Thorpe, *C. J.* 37, 358).—3. By distilling fuming H_2SO_4 with P_2O_5 in a current of HCl (Müller, *l.c.*).—4. By the reaction of HCl with crystallised fuming H_2SO_4 (Beckurts a. Otto, *B.* 11, 2058).—5. By the action of Cl, S_2Cl_2, or $S_2O_3Cl_4$, with conc. H_2SO_4; or of Cl with moist SO_2 in presence of Pt at a red heat. 6. By warming $S_2O_5Cl_2$ with water (Billitz a. Heumann, *B.* 16, 602).

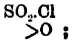
Preparation.—1. Three parts of the most conc. H_2SO_4 (preferably the residue from preparing SO_3) are warmed in a long-necked flask, and two parts PCl_5 are added little by little; when HCl ceases to be given off the contents of the flask are fractionated, the part boiling between c. 152°–156° being collected apart.—2. Very conc. oil of vitriol, 200 parts, is mixed with $POCl_3$, 226 parts, the mixture is gently heated and then distilled $[2(SO_2.OH.OH) + POCl_3 = 2(Cl.SO_2.OH) + HPO_3 + HCl]$ (Thorpe, *l.c.*).—

3. A mixture of P_2O_5 and fuming H_2SO_4 is distilled in a current of HCl, and the product is fractionated; this method removes all traces of P chlorides (Müller, *l.c.*).—4. Commercial crystalline fuming H_2SO_4 (approximately pure $H_2S_2O_7$) is placed in a retort connected with a good condenser, dry HCl gas is passed in so long as absorption occurs, the liquid is distilled, and the product fractionated; the yield is very satisfactory (Beckurts a. Otto, *B.* 11, 2058).

Properties.—A colourless liquid, fuming much in air, and having a powerful, penetrating odour. S.G. $\frac{0^\circ}{4^\circ}$ = 1·78474 (Thorpe, *C. J.* 37, 358); Michaelis (*J. Z.* 6, 235, 292) gives 1·776 at 18°. Boils at 155·3° at 760 mm. pressure (T., *l.c.*; *v.* also M., *l.c.*; Clausnitzer, *B.* 11, 2008; Beckurts a. Otto, *l.c.*; Behrend, *B.* 8, 1004). Ogier (*C. R.* 96, 616) gives H.F. [SO^3 solid, HCl] = 14,400. Baumstark (*A.* 140, 75) found V.D. 59·3 (calc. = 58·12) (temp. is not given); Williams (*C. J.* [2] 7, 304) found V.D. at 216° to be 32·8; Heumann a. Köchlin (*B.* 16, 602) found V.D. 34·7 at 184° and 30·4 at 410°. The gas is therefore dissociated at a temperature not much above its b.-p. When $ClSO_2.OH$ is repeatedly heated above 158° it is partly resolved into SO_2Cl_2; distilled, it gives SO_2Cl_2 (Williamson, *C. J.* 10, 97). By boiling the compound for a long time with an inverted condenser, Clausnitzer (*B.* 11, 2008) obtained H_2SO_4, SO_2, and Cl; Beckurts a. Otto (*l.c.*) heated $ClSO_2.OH$ for a long time in a sealed tube at c. 170°, and found that part remained unchanged, and that Cl and SO_2 were produced. Heumann a. Köchlin (*l.c.*) think that the decomposition at c. 440° is represented as follows: $2(ClSO_2.OH) = SO_2 + SO_3 + Cl_2 + H_2O$; they regard the high value obtained by Baumstark for the V.D. as due to presence of $S_2O_5Cl_2$ (*v.* also Claesson, *J. pr.* [2] 19, 235).

Reactions.—1. Action of *heat*, **v.** *supra*, *Propertics.*—2. *Water* produces HClAq and H_2SO_4Aq. 3. *Hydrogen sulphide* reacts at ordinary temperatures, forming HCl, S_2Cl_2, S, and H_2SO_4 (Prinz, *A.* 223, 371).—4. *Carbon disulphide*, at 100°, produces HCl, SO_2, S, and COS.—5. *Phosphorus pentoxide* or *pentachloride* produce $S_2O_5Cl_2$ (Billitz a. Heumann, *B.* 16, 482; Konswaloff, *C. R.* 96, 1146).—6. Heating with *silver nitrate* forms AgCl and $NO_2.SO_2.OH$ (Thorpe, *C. J.* 41, 297).—7. Fusion with *potassium sulphate* forms $K_2S_2O_7$ and HCl; heating with *sodium chloride* forms HCl and $Cl.SO_2.ONa$ (Müller, *B.* 6, 227). 8. The reactions of $ClSO_2.OH$ with several *elements* were examined by Heumann a. Köchlin (*B.* 15, 416).

Chlorosulphonates. The salts of $Cl.SO_2.OH$, which reacts as a monobasic acid, are formed by the reaction of the acid with metallic chlorides. It is very difficult to obtain these salts pure. When heated they form sulphates, giving off SO_2 and Cl; with water they decompose to chlorides and acid sulphates; and with alcohol HCl and salts of $Et.H.SO_4$ are formed (Müller, *B.* 6, 227). No accurate description of any salts has yet been given.

CHLOROSULPHONIC ANHYDRIDE 

$$\begin{matrix} SO_2.Cl \\ >O \\ SO_2.Cl \end{matrix}$$

; *v.* ***Pyrosulphuryl chloride***, under SULPHUR OXYCHLORIDES, p. 618.

FLUOSULPHONIC ACID AND SALTS $F.SO_2.OH$ and $F.SO_2.OM$. Only the acid has been isolated.

Fluosulphonic acid $F.SO_2.OH$. Isolated and examined by Thorpe a. Kirman (*C. J.* 61, 921 [1892]). Prepared by placing pure SO_3 in a Pt vessel, surrounded by ice and $CaCl_2$ (for description of apparatus *v.* Thorpe a. Hambly, *C. J.* 55, 163), leading in excess of pure HF (made by heating KHF_2), and removing excess of HF by passing in a stream of dry CO_2 for many hours, the liquid being kept at 25°–35°. A thin, colourless liquid, with a slightly pungent smell, and fuming in air; boils at 162·6°, a little being decomposed with formation of H_2SO_4, and probably also SO_2F_2. Reacts rapidly with Pb, forming $PbSO_4$ and PbF_2; slowly attacks glass. Reacts violently, and sometimes explosively, with water, forming H_2SO_4Aq and HFAq.

IMIDOSULPHONIC ACID AND SALTS $NH(SO_2.OH)_2$, $NH(SO_2.OM)_2$, and $NM(SO_2.OM)_2$. By passing dry NH_3 into SO_3, H. Rose (*P.* 32, 81; 47, 41; 49, 183 [1834–40]) obtained two compounds, which he named *sulphatammon* and *parasulphatammon*, and to both of which he assigned the composition $2NH_3.SO_3$. These compounds were examined by Jacquelain (*A. Ch.* [3] 8, 293 [1843]), Woronin (*J. R.* 3, 273 [1859]) and others; in 1875 Berglund (*Lunds Universitets Årsskrift*, 12 and 13; *Bl.* [2] 25, 455; 29, 422) showed that Rose's *parasulphatammon* was diammonium imidosulphonate $NH(SO_2.ONH_4)_2$, and that *sulphatammon* was probably the triammonium salt $N.NH_4(SO_2.ONH_4)_2$. Berglund's conclusions were confirmed, partly by Raschig (*A.* 241, 161 [1887]), and Mente (*A.* 248, 232 [1888], and partly by Divers a. Haga (*C. J.* 61, 943 [1892]). A full discussion of the constitution of Rose's compounds, with reference to the work of other chemists and an historical summary of researches on the imidosulphonates, will be found in the memoir by D. a. H.

Imidosulphonic acid $NH(SO_2.OH)_2Aq$. This acid is known only in solution, which is obtained by suspending lead imidosulphonate in water, decomposing by a stream of H_2S, and rapidly filtering from PbS. The solution gives a pp. with excess of BaOAq, soluble in HNO_3Aq; and a pp. of $NH(SO_2.OK)_2$ with $K.C_2H_3O_2Aq$. The acid solution is very unstable, soon becoming changed to $NH_2(SO_2.OH)Aq$ and H_2SO_4Aq (Jacquelain, *l.c.*; Fremy, *A. Ch.* [3] 15, 408; D. a. H., *l.c.* p. 945).

Imidosulphonates. The normal salts are of the types $NH(SO_2.OM)_2$ and $NM(SO_2.OM)_2$; besides these many basic salts have been isolated. The di-alkali imidosulphonates are prepared by mixing solutions of alkali nitrites and sulphites, dissolving the pp. which forms in water, heating this solution for some time, allowing to crystallise, and then boiling the nitrilosulphonate, $N(SO_2OM)_3$, thus obtained (*v.* p. 601, NITRILOSULPHONATES) with acidified water (for instance

$$N(SO_2.OK)_3 + H_2O = NH(SO_2.OK)_2 + KHSO_4);$$

also by heating the alkali amidosulphonates (*e.g.*

$$2(NH_2.SO_2.OK) = NH(SO_2.OK)_2 + NH_3);$$

the diammonium salt $NH(SO_2.ONH_4)_2$ is also obtained by the reaction of NH_3 with SO_3, $ClSO_2.OH$, SO_2Cl_2, or $S_2O_5Cl_2$. Most of the other di- salts are obtained by double decomposition from the alkali salts. The tri- salts are generally prepared by dissolving the di-salts in excess of an aqueous solution of the base and crystallising. A number of mixed salts, such as $N(NH_4)(SO_2.O)_2Ba$, have been prepared, generally by double decomposition. Basic salts, chiefly of such slightly positive metals as Pb or Hg, have also been isolated. For references *v.* Divers a. Haga (*C. J.* 61, 943). The di-alkali salts give off NH_3, N, and SO_2 when heated; water reacts to form amidosulphonates $NH_2(SO_2.OM)_2$ and sulphates.

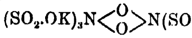
The chief imidosulphonates are those of NH_4, Ba, Ca, Hg, Pb, K, Ag, and Na; basic salts of Pb and Hg are known; mixed salts containing NH_4 and Na, NH_4 and Ba, Ba and Hg, Ba and Na, Ca and Na, Hg and K, and Ag and Na have been isolated; some of the imidosulphonates also form double compounds with KNO_3 and $NaNO_3$. Full accounts of the preparation and reactions of the chief imidosulphonates are given in the memoir of D. a. H.

NITRILOSULPHONIC ACID AND SALTS $N(SO_2.OH)_3$ and $N(SO_2.OM)_3$. The acid has not been isolated, and only a few salts are known.

Potassium nitrilosulphonate $N(SO_2.OK)_3$. Solutions of K_2SO_3 and KNO_2 are mixed in the ratio $4K_2SO_3:KNO_2$; after crystallisation occurs the mixture is heated at 100° till the crystals dissolve, a little water is added, and heating at 100° is continued for a little; on cooling the salt crystallises in well-formed crystals with $2H_2O$. The water of crystallisation is removed at 100°-110°; at a higher temperature decomposition occurs to K_2SO_4, $(NH_4)_2SO_4$, SO_3, and SO_2. The salt may be crystallised from dilute KOHAq; it is decomposed by water at 40° to $NH(SO_2.OK)_2$ and $KHSO_4$.

Claus prepared this salt in 1871 (*B.* 4, 186), giving it the formula $NH_2(SO_3K)_3$ and the name *potassium trisulphammonate*; Raschig (*B.* 20, 584 [1887]) showed that the salt was probably $N(SO_2.OK)_3$, and this composition was confirmed both by the earlier work of Berglund (*B.* 9, 252, 1896 [1876]) and by the more recent work of Divers a. Haga (*C. J.* 61, 943).

For description of a salt $NO(SO_3K)_3$ *v.* Raschig (*A.* 241, 225); this is the *trisulphooxyazotate* of Claus and Raschig. R. regards it as



$(SO_2.OK)_3N<\begin{smallmatrix}O\\ O\end{smallmatrix}>N(SO_2.OK)_3$.

Sodium nitrilosulphonate $N(SO_2.ONa)_3$. Formed by passing SO_2 into a solution of $NaNO_2$ and Na_2CO_3 (in the ratio $2NaNO_2:3Na_2CO_3.10aq$) until the solution is feebly acid to litmus (*v.* D. a. H., *l.c.*).

NITROSULPHONIC ACID $NO_2(SO_2.OH)$, AND DERIVATIVES. The acid and its potassium salt have been isolated. The anhydride $SO_2(NO_2).O.(NO_2)SO_2$, the chloride $NO_2(SO_2.Cl)$, and an oxy-anhydride $S_2O_5O(NO_2)_2$ have also been obtained.

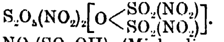
Nitrosulphonic acid $NO_2(SO_2.OH)$. (*Nitrosylsulphuric acid* $SO_2.OH.O(NO)$. *Lead chamber crystals. Nitrosyl hydrogen sulphate* $NO.H.SO_4$.) This acid is produced by the reaction between H_2SO_4 and any oxide of nitrogen except N_2O (Henry, *P.* 7, 135; A. Rose, *P.* 50, 161; Reibling, *J.* 1861. 152; Kuhlmann, *A. Ch.* [3] 1, 116; Sestini, *Bl.* [2] 10, 226). It is also formed in the leaden chambers in making H_2SO_4 (first observed by Clement a. Desormes, *A. Ch.* [2] 59, 329). The acid is produced by the reaction of SO_2 with NO or NO_2 in presence of water (Davy); also by burning 1 part S mixed with 2·5-3 parts KNO_3 in moist air (Girard a. Pabst, *Bl.* [2] 30, 531; Reinsch, *N. J. P.* 12, 3).

The acid is best prepared by leading NO_2 into well-cooled fuming H_2SO_4 till the whole solidifies, and then drying over H_2SO_4 (Weber, *J. pr.* 85, 425; 100, 37; Tilden, *C. J.* 28, 630); or by adding NO_2 in excess to conc. H_2SO_4, washing the crystals with liquid NO_2, and drying in a stream of dry air at 20°-30° or *in vacuo* (Müller, *A.* 122, 1; Gaultier de Claubry, *P.* 20, 467).

Colourless rhombic plates, melting at 73° (Tilden, *l.c.*, gives m.p. 85°-87°), and easily remaining liquid below this temperature (Weltzien, *A.* 115, 213; De la Provostaye, *A. Ch.* [2] 73, 362). On melting in air the anhydride ($S_2O_5(NO_2)_2$) is formed, and the water given off causes decomposition of part of the acid to H_2SO_4 and oxides of N (Michaelis a. Schumann, *B.* 7, 1075; Fremy, *C. R.* 70, 61). With dry NaCl reacts to give $NaHSO_4$ and NOCl; on heating for a little HCl is given off (Tilden, *l.c.*). Dissolves unchanged in H_2SO_4 (Döbereiner, *S.* 8, 239; *cf.* Lunge, *B.* 12, 1058; 21, 67). SO_2 is without action on dry $NO_2(SO_2.OH)$, but in presence of water, or H_2SO_4Aq with S.G. less than 1·55, decomposition occurs with formation of H_2SO_4, N_2O_3, and other oxides of N, according to Lunge (*l.c.*).

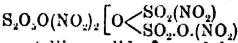
Potassium nitrosulphonate $NO_2(SO_2.OK)$ seems to be obtained by the reaction of SO_3 on KNO_2, also by adding liquid SO_2 to dry KNO_3; the salt cannot be prepared by neutralising the acid by KOHAq. The salt is decomposed by water (Schultz-Sellack, *B.* 4, 113).

Nitrosulphonic anhydride



$S_2O_5(NO_2)_2\left[O<\begin{smallmatrix}SO_2(NO_2)\\ SO_2(NO_2)\end{smallmatrix}\right]$. Formed by heating $NO_2(SO_2.OH)$ (Michaelis a. Schumann, *B.* 7, 1075); also by the reaction of SO_3 with NO in absence of O and moisture (H. Rose, *P.* 47, 605; Brüning, *A.* 98, 377); also by adding liquid NO_2 to liquid SO_2 without warming (De la Provostaye, *A. Ch.* [2] 73, 362); by passing electric sparks through a dry mixture of N, O, and SO_2, or of S vapour and N_2O or NO (Morren, *A. Ch.* [4] 4, 293; Chevrier, *C. R.* 69, 136). Hard, regular plates; S.G. 2·14; melts at 217°; may be distilled unchanged at c. 360°. Decomposed by water to NO, H_2SO_4Aq, and HNO_3Aq. $NO_2(SO_2.OH)$ crystallises from a solution in H_2SO_4.

OXYNITROSULPHONIC ANHYDRIDE



$S_2O_5O(NO_2)_2\left[O<\begin{smallmatrix}SO_2(NO_2)\\ SO_2.O.(NO_2)\end{smallmatrix}\right]$. A white, fusible, crystalline solid; formed by leading vapour of NO_2 into SO_3 till saturated. Gives $S_2O_5(NO_2)_2$ when heated (Weber, *P.* 123, 333; *cf.* Thorpe, *C. J.* 41, 297).

Nitrosulphonic chloride $NO_2(SO_2.Cl)$. (*Nitrosulphuryl chloride.*) A white, crystalline solid; formed by the action of SO_3 on NOCl in absence of moisture, also by the reaction of $AgNO_3$ with $SOCl_2$ (Thorpe, *C. J.* 41, 297); dissolves unchanged in fuming H_2SO_4; dissolves in conc. H_2SO_4, giving off HCl, and forming $Cl(SO_2.OH)$ on heating; decomposed by moist air or by water, giving HClAq, H_2SO_4Aq, HNO_3Aq, and NO (Weber, *l.c.*).

NITROSO-OXY-AMIDOSULPHONIC ACID AND SALTS $N(NO.OH)(SO_2.OH)$. (*Nitroso-hydroxylamine sulphonic acid* $N(NO)(SO_2.OH)OH$. *Dinitroso-sulphuric acid* $SO(NO)_2.(OH)_2$ or $(SO_2.OH).(NO)_2.H$.) The acid has not been isolated, but the NH_4, Ba, Pb, K, and Na salts are known. These salts are described as *Nitrososulphates* under SULPHATES,' p. 581.

OXY-AMIDOSULPHONIC ACID AND SALTS $NH(OH)(SO_2.OH)$. (*Hydroxylamine sulphonic acid* [Raschig]. *Sulphydroxylamic acid* [Claus]. *Sulphazidic acid* [Fremy].) The K salt of the acid is obtained by the action of water on $N(OH)(SO_2.OK)_2$ (*v.* OXY-IMIDOSULPHONIC ACID AND SALTS, *infra*). The acid itself is known only in aqueous solutions. Two Ba salts, a K salt, and a Na salt have been isolated. The salts have been investigated by Fremy (*A. Ch.* [3] 15, 408), Claus a. Koch (*A.* 152, 336; 158, 52, 194), Raschig (*A.* 241, 161), and Divers a. Haga (*C. J.* 55, 760).

Oxy-amidosulphonic acid $NH(OH)(SO_2.OH)Aq$. An aqueous solution of this acid (the acid has not been isolated) is prepared by heating an aqueous solution of $N(OH)(SO_2.OK)_2$ (*v. infra*) to boiling (whereby $NH(OH)(SO_2.OK)Aq$, H_2SO_4Aq, and $KHSO_4Aq$ are formed), neutralising by NH_3Aq, adding $BaCl_2Aq$, filtering off $BaSO_4$, adding BaOAq to ppt. $Ba(N(OH)SO_2.O)_2Ba.H_2O$, washing this pp., adding enough H_2SO_4Aq to ppt. half the Ba in the salt as $BaSO_4$, filtering, and so getting a solution of the (soluble) salt $(NH(OH)SO_2.O)_2Ba$. On now heating this solution with an equivalent quantity of H_2SO_4Aq (the Ba in solution must be estimated) and filtering, a solution of the acid is obtained (Fremy, modified by D. a. H.). The solution of $NH(OH)(SO_2.OH)$ is fairly stable, but slowly decomposes; in presence of hot acid the decomposition is more rapid, giving $2NH_2OH.H_2SO_4Aq$ and H_2SO_4Aq (Raschig, confirmed by D. a. H.).

Oxy-amidosulphonates. The normal salts are of the form $NH(OH)(SO_2.OM^I)$ and $(NH(OH)SO_2.O)_2M^{II}$, where $M^I = K$ or Na, and $M^{II} = Ba$; there is also a dibarium salt $Ba{<}\begin{smallmatrix}N(OH).SO_2.O\\N(OH).SO_2.O\end{smallmatrix}{>}Ba.H_2O$. The salts are best obtained from the solution of the soluble salt $(NH(OH).SO_2.O)_2Ba.H_2O$ (*v. supra*) by adding the equivalent quantity of a sulphate. The dibarium salt is itself prepared as described under the acid (*supra*); the monobarium salt is obtained by decomposing the di- salt by enough H_2SO_4Aq to ppt. half the Ba, filtering, and evaporating over H_2SO_4 (D. a. H.). The oxy-amidosulphonates are fairly stable; they are decomposed by heating with acid into hydroxylamine sulphate and H_2SO_4Aq; caustic alkalis produce only sulphite and hyponitrites (the latter rapidly undergo further change, giving off N_2O) (D. a. H., *l.c.*; *v.* also *C. J.* 61, 988 note). Basic oxides, such as CuO and Ag_2O, in presence of alkali produce sulphite, sulphate, and N_2O, and at the same time the basic oxide is reduced (D. a. H., *l.c.*, p. 770).

Raschig's *sulphazinate* (*A.* 241, 197) $(SO_2.OK)N(OH).O.(OK)N.(SO_2.OK)$ may be derived from $2NH(OH)(SO_2.OH)$ by replacing 2H by O.

OXY-IMIDOSULPHONIC ACID AND SALTS $N(OH)(SO_2.OH)_2$. (*Hydroxylamine disulphonic acid* $N(SO_2.OH)_2OH$ (Raschig). *Disulphydroxy-azic acid* (Claus).) Only the potassium salt has been isolated.

Potassium oxy-imidosulphonate $N(OH)(SO_2.OK)_2.2aq$ (Claus, *A.* 158, 83; Raschig, *B.* 20, 584; *cf.* Divers a. Haga, *C. J.* 51, 659). Prepared by passing a rapid stream of SO_2 through well cooled KNO_2Aq made strongly alkaline by KOHAq; allowing $N(SO_2.OK)_3$ (*v. Nitrilosulphonates*, p. 601) to crystallise out, pouring off, and allowing to stand. Large, lustrous crystals; almost insol. cold water, more sol. water at 40°–60°; heated with water gives $KHSO_4Aq$ and $NH(OH)(SO_2.OK)Aq$ (*v. supra*, OXY-AMIDOSULPHONIC ACID). Three Na salts and several other oxy-imidosulphonates have been prepared by D. a. H. (*C. J. Proc.* 1893–4. 61).

The salts described by Fremy (*l.c.*) as *sulphazotates*, and further examined by Raschig (*A.* 241, 211), and formulated by him as $N(OH)(SO_2.OK)_2.N(OM)(SO_2.OK)_2$, where M = K or Na, and $N(OK)(SO_2.OK)_2.N(OK)(SO_2.OK)_2$, may be regarded as derived from oxy-imidosulphonic acid $N(OH)(SO_2.OH)_2$.

The *oxysulphazotate* of Claus (*sulphazilinate* of Fremy) examined by Raschig (*l.c.*, p. 223) and formulated by him as $(SO_2.OK)_2N{<}\begin{smallmatrix}O\\O\end{smallmatrix}{>}N(SO_2.OK)_2$, may be looked on as derived from oxy-imidosulphonic acid by the removal of 2H from $2N(OH)(SO_2.OH)_2$.

M. M. P. M.

SULPHONO-DI-ACETIC ACID *v.* DI-METHYL SULPHONE DICARBOXYLIC ACID.

SULPHONO-DI-BUTYRIC ACID $SO_2(CHEt.CO_2H)_2$. [152°]. Formed by oxidation of sulphido-dibutyric acid (5 g.) in neutral solution by $KMnO_4$ (5 g.) in water (500 g.). Its ether is got from $SO_2(CH_2.CO_2Et)_2$, Na, and EtI (Lovén, *J. pr.* [2] 33, 104). Octahedra.

Sulphono-di-isobutyric acid $SO_2(CMe_2.CO_2H)_2$. [182°–186°]. Formed by oxidising $S(CMe_2.CO_2H)_2$ (Lovén). Plates.—BaA″ $2\frac{1}{2}$aq. Groups of needles (from hot water).

SULPHONO-DIPROPIONIC ACID *v.* DI-ETHYL-SULPHONE DICARBOXYLIC ACID.

SULPHONO-DI-ISOVALERIC ACID $SO_2(C_4H_8.CO_2H)_2$. Formed by oxidation of $S(C_4H_8.CO_2H)_2$ and by the action of PrI (2 mols.) on sulphono-di-acetic ether (1 mol.) and NaOEt (2 mols.) at 120°; the product being saponified by baryta (Lovén, *J. pr.* [2] 33, 114).—BaA″ 7aq.

SULPHO-OXY-BENZOIC ACID *v.* OXY-SULPHO-BENZOIC ACID.

SULPHO-PHENYL-ACETIC ACID $C_8H_8SO_5$ *i.e.* $CHPh(SO_3H).CO_2H$. Formed by saponifying the product of the action of K_2SO_3Aq on α-bromo-phenyl-acetic ether (Papilsky, *J.* 1880, 856). Very deliquescent mass.—Salts: K_2A''.—CaA″.—BaA″: plates, m. sol. hot water.—ZnA″.—PbA″.—CuA″: blue plates.—$Me(NH_4)A''$.—$CHPh(SO_3NH_4).CO_2Et$. Tables, v. sol. water.—$CHPh(SO_3K).CO_2Et$: thin plates, v. e. sol. Ag.

SULPHO-PHENYL-AMIDO-ACETIC ACID $C_8H_9NSO_5aq$ *i.e.* $SO_3H.C_6H_4.NH.CH_2.CO_2H$. [185°]. Formed by heating phenol (1 pt.) with hippuric acid (1 pt.) and H_2SO_4 (3 pts.) at 140° (Zehenter, *M.* 5, 332; 6, 523). Monoclinic prisms (containing aq); $a:b:c = \cdot93:1:1\cdot28$. Sol.

water and alcohol. Coloured violet by $FeCl_3$. Decomposed by HClAq at 140° into phenol, glycocoll, and H_2SO_4. Aqua regia gives $C_6H_2(OH)Cl(NO_2)_2$ [1:2:3:5].—$BaH_2A''_2\frac{1}{2}aq$.—$AgHA''$ 3aq : concentric groups of needles.

***p*-SULPHO-PHENYL-CARBAMIC ACID.** The acid ether $C_6H_4(SO_3H).NH.CO_2Me$ [188°] is formed by dissolving methyl phenyl-carbamate in fuming H_2SO_4 (Hentschel, *B.* 18, 979) and also by adding NaOH to a cooled mixture of $ClCO_2Me$ and aqueous *p*-amido-benzene sulphonic acid (Noelting, *Bl.* [2] 50, 622).

SULPHO-PHENYL-GLYCOCOLL *v.* SULPHO-PHENYL-AMIDO-ACETIC ACID.

***m*-SULPHO-PHENYL-PROPIONIC ACID** $C_9H_{10}SO_5$ *i.e.* $C_6H_4(SO_3H).CH_2.CH_2.CO_2H$. Formed by treating bromo-sulpho-phenyl-propionic acid with sodium-amalgam (Göring, *C. C.* 1877, 793, 808). Yields *m*-oxy-benzoic acid by potash-fusion.

***exo*-Sulpho-phenyl-propionic acid** $C_6H_5.C_2H_3(SO_3H).CO_2H$. Formed by boiling cinnamic acid with aqueous K_2SO_3 for 12 hours (Valet, *A.* 154, 62). Cinnamic aldehyde is converted by K_2SO_3 into $PhC_2H_3(SO_3K).CH(OH).SO_3K$, which crystallises in needles (containing 2aq) and is converted by boiling dilute H_2SO_4 into *exo*-sulpho-phenyl-propionic acid (Heusler, *B.* 24, 1805). Crystals, v. sol. water and alcohol. Converted by boiling conc. KOHAq into cinnamic acid. Not affected by boiling dilute H_2SO_4.—KHA''. S. 4 at 15°.—K_2A'' *x*aq. Efflorescent crystals. — CaA'' *x*aq. Plates. — BaA'' aq. — $K_2ZnA''_2$.—Ag_2A'' aq : white crystalline pp.

SULPHO-PHENYL-THIO-CARBAMIC ACID. *Anhydride* $C_7H_5NS_2O_3$ *i.e.* $C_6H_4\Big<\begin{smallmatrix}NH.CS\\SO_2.O\end{smallmatrix}$. [183°]. Formed from phenyl-thio-carbimide and SO_3 (Magatti, *B.* 11, 2267). Crystals (from benzene), insol. water, alcohol, and ether. Insol. acids and alkalis. Decomposed by water at 100° into H_2S, CO_2, and amido-benzene *p*-sulphonic acid.

SULPHO-PHLORETIC ACID $C_9H_{10}SO_6$. Formed from phloretic (oxy-phenyl-propionic) acid and SO_3 (Nachbaur, *J. pr.* 75, 45). Sour syrup. — Na_2A'' *x*aq. — BaA'' 3aq. — MgA'' 5aq. —CaA'' 4aq. Crystalline.

***c*-SULPHO-PHTHALIC ACID** $C_6H_3(SO_3H)(CO_2H)_2$[3:2:1]. (*α*)-*Sulpho-phthalic acid.* Formed by oxidising naphthalene (*α*)-sulphonic amide by $KMnO_4$ (Remsen, *Am.* 5, 107), and got also, in small quantity, together with the (*β*)- acid, by the action of fuming H_2SO_4 on phthalic acid (Rée, *C. J.* 49, 514). Minute crystals, v. sol. water, m. sol. alcohol. Soda-fusion gives *c*-oxy-phthalic acid.—$Ba_3A'''_2$ 8aq. Needles, sl. sol. hot water.—$PbHA'''$ $1\frac{1}{2}$aq.—Ag_2KA''' 2aq. Ppd. by adding $AgNO_3$ to a solution of the K salt (Stokes, *Am.* 6, 280).

Amic acid $C_8H_7NSO_6$ *i.e.* $C_6H_3(SO_2NH_2)(CO_2H)_2$. [155°–160°]. Formed by oxidation of naphthalene (*α*)-sulphonic amide by alkaline $KMnO_4$. Thick needles (containing aq). At 155° it splits up into H_2O and the anhydride. Conc. HClAq at 150° forms *c*-sulpho-phthalic acid.—KHA'': slender needles, v. sl. sol. cold water.—K_2A''. [300°]. Amorphous, v. e. sol. water. Yields, when heated, the compound $C_6H_3(COCl)\Big<\begin{smallmatrix}SO_2\\CCl_2\end{smallmatrix}\Big>N.POCl_2$ [120°–126°] whence MeOH produces $C_6H_3(CO_2Me)\Big<\begin{smallmatrix}SO_2\\C(OMe)_2\end{smallmatrix}\Big>NH$ [144°] (Stokes, *Am.* 6, 274).—PbA''.—$AgHA''$: needles.—Ag_2A''. Insol. hot water.

Anhydride of the Amic Acid $C_6H_3(CO_2H)\Big<\begin{smallmatrix}SO_2\\CO\end{smallmatrix}\Big>NH$. Formed as above. Begins to sublime at 200°, but is not melted at 240°. Its silver salt $C_8H_4AgNSO_4$ is converted by MeI into $C_6H_3(CO_2H)\Big<\begin{smallmatrix}SO_2\\CO\end{smallmatrix}\Big>NMe$ [191° cor.]. The compound $C_6H_3(CO_2Me)\Big<\begin{smallmatrix}SO_2\\CO\end{smallmatrix}\Big>NMe$ [180° cor.] has also been prepared.

***i*-Sulpho-phthalic acid** $C_6H_3(SO_3H)(CO_2H)_2$[4:2:1]. (*β*)-*Sulpho-phthalic acid.* (*γ*)-*Sulpho-phthalic acid.* [140°] (when hydrated). The chief product of the sulphonation of phthalic acid or anhydride at 100°-200° (Loew, *A.* 143, 257; Rée, *B.* 18, 1629). Formed also by oxidation of naphthalene (*β*)-sulphonic amide (Remsen, *Am.* 5, 110) and by the action of hot HNO_3 (S.G. 1·3) on potassium di-nitro-(*α*)-naphthol sulphonate (*naphthol yellow S*) (Graebe, *B.* 18, 1126; Rée, *C. J.* 49, 516). Crystalline (containing aq), very hygroscopic, v. sol. water and alcohol, insol. ether. At 180° it yields the anhydride $C_8H_4SO_6$. Soda-fusion forms *i*-oxy-phthalic acid. The K salt fused with sodium formate yields trimellitic acid. Heated with resorcin it yields fluoresceïn sulphonic acid. PCl_5 forms $C_6H_3(SO_2Cl)(CO_2H)_2$ [170°], oily $C_6H_3(SO_2Cl)\Big<\begin{smallmatrix}CO\\CCl_2\end{smallmatrix}\Big>O$ and $C_6H_3Cl\Big<\begin{smallmatrix}CO\\CCl_2\end{smallmatrix}\Big>O$. The mono-chloride is converted by NH_3 into $C_6H_3(SO_2NH_2)(CO_2H)_2$ [192°–202°] which crystallises in plates, sol. water, alcohol, and ether.

Salts.—KH_2A''' 2aq. Needles, v. sol. water. —K_2HA''' 2aq.—$(NH_4)_2HA'''$ $1\frac{1}{2}$aq. At 200° it yields $C_6H_3(SO_3NH_4)\Big<\begin{smallmatrix}CO\\CO\end{smallmatrix}\Big>NH$ [c. 300°]. Crystallising in monoclinic prisms.—$Ba_3A'''_2$ 2aq.—$BaH_4A'''_2$ 5aq. S. 5 at 15°; 50 at 100°. At 250° it yields $Ba(C_8H_3SO_6)_2$.—$BaHA'''$ 2aq.

***s*-Sulpho-isophthalic acid** $C_6H_3(SO_3H)(CO_2H)_2$[5:3:1]. [258°]. Obtained by sulphonation of isophthalic acid (Aronstein a. Kramps, *B.* 13, 489; Lönnies, *B.* 13, 704). Long deliquescent needles (containing 2aq). Potash-fusion yields *s*-isophthalic acid.—KH_2A''' 3aq : long needles.—K_3A''' *x*aq : prisms. —$Ba_3A'''_2$ 8aq : needles, v. sol. water.

***i*-Sulpho-isophthalic acid** $C_6H_3(SO_3H)(CO_2H)_2$[4:3:1]. [244°]. Formed by oxidation of *m*-xylene (*α*)-sulphonic acid (Jacobsen a. Lönnies, *B.* 13, 1556), and by oxidation of $C_6H_3Me(SO_2NH_2).CO_2H$ (Remsen a. Iles, *Am.* 1, 114; Remsen a. Coale, *Am.* 3, 206). Hygroscopic needles (containing 2aq), v. e. sol. water. Potash-fusion yields (*α*)-oxy-isophthalic acid.—**Salts**: KH_2A''' 2aq : needles, sl. sol. cold water. S. 1·59 at 26°.—K_2A'''.—$CaHA'''$ $4\frac{1}{2}$aq. Crystals.—$BaHA'''$ 3aq : small needles. S. ·073 at 23·5°. —$BaHA'''$ 4aq.—$Ba_3A'''_2$ 3aq.

Amic acid $C_8H_7NSO_6$ *i.e.* $C_6H_3(SO_2NH_2)(CO_2H)_2$. Formed by oxidation of $C_6H_3Me(SO_2NH_2).CO_2H$ by $KMnO_4$ (Remsen, *B.* 11, 464; 12, 1436; *Am.* 1, 122; 3, 209). When set free from its salts it changes at once to the anhydride $C_6H_3(CO_2H)\Big<\begin{smallmatrix}SO_2\\CO\end{smallmatrix}\Big>NH$ [284°], S. ·45 at 10°.—KHA″ aq. S. 2·3 at 26°.—K_2A'' 4aq: v. e. sol. water. — $CaH_2A''_2$ 2aq. — CaA″ 5aq. — $BaH_2A''_2$ 2aq: monoclinic tables.—BaA″ 3aq.— $Ag_3C_8H_4NSO_6$: crystalline pp. (Jacobsen, *B.* 12, 2320).

c-Sulpho-isophthalic acid. *Amic acid* $C_6H_3(SO_2NH_2)(CO_2H)_2$ [2:3:1]. Formed by oxidation of the corresponding *m*-xylene sulphonic amide (Jacobsen, *B.* 11, 902). Its acid potassium salt is sl. sol. water.

a-SULPHO-PROPIONIC ACID $C_3H_6SO_5$ *i.e.* $CH_3.CH(SO_3H).CO_2H$. Formed by boiling *a*-chloro-propionyl chloride with aqueous ammonium sulphite and also by warming propionic acid with $ClSO_3H$ (Kurbatoff, *B.* 6, 563; *A.* 173, 5). Syrup, v. sol. water and alcohol.—K_2A'' aq: needles (Rosenthal, *A.* 233, 27).—$(NH_4)_2A''$ aq: prisms.—BaA″ 2aq. S. (of BaA″) 7·45 at 18°. —CaA″ 2aq.—CdA″ 2aq.—Ag_2A'': small needles. Got also by mixing propionic anhydride with SO_3 (Franchimont, *R. T. C.* 7, 27).

β-Sulpho-propionic acid $CH_2(SO_3H).CH_2.CO_2H$. [68°]. Formed by boiling β-iodo-propionic acid with an aqueous solution of $(NH_4)_2SO_3$. Got also by the action of ammoniacal $AgNO_3$ on the compound of acroleïn with $NaHSO_3$ (Rosenthal, *A.* 233, 15) and obtained likewise by the oxidation of thiohydantoic acid $NH{:}C(NH_2).S.CH_2.CH_2.CO_2H$ (Andreasch, *M.* 6, 838; 7, 169). Hygroscopic crystals, sol. water and alcohol. Decomposes at 150°. Successive treatment with PCl_5 and with tin and HClAq converts it into sulphydro-propionic acid.

Salts.—K_2A'' aq.—KHA″ aq.—Na_2A'' aq.—$(NH_4)_2A''$ 4aq. Hygroscopic. — HNH_4A''. — BaA″ 5aq.—$BaH_2A''_2$.—SrA″ 5aq. – CaA″ 2½aq. —CaA″ aq.—MgA″ 4aq.— ZnA″ 4aq.— CuA″.— MnA″ 4aq.—PbA″. — CdA″ aq. — Ag_2A'' ½aq. — HAgA″ ½aq.

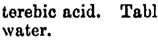
Ethyl ether Et_2A''. Liquid.

Sulpho-dipropionic acid is DI-ETHYL-SULPHONE DICARBOXYLIC ACID.

SULPHO-PROPYL-BENZOIC ACID *v.* SULPHO-CUMINIC ACID.

SULPHO-ISOPROPYL-SUCCINIC ACID $CMe_2(SO_3H).CH(CO_2H).CH_2.CO_2H$. [c. 167°]. Got by action of HNO_3 on sulphocamphylic acid (Königs a. Hoerlin, *B.* 26, 2044). When heated *in vacuo* at 170° it splits up into water, SO_2, and terebic acid. Tables (containing 3aq), v. e. sol. water.

SULPHO-PYROMUCIC ACID $C_5H_4SO_6$ *i.e.*



$\begin{matrix}CH{:}C(CO_2H)\\ CH{:}C(SO_3H)\end{matrix}{>}O$. Formed by dissolving pyromucic acid in cold fuming H_2SO_4, and got also by the action of zinc-dust and ammonia on dibromo-sulpho-pyromucic acid (Schwanert, *A.* 116, 268; Hill a. Palmer, *B.* 18, 2095; *Am.* 10, 373, 409). Deliquescent prisms.—K_2A'' 4aq.—KHA″.—Na_2A'' 5aq. — NaHA″ aq. — BaA″ 4aq. Small prisms. Yields fumaric acid when heated with excess of bromine.—Salts: $BaH_2A''_2$ 4aq.—$BaH_2A''_2$ 6aq.—CaA″ 3aq.—PbA″ 2aq.—Ag_2A''.

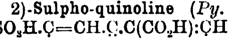
Amide $C_5H_2SO_4(NH_2)_2$ [213°]. Crystalline.

(β)-Sulpho-pyromucic acid $C_4H_2O(SO_3H)(CO_2H)$. Formed by sulphonation of bromo-pyromucic acid and debromination of the product by zinc-dust and NH_3 (H. a. P.).—Salts: K_2A'' 2½aq.—CaA″ 2aq.—$BaH_2A''_2$ 3aq. —BaA″ 3aq.—BaA″ aq: small concentric prisms.

SULPHO-PYROTARTARIC ACID $C_5H_8SO_7$ *i.e.* $C_3H_5(SO_2H)(CO_2H)_2$. Formed by boiling ita-, citra-, and mesa- conic acids with aqueous K_2SO_3 (Wieland, *A.* 157, 34). Crystalline, v. e. sol. water.—$Ca_3A'''_2$ 7aq. Sl. sol. cold water.

SULPHO-QUINOLINE CARBOXYLIC ACID $C_9H_5N(SO_3H).CO_2H$. (*a*)-*Sulpho-cinchoninic acid.* Formed by heating cinchonic acid with SO_3 or with H_2SO_4 and P_2O_5 at 180° (Weidel a. Cobenzl, *M.* 1, 844). Triclinic crystals (containing aq), m. sol. hot water, insol. alcohol and ether. Tastes bitter. Potash-fusion gives (*a*)-oxy-cinchoninic acid.—$(NH_4)_2A''$ 2aq. Monoclinic crystals; *a*:*b*:*c* = 1·19:1:3·53; β = 95°14′.—CaA″ 2½aq. Monoclinic crystals.—BaA″ 3aq.—PbA″ aq.—CuA″ aq: minute sea-green crystals.

(*B.* 2)-Sulpho-quinoline (*Py.* 1)-carboxylic acid



$\begin{matrix}SO_3H.C{=}CH.C.C(CO_2H){:}CH\\ CH{:}CH.C.N{=\!=\!=}CH\end{matrix}$. (β)-*Sulpho-cinchoninic acid.* Formed at the same time as the preceding acid (Weidel, *M.* 2, 565) and prepared by heating cinchoninic acid (1 pt.) with H_2SO_4 (7 pts.) at 300° (Von Georgievitch, *M.* 8, 639). The same acid (crystallising with aq) appears to be formed by oxidation of benzylidene-lepidine sulphonic acid by alkaline $KMnO_4$ (Busch a. Koenigs, *B.* 23, 2683). Colourless needles (containing 2aq), v. sol. hot water. Very bitter. Potash-fusion yields (β)-oxy-cinchoninic acid.—$(NH_4)HA''$ 2aq.—BaA″ aq.—PbA″ 4aq.

SULPHO-SALICYLIC ACID *v.* OXY-SULPHO-BENZOIC ACID.

SULPHO-SUCCINIC ACID $C_4H_6SO_7$ *i.e.* $CO_2H.CH_2.CH(SO_3H).CO_2H$.

Formation.—1. By exposing cooled succinic acid to SO_3 vapour (Fehling, *A.* 38, 285; 49, 203).—2. By boiling fumaric and maleïc acids with aqueous K_2SO_3 (Credner, *Z.* [2] 6, 77; Strecker a. Messel, *A.* 157, 15; *Z.* [2] 6, 459, 671).—3. From succinyl chloride and Ag_2SO_4 (Carius a. Kämmerer, *A.* 131, 167).—4. By oxidation of thio-malic acid with HNO_3 (Carius, *A.* 129, 9).

Properties.—Deliquescent mass, v. e. sol. water, alcohol, and ether. Yields fumaric acid when fused with potash.

Salts.—K_3A''' aq: efflorescent crystals.— K_3A''' 2½aq.—K_3A''' 1½aq. Crystals.—KH_2A'''.— K_2HA''' 2aq.—$K_4H_5A'''_3$ 1½aq.—$(NH_4)_3A'''$ aq.— $(NH_4)H_2A'''$ aq: crystals.—$Ba_3A'''_2$ (dried at 100°). Pp.—$Ca_3A'''_2$ 6aq.—$Pb_3A'''_2$ 4aq.—$Pb_3A'''_2$ 3aq.— $Pb_4OA'''_2$.—$Pb_5O_2A'''_2$.—Ag_3A''': m. sol. water.

SULPHO-TEREPHTHALIC ACID $C_8H_6SO_7$ *i.e.* $C_6H_3(SO_3H)(CO_2H)_2$[2:4:1].

Formation.—1. By heating terephthalic acid with fuming H_2SO_4 at 250° (Ascher, *A.* 161, 2; Schoop, *B.* 14, 223).—2. By oxidation of sulpho-*p*-toluic acid (Remsen a. Burney, *Am.* 2, 410; Weber, *B.* 25, 1740), of *p*-xylene sulphonic acid (Remsen a. Kuhara, *Am.* 2, 414), and of $C_6H_3Me(SO_2NH_2).CO_2H$ (Hall a. Remsen, *B.* 12, 1432; *Am.* 2, 56).

Properties.—Hygroscopic needles or tables.

Salts.—KH_2A''' ½aq. Needles (Remsen a. Keiser, *Am.* 5, 170).—KH_2A''' aq (W.).—K_3A''' aq. —BaHA‴ aq.—CaHA‴ 1½aq.—BaHA‴ 1½aq.— BaHA‴ aq. — $Ba_3A'''_2$ 8aq. — $BaH_4A'''_2$ 5aq. — PbHA‴ 2aq.—Ag_2HA'''.

Amic acid $C_6H_3(SO_2NH_2)(CO_2H)_2$. Formed by oxidising *p*-xylene sulphonic amide with alkaline K_3FeCy_6 (Noyes a. Walker, *Am.* 9, 94).

Concentric needles, sol. hot water. Not melted at 310°.—KHA'' ½aq.—BaA'' aq : nodules.

Imide $C_6H_3(CO_2H){<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NH$. [284°] (W.); [299° cor.] (N. a. W.). Formed by oxidation of $C_6H_3Me(SO_2NH_2).CO_2H$ by $KMnO_4$. Short thin prisms (from ether), m. sol. cold water. $AgNO_3$ gives a pp. insol. HNO_3.—$KC_8H_4NSO_5$ aq.—$BaC_8H_3NSO_5$ 3aq. Scales, v. sl. sol. water.—$Ag_2C_8H_3NSO_5$.

SULPHO-TOLUENE DICARBOXYLIC ACID. *Amic acid* $C_6H_2Me(SO_2NH_2)(CO_2H)_2$[1:4:3:5]. [c. 300°]. Formed by oxidation of ψ-cumene sulphonic amide (Jacobsen a. Meyer, *B.* 16, 190). Needles, sol. water, alcohol, and ether. — BaA'' 2½aq : small prisms, sl. sol. water.

SULPHO-*o*-TOLUIC ACID $C_8H_8SO_5$ *i.e.* $C_6H_3Me(SO_3H).CO_2H$ [2:3:1]. Formed by heating *o*-toluic acid with H_2SO_4 (5 pts.) for 3 hours at 160° (Jacobsen a. Wierss, *B.* 16, 1960). Crystalline, v. e. sol. water. Potash-fusion yields *o*-oxy-toluic acid.

Sulpho-*o*-toluic acid. *Amic acid* $C_6H_3Me(SO_2NH_2).CO_2H$ [2:5:1]. [243°]. Formed, together with about an equal quantity of the (2,4,1)- isomeride, by oxidation of *m* - xylene *o*-sulphonic amide by alkaline $KMnO_4$ (Jacobsen, *B.* 14, 38). Long needles, sol. alcohol, ether, and water. Potash-fusion yields the corresponding oxy-toluic acid. Further oxidised by $KMnO_4$ to $C_6H_3(SO_2NH_2)(CO_2H)_2$.

Sulpho-*o*-toluic acid. *Amic acid* $C_6H_3Me(SO_2NH_2).CO_2H$ [2:4:1]. [217°]. Formed as above. Long needles, sl. sol. cold water, v. sol. alcohol and ether.—KA' : crystals.

***s*-Sulpho-*m*-toluic acid** $C_6H_3Me(SO_3H).CO_2H$ [3:5:1]. Formed, together with the (3,4,1)- isomeride, by sulphonating *m*-toluic acid with fuming H_2SO_4 at 180° (Jacobsen, *B.* 14, 2355).

Sulpho-*m*-toluic acid. *Amic acid* $C_6H_3Me(SO_2NH_2).CO_2H$ [3:4:1]. [248°]. S. 2 at 15°. Formed by oxidation of *m*-xylene sulphonic amide (Remsen, *Am.* 1, 37 ; 3, 205 ; Jacobsen, *B.* 11, 895). Needles (from water), m. sol. alcohol, sl. sol. ether. Potash-fusion gives (4,3,1)-oxy-*m*-toluic acid. $KMnO_4$ yields sulpho-isophthalic acid.—CaA'₂ 1½aq : small concentric needles.—BaA'₂ 4aq.—BaA'₂ 5aq.—AgA' : needles (from hot water).

Sulpho-*m*-toluic acid. *Amic acid* $C_6H_3Me(SO_2NH_2).CO_2H$ [3:2:1]. [203°]. Formed by oxidation of the corresponding *m*-xylene sulphonic amide [96°] (J.). Converted by potash-fusion into the corresponding oxy-toluic acid.

Sulpho-*p*-toluic acid $C_6H_3Me(SO_3H).CO_2H$ [4:3:1].

Formation. — 1. By oxidation of thiocarvacrol (Flesch, *B.* 6, 480; Bechler, *J. pr.* [2] 8, 170).—2. By oxidation of cymene sulphonic acid (Remsen, *Am.* 2, 411 ; R. Meyer a. Baur, *A.* 220, 18).—3. From *p*-toluic acid and SO_3 (Fischli, *B.* 12, 616).—4. By oxidation of *p*-xylene sulphonic acid (Remsen, *Am.* 8, 264). Needles (containing 2aq). Not hygroscopic. V. sol. water, insol. ether. Decomposes at 185°–190° without melting. Potash-fusion gives oxy-*p*-toluic acid [204°]. Conc. HClAq at 190° forms *p*-toluic acid.

Salts. — KHA'' 3aq. — KHA'' 2aq.— K₂A'' 1½aq. — MgA'' 3aq. — MgA'' 7aq. — BaA'' 3aq.—BaA'' 4aq.—PbA'' aq.—PbA'' 3aq.—PbA'' 3½aq.—Ag₂A'' aq.

Amide $C_6H_3Me(SO_2NH_2).CONH_2$ ½aq. [218°].

Amic acid $C_6H_3Me(SO_2NH_2).CO_2H$. [267°]. Formed by oxidation of cymene sulphonic amide and of *p*-xylene sulphonic amide by chromic acid mixture (Remsen a. Hall, *Am.* 2, 50 ; *B.* 11, 229 ; Noyes a. Walker, *Am.* 9, 98). Needles, sol. cold alcohol, insol. ether, sl. sol. cold water.—BaA'₂ 2aq. — CaA'₂ 4aq. — MnA'₂ 5aq : needles. Probably the same amic acid [242°] is formed by oxidising *p*-butyl-toluene sulphonic amide by $KMnO_4$ (Kelbe a. Baur, *B.* 16, 2565). Sl. sol. water, nearly insol. alcohol.

Sulpho-*p*-toluic acid $C_6H_3Me(SO_3H).CO_2H$ [4:2:1]. [182°] (W.) ; [190°] (F.). Got by oxidising thio-thymol (Fittica, *A.* 172, 329) and by evaporating its imide with HClAq (Weber, *B.* 25, 1741). Crystals (containing 3aq).—NH₄HA''.—MgA''.—Ag₂A''.

Anhydride $C_6H_3Me{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}O$. [97°]. Got by treating the acid with AcCl.

Amic acid $C_6H_3Me(SO_3H).CONH_2$. [186°]. Prisms (containing aq).—NH₄A'. Got from the anhydride in benzene by the action of dry NH_3.—AgA' aq : scales (from water).

Amic acid $C_6H_3Me(SO_2NH_2).CO_2H$. [185°]. Got by boiling the imide with water (Weber, *B.* 25, 1739). Yellowish crystals. Probably identical with the preceding amic acid.—BaA'₂ 2aq.—AgA'.—MeA'. [145°].—EtA'. [95°].

Imide $C_6H_3Me{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NH$. *Methyl - saccharin.* [246°]. Got from *p*-toluidine sulphonic acid *viâ* $C_6H_3MeCy.SO_3H$, $C_6H_3MeCy.SO_2Cl$, $C_6H_3MeCy.SO_2NH_2$, $C_6H_3Me(CO_2H)(SO_2NH_2)$, the last body being heated (Kreis, *G. P.* 48,583 ; *B.* 22, Ref. 719 ; Weber, *B.* 25, 1737). Sl. sol. cold water, v. sol. alcohol, ether, and alkalis. Yields $C_6H_3Me{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NAg$, whence MeI forms $C_6H_3Me{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NMe$ [153°], while EtI gives $C_6H_3Me{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NEt$ [106°] (Weber). The imide is converted by warming with aqueous KOCl into *p*-toluidine sulphonic acid.

Di-sulpho-*o*-toluic acid $C_6H_2Me(SO_3H)_2CO_2H$ [2:3:5:1]. Formed by sulphonation of *o*-toluic acid with H_2SO_4 containing SO_3 (Jacobsen a. Wierss, *B.* 16, 1960). Minute needles, v. e. sol water.—×Ba₃A'''₂ : amorphous, v. sol. water.

Di-sulpho-*p*-toluic acid $C_6H_2Me(SO_3H)_2CO_2H$. Formed by heating *p*-toluic acid with fuming H_2SO_4 and P_2O_5 (Weinreich, *B.* 20, 982).—BaHA''' 5aq. Crystals.

Reference.—NITRO-SULPHO-TOLUIC ACID.

SULPHO-UVITIC ACID $C_9H_8SO_7$ *i.e.* $C_6H_2Me(SO_3H)(CO_2H)_2$ [5:6:3:1]. Formed by evaporating its amic acid with conc. HClAq (Jacobsen, *A.* 206, 185). Needles (from dilute H_2SO_4). Potash-fusion yields oxy-uvitic acid.—KH₂A''' 2aq.—Ba₃A'''₂. S. 3·23 at 12·5°. Needles.

Amic acid $C_6H_2Me(SO_2NH_2)(CO_2H)_2$. A product of oxidation of mesitylene sulphonic amide with $KMnO_4$ (Hall a. Remsen, *Am.* 2, 136 ; Jacobsen). When set free from its salts it changes at once into the anhydride $C_9H_7NSO_6$. [270°], S. 5 at 100°.—KHA''.—BaA''.—BaA'' 3aq.

SULPHO-ISOVALERIC ACID $C_5H_{10}SO_5$ *i.e.* $C_4H_8(SO_3H).CO_2H$. Formed by heating isovaleric acid (1 pt.) with $ClSO_3H$ (1 pt.) at 150° (De Varda, *G.* 18, 91). Deliquescent crystalline mass. Its aqueous solution partially decomposes when heated.—BaA'' aq.—PbA'' 2aq.

SULPHOXIDES. Organic compounds R.SO.R' formed by the action of conc. HNO_3 on sulphides. Decomposed by heat. Reduced by Zn and H_2SO_4 and by HI to sulphides. Attacked by PCl_5, sulphides being formed. They reduce $KMnO_4$, being converted into sulphones. Sulphoxides containing monovalent alcohol radicles form unstable compounds with HNO_3, such as Et_2SO,HNO_3 (Beckmann, *J. pr.* [2] 17, 475).

SULPHO-XYLENE CARBOXYLIC ACID. *Amic acid* $C_6H_2Me_2(SO_2NH_2).CO_2H$ [1:3:4:5]. [268° cor.]. Formed by oxidising ψ-cumene sulphonic amide (Jacobsen a. Meyer, *B.* 16, 190). Long needles, sl. sol. hot water.—KA'aq.—$BaA'_2 2\frac{1}{2}aq$.

SULPHUR. S. At. w. 31·98. Mol. w. 63·96; probably also 191·88 and 255·84 (*v. infra*). *The following data apply to ordinary rhombic S.* Melts at c. 115°; different observers give from 111° to 115° (*v.* Helff, *Z. P. C.* 12, 219; Spring, *A. Ch.* [5] 22, 170; Kopp, *A.* 93, 129; Brodie, *J. pr.* 62, 336; Gernez, *C. R.* 83, 217; for m.p. at high pressures *v.* Hopkins, *J.* 1854. 48). Boils at 440° (Dumas, *A. Ch.* [2] 36, 83; Troost a. Hautefeuille, *C. R.* 76, 76, 219). Callendar a. Griffiths (*T.* 182, 119) give 444·53° as 'within ·1° of the true temperature of the vapour of sulphur boiling freely under a pressure of 760 mm.' (This determination was made with Pt resistance thermometers with great care, but unfortunately no special precautions were taken to insure the purity of the S used. For other determinations *v.* Carnelley's *Melting- and Boiling-point Tables*, 1, 11. For b.p. under different pressures from 1 to 760 mm. *v.* Monckman, *Pr.* 46, 136.) S.G. c. 2·03 (for numerous data *v.* Clarke's *Table of Specific Gravities*, 2nd ed., 9). S.G. molten S 1·801 to 1·815 (Playfair a. Joule, *C. S. Mem.* 3, 76); S.G. at b.p. 1·46 to 1·51 (Ramsay, *C. J.* 35, 471). V.D. varies from c. 122 to c. 62; *v. infra, Molecular Weight of S.* S.H. (17°–45°) ·163 (Kopp, *T.* 1865. 71); (0°–100°) ·1776 (Bunsen, *P.* 141, 1). S.H. (liquid) ·2346 (Person, *A. Ch.* [3] 21, 295). Latent heat of fusion = 9·368 (for 1 g. S) (Person, *l.c.*). S.V.S. 15·9. S.V. of S in combination varies from 28·6 to 22·6; S.V. at b.p. 21·6 (Ramsay, *C. J.* 35, 471). C.E. (linear) ·00006413 (at 40°) (Fizeau, *C. R.* 68, 1125; *v.* also Kopp, *A.* 93, 129; Pisati, *G.* 1874. 29; Spring, *J.* 1881. 1085; Moitessier, *J.* 1866. 27, who gives C.E. for each c. 20° from 110° to 440°). S. in CS_2; 16·54 at −11°, 18·75 at −6°, 23·99 at 0°, 37·15 at +15°, 41·65 at 18·5°, 46·05 at 22°, 94·57 at 38°, 146·21 at 48·5°, 181·34 at 55° (Cossa, *B.* 1, 138; Payen, *C. R.* 84, 456, 508). For S.G. of solutions in CS_2 *v.* Macagno (*C. N.* 43, 192). For S. in C_6H_6 and other solvents *v.* Pelouze (*C. R.* 68, 1179; 79, 56). Refraction-equivalent $\left(\frac{\mu-1}{d}.\text{at.w.}\right)$ for D line 16·0 (solid), 16·47 (liquid), 16·1 (gaseous, for C line), 16·0 (in solution), 16·0 (calculated from data for SCl_2), 16·1 (from data for S_2Cl_2) (Gladstone, *P. M.* [5] 35, 204). H.C. $[S,O^2] = 71,080$ (*Th.* 2, 247). The E.C. of S is very small; it varies much with temperature (*v.* Monckman, *Pr.* 46, 136). The fundamental form of rhombic S is a simple pyramid, or elongated octahedron; $a:b:c = {\cdot}8106:1:1{\cdot}898$. For emission-spectrum *v.* Salet, *C. R.* 68, 404; 73, 559; *Bl.* [2] 11, 302; Mulder, *J. pr.* 91, 112; Barrett, *J.* 1865. 138; Seguin, *C. R.* 53, 1272; Chautard, *C. R.* 79, 1123; Plücker a. Hittorf, *J.* 1863. 109. For absorption-spectrum of S vapour *v.* Salet, *C. R.* 74, 865; Gernez, *C. R.* 74, 803; Ciamician, *W. A. B.* 77 [2] 839. For vapour-pressures of S vapour *v.* Regnault (*J.* 1863. 65). Ignition point c. 250° (Hill, *C. N.* 61, 125; Blount, *C. N.* 61, 153).

The following data apply to monoclinic S. Melts at 117·4° (Gernez, *C. R.* 83, 217); at 120° (Brodie, *J. pr.* 62, 336). S.G. 1·982 (Marchand a. Scheerer, *J. pr.* 24, 129); 1·958 (Deville, *J.* 1, 365). S.V.S. 16·4. H.C. $[S,O^2] = 71,720$ (*Th.* 2, 247; Petersen, *Z. P. C.* 8, 601). For volumes occupied at different temperatures *v.* Toepler (*W.* 47, 169). Crystallises in secondary forms of a monoclinic prism; $a:b:c = 1{\cdot}004:1:1{\cdot}004$, angle $b:c = 84° 14'$. Sol. CS_2, from which solution rhombic S crystallises out.

Insoluble sulphur is amorphous; insol. CS_2; S.G. c. 2·04 (Troost a. Hautefeuille, *C. R.* 69, 248); S.G. after compression at 8,000 atmos. 1·9556 at 0°, 1·9643 at 100° (Spring, *Bl. Acad. Belg.* [3] 2, 83).

Cf. Allotropy of Sulphur (p. 609).

Occurrence.—Native, in beds, in Sicily, Mexico, New Zealand, &c.; in the lava fissures of volcanic districts; in small quantities in the mud from the sea-bottom (Buchanan, *Pr. E.* 1891. 1). Many metallic sulphides also occur native—*e.g.* sulphides of Sb, As, Cu, Fe, Pb, Hg, and Zn. Sulphates occur in large quantities—*e.g.* gypsum, celestine, heavy spar; these and other sulphates are found in the earth's crust, in the sea, and in many river and spring waters. (For more details *v.* DICTIONARY OF APPLIED CHEMISTRY, iii. 682.) S is a constituent of albumen, hair, feathers, horn, and some other parts of animals; it is also found in many plants. Small quantities of S compounds are found in the atmosphere near volcanoes. According to Young sulphur occurs in the solar atmosphere (*Am. S.* [3] 4, 356).

Sulphur has been known from very early times. The quantitative work of Lavoisier, in 1772, on burning S showed this substance to be an element, but it was not finally placed on the list of elements until after the experiments of Gay-Lussac and Thénard in 1809.

Formation.—1. By the interaction of SO_2 and H_2S; $2SO_2 + 4H_2S = 3S_2 + 4H_2O$.—2. By the partial oxidation of H_2S, either by incomplete combustion or by exposure of H_2SAq to a limited quantity of air; $2H_2S + O_2 = 2H_2O + S_2$. Also by the oxidation of FeS by exposure to moist air; $2FeS + 3O = Fe_2O_3 + S_2$.—3. By distilling certain metallic sulphides out of contact with air, *e.g.* $3FeS_2 = Fe_3S_4 + S_2$.—4. By decomposing solution of an alkali or alkaline polysulphide by acid; *e.g.* $CaS_5Aq + 2HClAq = CaCl_2Aq + H_2S = 2S_2$. Also by adding acid to solution of a thiosulphate; *e.g.* $Na_2S_2O_3Aq + 2HClAq = 2NaClAq + H_2O + SO_2Aq + S$.—5. By decomposing S_2Cl_2 by water ($2S_2Cl_2 + 2H_2O + Aq = 4HClAq + SO_2 + 3S$).—6. When sulphates, *e.g.* $CaSO_4$, are in prolonged contact with decaying organic matter (such as plant-leaves) they are reduced to sulphides, and if these come into contact with acids S is among the products of the reactions that occur. For a fuller account of some of these processes, whereby native S is probably formed, *v.* DICTIONARY OF APPLIED CHEMISTRY, iii. 683. For methods of forming the various varieties of S *v. infra*, *Preparation*.

Preparation.—1. Ordinary S is dissolved in pure, dry CS_2; a part of the CS_2 is distilled off, and the rest is allowed to deposit crystals of S. This process is repeated once or twice; the S crystals are powdered, kept *in vacuo* for some days to remove all CS_2, and then repeatedly distilled *in vacuo*, the middle portion of the distillate being collected each time.—2. Ppd. S is distilled several times in S_2Cl_2 to remove H compounds; the distillate is then repeatedly distilled *in vacuo*, the middle portion only being collected; the distilled S is finely powdered, repeatedly washed with water, dried, distilled over a few small pieces of pure Zn *in vacuo* (to remove traces of S_2Cl_2), and then repeatedly distilled *in vacuo*.—3. S is ppd. by adding HClAq to pure $Na_2S_2O_3Aq$, the pp. is repeatedly washed till free from chlorides, dried, distilled repeatedly, and finally distilled several times *in vacuo* (*v.* Monckman, *Pr.* 46, 149).

Ordinary rhombic sulphur is prepared by melting S and allowing to cool *very slowly* at 90° (Schützenberger, *C. R.* 66, 746), or by melting and throwing in a crystal of rhombic S when the liquid has cooled nearly to the crystallisation point (Gernez, *C. R.* 83, 217); also by crystallising from CS_2; and, in very well formed crystals, by saturating pyridine or picoline with H_2S and allowing to stand (Ahrens, *B.* 23, 2708).

Monoclinic sulphur is prepared by melting a considerable quantity of roll sulphur in a Hessian crucible, allowing to cool till a crust forms on the surface, piercing this crust, and pouring out the S that is still liquid; the walls of the crucible are covered with monoclinic crystals. This form of S can also be prepared by evaporating alcoholic solutions of $(NH_4)_2S$ (Mallard, *J.* 1885. 383; Ruys, *J.* 1884. 336; Gernez, *C. R.* 100, 1539; 101, 312); also, along with rhombic crystals, from solution of S in boiling alcohol, benzene, &c. (Maquenne, *Bl.* [2] 41, 238). By melting S, and throwing in a crystal of the monoclinic form when the liquid is near the crystallisation point, the S solidifies in monoclinic crystals (Gernez, *C. R.* 83, 217).

Soft soluble sulphur is prepared by decomposing S_2Cl_2 by water, or $Na_2S_2O_3Aq$ or a soluble polysulphide by a limited quantity of acid, or many metallic sulphides by fuming HNO_3, or SO_2Aq by H_2SAq (Weber, *A.* 141, 432; Rose, *P.* 47, 166; Deville, *Ph. C.* 1848. 200; Fordos a. Gélis, *Ph. C.* 1854. 294). This preparation is not homogeneous; it contains both soluble and insoluble S.

Insoluble sulphur (insol. in CS_2) is prepared by heating ordinary S nearly to boiling and then cooling rapidly (most easily by slowly pouring into a large quantity of cold water), rubbing the plastic mass so obtained with a glass rod, under water, till it becomes hard, and removing soluble S by treatment with warm CS_2 (*cf.* Deville, *Ph. C.* 1848. 200). Insoluble S is generally present in 'flowers of sulphur' (which is formed by rapidly cooling vapour of S); by treating this with CS_2 the soluble S is removed, and the insoluble form remains. Soluble S becomes covered with a film of the insoluble variety by exposure to sunlight or electric light when melted (Berthelot, *J. pr.* 31, 396; Lallemand, *C. R.* 70, 182). Insoluble S is also said to be obtained by decomposing $Na_2S_2O_3Aq$ by HClAq, dissolving the ppd. S in $CHCl_3$, evaporating, and keeping the crystals that separate for some time (for details *v.* Engel, *C. R.* 112, 866; Friedel, *C. R.* 112, 834). Insoluble S is also formed, mixed with the soluble variety, by the incomplete combustion of H_2S or CS_2; by decomposing H_2S by fuming HNO_3, *aqua regia*, Fe_2Cl_6Aq, S_2Cl_2, or CrO_3Aq; and by the reaction of HNO_3Aq, SO_2, or halogens with melted S (*v.* Wöhler, *A.* 86, 373; Vogel, *J. Ph.* [3] 29, 433; Schiff, *A.* 115, 68; Nöllner, *A.* 108, 49; Dietzenbacher, *C. R.* 56, 39). Insoluble S is also formed by decomposing thiosulphates by acid, or S_2Cl_2 or S_2Br_2 by water, &c., and washing the soft magma so obtained with CS_2 to remove soluble S (*cf. Preparation of soft soluble sulphur, supra*; and *v.* Weber, *A.* 141, 432; Rose, *P.* 47, 166; Deville, *Ph. C.* 1818. 200).

Colloidal sulphur, soluble in water, is prepared by passing H_2S into SO_2Aq at a little above 0° till all the SO_2 is decomposed, filtering, and concentrating over KOH *in vacuo*. The yellow solid so obtained is sol. water, but changes to ordinary S on keeping (Debus, *C. J.* 53, 282). According to Engel (*C. R.* 112, 866) this form of S exists in the solution obtained by adding 1 vol. $Na_2S_2O_3Aq$, saturated at the ordinary temperature, to 2 vols. HClAq saturated at 25°–30° and let cool to c. 10°, and filtering from NaCl that separates. This form of S has not been isolated in a state of purity.

Regarding the formation of the varieties of S one from the other, *cf. Allotropy of sulphur*, p. 609.

Properties.—S exists in several modifications. The chief are (1) soluble in CS_2, (2) insoluble in CS_2, (3) soluble in water.

1. Soluble sulphur exists in two, perhaps in three, varieties, differing in S.G., crystalline form, &c.

A. *Ordinary rhombic (octahedral) sulphur* is a pale-yellow, tasteless, very brittle solid. By crystallisation from CS_2 it forms clear, yellow, transparent, lustrous crystals; the colour becomes paler at low temperatures, until at −50° the crystals are almost colourless (Schönbein, *J. pr.* 55, 161); by immersion in boiling water it becomes easily powdered (Daguin, *C. R.* 20, 1667). The crystals are derived from the fundamental form of a rhombic pyramid; about thirty varieties are known. When held in the hand S emits a distinct odour, probably because of slight volatilisation; according to Berthelot (*C. R.* 100, 1326) S is wholly volatilisable at a temperature not much above the ordinary. S is said to phosphoresce in air or O at 200° (Heumann, *B.* 16, 139). When S is rubbed it becomes strongly (negatively) electrified. S is a bad conductor of heat, and a very bad conductor of electricity; the conductivity varies slightly, according as the light is or is not allowed to fall on the S (Monckman, *Pr.* 46, 136). Insoluble in water; easily sol. CS_2 (data at beginning of article); also sol. C_6H_6, $CHCl_3$, &c. Sol. warm conc. acetic acid (Liebermann, *B.* 10, 866); sol. liquid SO_2 (Sestini, *Z.* 1868. 718). As octahedral S changes to prismatic S near the m.p. of the former, it is evident that hot solutions of the former, in solvents which boil near to, or above, the m.p. of S must contain some prismatic S. Rhombic S slowly changes to monoclinic S when kept near its m.p. (*v.* p. 609, *Allotropy of sulphur*); the change is accompanied by absorption of heat (c. 650 g.-units for 32 grams S) and expansion of volume (*v.* Petersen, *Z. P. C.* 8, 601). According to Gernez (*C. R.* 83, 217), if a fair quantity of rhombic S is heated till melting begins on the surface, the interior portions change to microscopic monoclinic crystals, and the surface parts solidify again; this occurs only if the m.p. of monoclinic S (117·4°) is not exceeded. S melts to a clear yellow liquid; at c. 150° the liquid begins to darken and thicken; between 170° and 200° it is black, and so viscid that it does not pour out when the vessel containing it is inverted; at 330°–340° the liquid becomes thin, but it remains dark coloured until it boils at c. 444°. These changes are accompanied by very considerable changes in the electrical conductivity of S: the conductivity is almost constant from 270°–290°; it increases considerably up to 340°–350°, and then very rapidly up to the b.p. (*v.* Monckman, *Pr.* 46, 136). The expansion-coefficient, for each interval of 10°, decreases from 110° to 180°, and then increases gradually, but not regularly, to the b.p. (*v.* Moitessier, *J.* 1866. 27). Melted S may be cooled below 95° without solidifying (*cf.* Gernez, *C. R.* 97, 1298, 1366, 1433). For S.G., S.H., and other physical properties of S, *v.* beginning of this article.

B. *Monoclinic sulphur*, obtained by cooling molten S, forms transparent, yellowish brown needles; as obtained by crystallisation from solutions the crystals are nearly colourless. The crystals gradually become pale yellow and opaque, due to change into the rhombic form. The crystals are secondary forms of a monoclinic prism. This form of S is sol. CS_2; rhombic S crystallises from this solution; it also dissolves in alcohol, C_6H_6, $CHCl_3$, &c. On evaporation, crystals, both of rhombic and monoclinic S, separate (Maquenne, *Bl.* [2] 41, 238); monoclinic S may be recrystallised from alcoholic solution of $(NH_4)_2S$ (for references *v.* p. 607, *Preparation of monoclinic S*). The change of monoclinic to rhombic S is hastened by scratching with a glass rod, or by covering with CS_2; heated to 95·1° at 760 mm. pressure, monoclinic changes to rhombic S; the change is accompanied by appearance of heat and contraction of volume (*v.* p. 609, *Allotropy of sulphur*). For S.G. &c. of monoclinic S *v.* beginning of this article.

C. *Soft soluble sulphur* (*v. Preparation of soft soluble sulphur*, p. 607) is only partly sol. CS_2; it contains both soluble and insoluble amorphous S; it is a very pale yellow, or nearly white, soft, amorphous, magma that gradually hardens; when heated it gives off H_2S (Weber, *A.* 141, 432; Rose, *P.* 47, 166; Deville, *Ph. C.* 1848. 200; Fordos a. Gélis, *Ph. C.* 1854. 294).

2. **Insoluble sulphur.** It is doubtful whether more than one variety of this form of S exists, or whether substances described as varieties are not merely mixtures of ordinary insoluble S with impurities.

D. *Plastic sulphur* is a citron-yellow, soft, caoutchouc-like, amorphous solid, formed by suddenly cooling molten S (*v.* p. 607, *Preparation of insoluble sulphur*); as prepared from ordinary S it is dark brown, but Mitscherlich (*J. pr.* 67, 369) found that the dark colour is caused by the presence of small quantities of fatty substances (*cf.* Dietzenbacher, *C. R.* 56, 39). The S.G. of brown, plastic S is c. 1·91 to 1·96; but the substance is not homogeneous; it contains both soluble and insoluble S. Plastic S soon hardens and becomes yellow, more quickly when broken up and rubbed with a glass rod, or when immersed in turpentine, or when heated to c. 100°; heat is given out in this change (*v.* p. 609, *Allotropy of sulphur*). For determinations of the volumes occupied at different temperatures by plastic S *v.* Toepler (*W.* 47, 169).

E. *Amorphous yellow sulphur* is prepared from plastic S, or flowers of S, or the S obtained by decomposing thionates by acid, or H_2S by oxidisers &c. (*v.* p. 607, *Preparation of insoluble sulphur*), by washing with warm CS_2 till all soluble S is removed. This variety is an amorphous, buff-yellow powder; kept under CS_2 it seems white; when dried and rubbed it forms a loose, flocculent powder. Insol. CS_2; somewhat sol. $CHCl_3$, Et_2O, and alcohol, according to Deville (*J. pr.* 56, 359). Unchanged at the ordinary temperature, but slowly converted to crystalline soluble S at 100° (*v.* Berthelot, *J. pr.* 70, 941; 71, 364; Favre, *J. Ph.* [3) 24, 344; F. a. Silbermann, *A. Ch.* [3] 34, 447). S.G. 2·046 (*v.* data at beginning of this article). H.C. $[S,O^2] = 71{,}990$ (Petersen, *Z. P. C.* 8, 601). The accounts of this variety of S vary considerably.

F. *Black sulphur.* When S mixed with a very little oil is thrown into a hot Pt dish, a black substance is obtained which has been looked on as a modification of S (Magnus, *P.* 92, 367; 99, 145; Dietzenbacher, *P.* 124, 644; Gross, *B. B.* 1879. 788; Jones, *C. N.* 41, 244; Keller, *Bl.* [2] 4, 346). Knapp (*J. pr.* [2] 38, 48; 43, 305) has shown that the black substance contains c. 65 p.c. S and c. 33 p.c. carbonaceous matter; K. thinks it is probably a modification of S adhering to carbonised products of the oil. This substance is said to be non-volatile above the b.p. of S; it is a lustrous, amorphous, solid, insol. CS_2, alcohol, Et_2O, oils, H_2SO_4, &c.

3. **Colloidal sulphur soluble in water.** This form of S is said to exist in *Wackenroder's solution* (the milky liquid formed by passing H_2S into SO_2Aq), and also in the solution obtained by adding HClAq to $Na_2S_2O_3Aq$ (*v.* p. 607, *Preparation of colloidal sulphur*). This form of S has not yet been obtained free from impurities; it is a plastic, gummy, pale-yellow solid; it dissolves in water, forming a turbid liquid. By ppg. by NaCl, filtering, drying on bibulous paper, shaking with water, and repeating this treatment, Debus (*C. J.* 53, 284] obtained colloidal S that dissolved in water so as to form an almost clear, opalescent liquid which became quite clear on warming, and turbid

on cooling. This solution yielded ordinary S on addition of several salts; evaporation left a viscous, transparent residue; the S in solution did not diffuse through a porous membrane.

Other modifications of sulphur. Various experimenters have described forms of S different from those usually recognised, but there is much doubt as to whether any of these are really distinct varieties, or merely mixtures of known varieties (*v.* Maquenne, *Bl.* [2] 41, 238; Gernez, *A. Ch.* [6] 3, 266; *C. R.* 100, 1326; Engel, *C. R.* 112, 866; Berthelot, *C. R.* 100, 1328; Braine, *C. R.* 101, 533, 639).

Allotropy of sulphur. The following table presents the best established allotropic forms of S:—

Insoluble in water.

Soluble in CS_2	*Insoluble in* CS_2
Rhombic; S_α	Plastic; S_γ
Monoclinic; S_β	Amorphous, yellow
Amorphous, soft	

Soluble in water.

Colloidal; S_δ

The amorphous forms of S (soft, soluble; yellow, insoluble; and plastic, insoluble) and colloidal S have not been obtained pure; the soluble amorphous always contains insoluble, and the insoluble forms always contain soluble S; the colloidal contains S insoluble in water (*cf.* Magnus, *J. pr.* 70, 215; 72, 48; Weber, *J. pr.* 70, 354). It would probably be more accurate to make only three divisions of amorphous S: soluble in water, insol. water but sol. CS_2, insol. both water and CS_2. Berthelot (*J. pr.* 71, 364; 78, 244) holds that there are two main varieties of S: soluble in CS_2, and insoluble in CS_2. S separated from compounds wherein it acts as the positive radicle, or part of the positive radicle (*e.g.* S_2Cl_2, SO_2Aq), is insoluble, according to B.; whereas when separated from compounds wherein it forms the negative radicle, or part of the negative radicle (*e.g.* H_2S, K_2S), S is soluble in CS_2. B. distinguishes the two varieties of S as electro-positive and electro-negative. Cloëz (*J. pr.* 74, 266; 78, 241) asserts that insoluble S is obtained from S_2Cl_2 when this compound is rapidly shaken with water, but that soluble (crystalline) S separates from the same compound by the gradual action of moist air; and that insoluble S is obtained by electrolysing H_2SAq provided the electrolysis is rapid (*cf.* Weber, *P.* 141, 432).

Any form of S changes gradually to the rhombic crystals (S_α); this change is hastened by raising the temperature within certain limits. Berthelot (*J. pr.* 71, 360) examined the amount of soluble (crystalline) S changed to insoluble at different temperatures; he found that rhombic S heated to 130°-140° and rapidly cooled was still wholly soluble in CS_2, that much insoluble S was formed by heating to c. 170°, and not much more at c. 230°. These results can be taken only as very roughly approximate, on account of difficulties in cooling, &c. (*cf.* Deville, *J. pr.* 56, 365; Frankenheim, *J. pr.* 54, 436). According to experiments of Gernez (*C. R.* 97, 1298, 1366, 1433; 100, 1343, 1382), Ruys (*R. T. C.* 3, 1), and Reicher (*J.* 1885. 247), monoclinic S (S_β) changes to rhombic (S_α) in c. 12 days at $-36°$ to $-15°$, and in c. 30 minutes at 40°. Reicher (*R. T. C.* 2, 246; *Z. K.* 8, 593) says that the temperature of change of S_β to S_α is 95·6° at the ordinary pressure, and rises ·05° for each increase of 1 atmosphere pressure; at 96·1° S_α changes to S_β, and at 95·1° S_β changes to S_α. The change of any form of S to rhombic crystals is accompanied by the appearance of heat and contraction of volume; the data for the heats of combination of S_α, S_β, and amorphous insoluble S give c. 650 gram-units as the quantity of heat produced when 32 grams S_β change to S_α, and c. 900 gram-units for the change of 32 grams insoluble amorphous S to S_α (*cf.* Berthelot, *C. R.* 70, 941; and Mitscherlich, *P.* 88, 328). By keeping S molten for some time at 100°, and then inducing crystallisation by dropping in a crystal of S, either rhombic or monoclinic crystals can be obtained, according as the crystal dropped in is rhombic or monoclinic. When rhombic S is melted and allowed to cool under ordinary conditions the solid contains both S_α and S_β; if the cooling is rapid, some amorphous S (both soluble and insoluble) is also produced; hence ordinary 'flowers of sulphur,' formed by rapidly cooling S vapour, contains both soluble and insoluble S, and generally also, when freshly prepared, both rhombic and monoclinic crystals. The crystals of S that separate from solutions in CS_2 are rhombic; both forms of crystals separate from solutions in alcohol, C_6H_6, $CHCl_3$, &c.; and monoclinic crystals separate from solutions in alcoholic $(NH_4)_2S$. Light brings about the change of soluble into insoluble S; if bright sunlight, or light from the electric arc, falls on molten S at c. 130°, a film of insoluble S is produced. Similarly, light concentrated by a lens and directed on to a conc. solution of S in CS_2 quickly causes the formation of a speck of insoluble S, which soon increases in size till the liquid becomes turbid (Berthelot, *J. pr.* 31, 396; Lallemand, *C. R.* 70, 182). No differences have been observed between the chemical behaviour of the soluble and insoluble varieties of S (*v.* Schmitz-Dumont, *B.* 25, 2659).

Atomic weight of sulphur. The at. w. of S has been determined (1) by converting AgCl into Ag_2S (Berzelius, *P.* 65, 319 [1845]; Svanberg a. Struve, *J. pr.* 44, 320 [1848]); (2) by reducing Ag_2SO_4 to Ag by H (Struve, *A.* 80, 203 [1851]; Stas, *Stas R.* 125 [1860]); (3) by direct synthesis of Ag_2S (Dumas, *A. Ch.* [3] 55, 147 [1859]; Stas, *Stas R.* 53 [1860]); (4) by determining S.H. of S (Kopp, *T.* 1865. 71); (5) by determining V.D. of, and analysing, SH_2, SO_2, S_2Cl_2, &c.

Molecular weight of sulphur. The V.D. determinations of Dumas (*A. Ch.* [2] 50, 170) gave c. 95 at 450°-500°, pointing to the molecular formula S_6; Bineau (*C. R.* 49, 799) found V.D. 39 from 714° to 743°, and 34 between 840° and 1160°, indicating the molecular weight S_2. The determinations by Deville a. Troost (*C. R.* 56, 891) at 860°-1040° confirmed the number 32 and the molecular weight S_2. Troost (*C. R.* 95, 30) got the number 42·5 at 665°, indicating a mol. w. of c. S_3 (V.D. corresponding to $S_3 = 48$). In 1888 Biltz determined V.D. of S at intervals from 468° to 606°, and got results ranging from 113·2 at the lower temperature to 68·4 at the higher ($S_7 = 112$; $S_4 = 64$). The V.D. constantly decreased as temperature rose; the V.D. was constant only between 502° and 524°, but the values were between those calculated for S_6 and S_2. Biltz concluded that the only molecules which exist as gas through any considerable range of temperature have the composition S_2. Ramsay (*Z. P. C.* 3, 67 [1889]) thought that Biltz's results did not negative the existence of gaseous molecules more complex than S_2. Schall (*B.* 23, 1701 [1890]) got numbers for V.D. varying from 115 to 122, at 573° and pressures from 10-20 mm., in an atmosphere of N or CO_2; S. concluded that molecules S_8 probably exist in the vapour of S. Riecke (*Z. P. C.* 6, 430 [1890]) regarded the decrease of V.D. with increasing temperature as a dissociation of S_8 to S_4 and S_2; by making certain assumptions, his calculated results agreed well with the experimental numbers of Biltz. In 1888 Paterno a. Nasini (*B.* 21, 2153) determined the depression in the freezing-point of benzene caused by dissolving S therein; their results indicated S_6 as the molecular formula of S in solution in benzene. By determining the increase in the boiling-point of CS_2 produced by dissolving S in that solvent, Beckmann (*Z. P. C.* 5, 76 [1889]) got values for the mol. w. of S varying from 245 to 280 ($S_8 = 256$). Sakurai also used this method in 1892 (*C. J.* 61, 989); his values for mol. w. of S in CS_2 varied from 252·3 to 254·9. From observations of the effect of dissolving S in naphthalene on the f.p. of the solvent, Hertz (*Z. P. C.* 6, 358 [1890]) concluded that the mol. w. of S in solution in naphthalene is 256 = S_8. Helff (*Z. P. C.* 12, 196) in 1893 also got S_8 for mol. w. of S in CS_2, and in molten P. These results leave little doubt that molecules S_8 exist in solutions of S in CS_2 and in naphthalene, and S_6 in solutions in benzene; that molecules of greater complexity than S_2—probably as complex as S_8—exist in S vapour, but these are stable only through a small range of temperature, and gradually dissociate as temperature rises until all the molecules existing above c. 700° have the composition S_2. Biltz a. Meyer (*B.* 22, 725 [1889]) have shown that the V.D. of S corresponds with the mol. w. S_2 up to 1600°-1700°.

Reactions.—1. Reacts with *water* at 100° to form H_2S. Cross a. Higgin (*C. J.* 35, 249; *B.* 16, 1195) found that the solution contained thionic acids; they supposed that these were produced by reactions between the H_2S and SO_2 formed by the action of the S on the water (*cf.* Payen, *J. Ph.* 8, 371; Mulder, *J.* 1858. 84; Meyer, *C. R.* 74, 195; Gélis, *C. R.* 56, 1004). Senderens (*Bl.* [3] 6, 800) regarded the production of H_2S as due to interactions between the S and the glass vessels employed; C. a. H. (*C. J.* 35, 252) found H_2S was produced when dilute H_2SO_4Aq was used in place of water, and they concluded that the alkaline constituents of the glass were without influence. Becquerel (*C. R.* 56, 287) says that when water containing S in suspension is electrolysed, H_2SO_4 forms at the positive, and H_2S at the negative, electrode (*cf.* Colson, *Bl.* [2] 34, 66). When S is moistened with water and let stand in the air, H_2SO_4Aq is said to be produced (Polacci, *C. C.* 1884. 484; Böhm, *M.* 8, 224).—2. S is oxidised to H_2SO_4Aq by heating with *nitric acid*, *aqua regia*, or *potassium chlorate and hydrochloric acid*.—3. *Conc. hot sulphuric acid* is reduced, giving off SO_2.—4. *Conc. hydriodic acid* gives H_2S and I (I decomposes dilute H_2SAq to $HIAq + S$).—5. *Chlorosulphonic acid* when heated with S produces S_2Cl_2, SO_2, and HCl (Heumann a. Köchlin, *B.* 15, 416).—6. S dissolves in boiling *alkali solutions*, also in *molten alkalis and alkaline carbonates*, to form mixtures of polysulphides and thiosulphates. Boiling *ammonia solution* forms polysulphides; heated in a sealed tube above 100° some $(NH_4)_2S_2O_3Aq$ is produced (*v.* Brunner, *D. P. J.* 150, 371).—7. *Sulphur trioxide* dissolves S, forming a blue solution of S_2O_3 (*v.* SULPHUR OXIDES).—8. *Carbon dioxide* reacts with boiling S to form COS (Cossa, *B.* 1, 117; Berthelot, *Bl.* [2] 40, 364). The same compound is produced by volatilising S, by an electric current, in *carbon monoxide* (Chevrier, *C. R.* 69, 56).—9. $PSCl_3$ is formed by the interaction of S and *phosphorus trichloride* at 130° (Henry, *Bl.* 13, 495). *Phosphorus pentachloride* forms PCl_3 and S_2Cl_2 (Goldschmidt, *C. C.* 1881. 489).—10. S decomposes many *sulphates* and *carbonates* at high temperatures, forming sulphides and SO_2, or CO_2 (*v.* Sestini, *Bl.* [2] 34, 490; Berthelot, *Bl.* [2] 40, 364).—11. *Solutions of salts* are very often reduced by boiling with S, sulphides being generally ppd. (*v.* Vortmann a. Padberg, *B.* 22, 2642; and, more fully, Senderens, *Bl.* [3] 6, 800; 7, 511).

Combinations.—1. Sulphur combines directly with most of the *elements*. The binary compounds of S—with the exception of those with Br, Cl, F, I, or O, and also compounds of S with more than one other element (except these be some of the five just mentioned)—are described under the least negative of the component elements; *e.g.* compounds of S with P and Cl are described (as sulphochlorides) under PHOSPHORUS. For the conditions of formation of the binary compounds of S reference must be made to the various elements, except in the cases of bromide, chloride, fluoride, iodides, and oxides of S, which are described in this article in their proper (alphabetical) places.—2. *Chlorine monoxide* Cl_2O is said to combine directly with S (suspended in S_2Cl_2), at −12°, to form $SOCl_2$ (Wurtz, *C. R.* 62, 460).

Sulphur, acids of. Reference should be made to HYDROGEN SULPHIDE, vol. ii. p. 725; SULPHUR OXYACIDS, this vol. p. 619; SULPHUR OXYACIDS, NITROGEN DERIVATIVES OF, this vol. p. 619; SULPHOCYANIC ACID, vol. ii. p. 303; SULPHONIC ACIDS AND DERIVATIVES, this vol. p. 599; THIOCARBONIC ACID, vol. i. p. 703. For acids, and salts of acids, containing S and P, and S, P and O, *v.* PHOSPHORUS SULPHIDES, this vol. p. 145 (beginning of article); also PHOSPHOROUS SULPHIDE, *Reactions* 7 and 8 (p. 146), PHOSPHORIC SULPHIDE, *Reaction* 8, and also end of that article (p. 147).

Sulphur, bromides of. It is very doubtful whether any definite compound of S and Br exists. Powdered S dissolves in Br with evolution of a little heat; the deep ruby-red liquid begins to distil over at c. 60° and the thermometer rises steadily to c. 190°, when it ascends slowly to c. 200°, after which it steadily rises till S remains; the fraction coming over at 190°–200° agrees fairly in composition with the formula S_2Br_2 (Pattison Muir, *C. J.* 28, 845). M. found that by passing CO_2 through a solution of S in excess of Br for some hours, at 15°, 50°, and 90°, the residual liquid had nearly the composition S_2Br_2; Hannay, however, by passing air through such a liquid for 400–500 hours found that the whole of the Br was removed and that pure S remained (*C. J.* 33, 284; 35, 16). It is, however, possible that at the temperature of this experiment, c. 15°, dissociation of S_2Br_2 was induced by the stream of air. H. also found that the vapour given off by the supposed S_2Br_2, even at 0°, showed the absorption-spectrum of Br. Spring a. Lecrenier (*Bl.* [2] 45, 867) examined the reaction of the supposed S_2Br_2 with K_2SO_3. S. had before shown that S_2Cl_2 and K_2SO_3 produce KCl and $K_2S_4O_6$; but Cl and S acting as free elements produce K_2SO_4, KCl, $K_2S_2O_3$ and SO_2. S_2Br_2 ought then to produce KBr and $K_2S_4O_6$, whereas S and Br would form K_2SO_4, KBr, $K_2S_2O_3$, and SO_2; by determining the quantities of the products S. a. L. calculated that the supposed S_2Br_2 contains c. 27 p.c. of the elements uncombined. Various reactions of the supposed S_2Br_2 are described in the memoirs already referred to (*v.* also Rose, p. 44, 327; Michaelis, *J. Z.* 6, 297; Ogier, *C. R.* 92, 922).

Sulphur, chlorides of. Three compounds of S and Cl are known: S_2Cl_2, SCl_2, and SCl_4. These compounds are liquids; S_2Cl_2 boils unchanged at c. 138°, SCl_2 begins to decompose to S_2Cl_2 and Cl at c. 10°, and the decomposition of SCl_4 to SCl_2 and Cl begins at c. −20°.

SULPHUR MONOCHLORIDE S_2Cl_2. (*Sulphur protochloride*, *Sulphur sulphochloride*, *Sulphothionyl chloride*, *Thio-thionyl chloride.*) Mol. w. 134·7. Boils at 138·12°; S.G. $\frac{0^\circ}{4^\circ}$ 1·70941, S.G. at b.p. 1·49201 (Thorpe, *C. J.* 37, 356). S.V. 90·28 (T., *l.c.*, p. 372). V.D. 68·4 (Dumas, *A. Ch.* [2] 49, 204; Marchand, *J. pr.* 22, 507). $\mu_{H_\alpha} = 1{\cdot}64449$ (Haagen, *P.* 131, 117). H.F. $[S^2,Cl^2]$ (from S_x) = 14,257 (*Th.* 2, 310); 17,600 (Ogier, *C. R.* 92, 922).

Formation.—1. By the interaction of S and Cl.—2. By distilling S with 9 parts $SnCl_2$ or 8·5 parts $HgCl_2$.—3. By reacting on PCl_5 with S (Goldschmidt, *C. C.* 1881. 489).—4. By decomposing $PSCl_3$ by Cl or by heating to redness.—5. By the interaction of P_2S_5 and $SOCl_2$, the other product being P_2O_5 (Carius, *A.* 106, 331).—6. By the action of CS_2 on ICl_3 (Weber, *P.* 128, 459).

Preparation.—A stream of dry Cl is passed into a flask, or retort, containing S (flowers or sticks) until most, but not quite all, S is dissolved to a yellowish-red liquid, the vessel being gently warmed. The liquid is repeatedly distilled until it boils constantly at 138°–139°. If the passage of Cl is continued until the S is completely dissolved, the liquid must be distilled from a little S (to decompose SCl_2 quickly).

Properties.—A yellowish-red, oily liquid, with a very characteristic, rather disagreeable, odour and an acid taste; the vapour affects the mucous membranes rapidly, causing tears, and affecting the breathing. Does not become viscid at −75° (Haase, *B.* 26, 1052). Fumes in air. Dissolves in CS_2 and C_6H_6, also in alcohol and ether with decomposition. S_2Cl_2 dissolves large quantities of S; solution of S_2Cl_2, containing free S, in CS_2 is used for vulcanising (*v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 706).

Reactions and Combinations.—1. S_2Cl_2 sinks in *water*, and then decomposes, giving HClAq, SO_2Aq, and S, with a little H_2SAq, $H_2S_2O_3Aq$, and some of the thionic acids.—2. *Hydrogen sulphide* produces HCl and S; *hydrogen iodide* reacts at the ordinary temperature to form HCl, I, S_2I_2, and then H_2S (Hautefeuille, *Bl.* [2] 7, 198).—3. By passing S_2Cl_2 vapour, mixed with *air* or *oxygen*, through a red-hot tube, SO_2, SO_3, and Cl are formed (Donny a. Mareska, *C. R.* 20, 817; Spring a. Lecrenier, *Bl.* [2] 45, 867).—4. Heating with *phosphorus* produces PCl_3, $PSCl_3$, and S if a little P is used; or PCl_3, P sulphides, and red P if much P is used (Wöhler a. Hiller, *A.* 93, 274; Chevrier, *C. R.* 63, 1003).—5. Heated with many *metals*, S_2Cl_2 gives metallic chlorides and S; the more volatile the metallic chloride the more readily does the reaction occur (*v.* Chevrier, *C. R.* 64, 302).—6. S_2Cl_2 combines with *chlorine*, forming SCl_2 and SCl_4 (*q.v.*, *infra*). Br and I are absorbed by S_2Cl_2; according to Evans a. Ramsay (*C. J.* 45, 65) no compound is formed with Br.—7. With *oxides of arsenic and antimony* S_2Cl_2 forms $AsCl_3$ and $SbCl_3$, giving off SO_2 and separating S; *selenion dioxide* produces Se_2Cl_2 and SO_2; *oxides of phosphorus, boron, and silicon* do not react (Prinz, *A.* 223, 355).—8. S_2Cl_2 absorbs *sulphur trioxide*, below 0°, forming a brownish-yellow liquid, from which excess of SO_3 crystallises out; a little above 6° SO_2 is given off, rapidly at 10°; $S_2O_5Cl_2$ is formed on distillation (Rose, *P.* 44, 291).—9. By passing vapour of S_2Cl_2 along with the vapours from *sulphonic acid* through a hot tube, SO_2, H_2S, S, HCl, and Cl are produced (Brault a. Poggiale, *J. Ph.* 21, 140).—10. Heating S_2Cl_2 with *sulphates* generally produces SO_2Cl_2, chlorides, S, and SO_2; heated with *sulphuryl chloride* to 250°, S_2OCl_4 is formed (*v.* Schneider, *J. pr.* 104, 83; [2] 32, 18; Demarçay, *C. R.* 92, 726).—11. S_2Cl_2 combines with *ammonia gas* to form $S_2Cl_2.4NH_3$, stable in air, sol. alcohol, decomposed by water giving NH_4ClAq, $(NH_4)_2S_2O_3Aq$, and S (Brault a. Poggiale, *J. Ph.* 21, 140).—12. Reacts with *organic compounds containing oxygen*, generally forming Cl compounds and small quantities of S compounds, and also HCl, SO_2, and S.—13. Combines with *unsaturated hydrocarbons*; *e.g.* with C_2H_4 forms $C_2H_4S_2Cl_2$.

SULPHUR DICHLORIDE SCl_2. Mol. w. (in solution in benzene or acetic acid) 102·72. S.G. 1·6482 at 15·4° (Costa, *G.* 20, 367). $\mu_{H_\alpha} = 1{\cdot}5716$ (Costa, *l.c.*). No constant b.p. (*v. infra*). This compound was prepared by *H.* Rose in 1831 (*P.* 21, 431; 27, 117); the experiments of Dumas (*A. Ch.* [2] 49, 204) and Marchand (*J. pr.* 22 507) led to its recognition as a definite compound (*v.* also Carius, *A.* 106, 291); Hübner a. Guerout (*Z.* 1870. 455) isolated the compound satisfactorily, and their results were confirmed by Thorpe a. Dalzell, in 1871 (*C. N.* 24, 159). Costa, in 1890 (*G.* 20, 367), determined the mol. w. of the compound in solution.

Preparation.—Dry Cl is led into S_2Cl_2, surrounded by a freezing mixture, until the liquid becomes deep red; excess of Cl is removed by a stream of dry CO_2. The temperature must not rise above 6°; the vessel containing the S_2Cl_2 should be kept filled with Cl continually, and should not be exposed to direct sunlight (H. a. G., *l.c.*; C., *l.c.*; T. a. D., *l.c.*; also Soubeiran *A. Ch.* [2] 67, 64; Michaelis, *A.* 170, 1).

Properties. — A thin, dark, brownish-red, liquid, with smell and taste like S_2Cl_2; does not solidify at $-30°$; gives off Cl when exposed to sunlight, and should, therefore, be kept in a sealed tube in the dark. Easily decomposed by heat to S_2Cl_2 and Cl; Michaelis (*B.* 6, 995) gives a table showing amount of dissociation from 20° to 130°; the temperature whereat 50 p.c. of the SCl_2 is dissociated is c. 86°. SCl_2 reddens dry litmus paper. The depression of the freezing-point of benzene or glacial acetic acid by solution therein of SCl_2, shows that the mol. w. agrees with the formula SCl_2 (Costa, *G.* 20, 367).

Reactions and Combinations.—1. *Heat*, or direct *sunlight*, causes dissociation to S_2Cl_2 and Cl (*v. supra*, *Properties*).—2. *Water* produces HClAq and $H_2S_2O_3$Aq.—3. Oxidised violently by *nitric acid* to HClAq and H_2SO_4Aq.—4. *Ammonia solution* produces NH_4ClAq, N, and S; *ammonia gas* combines to form $SCl_2.2NH_3$ and $SCl_2.4NH_3$, soluble, unchanged, in absolute alcohol and ether (Soubeiran, *A. Ch.* [2] 67, 74).—5. *Thionyl chloride* ($SOCl_2$), when heated with SCl_2, forms S_2OCl_4 (Ogier, *Bl.* [2] 37, 293).—6. *Alkali sulphites* produce chlorides and trithionates (Spring a. Lecrenier, *Bl.* [2] 45, 867).—7. Some *metals*, *e.g.* Cu, Fe, K, react with SCl_2, with production of heat and light, and formation of chlorides and sulphides.—8. Combines with *arsenious chloride*, forming $AsCl_3.SCl_2$ according to H. Rose (*P.* 27. 107).—9. SCl_2 reacts with *oxygenised carbon compounds* similarly to, but more readily than, S_2Cl_2; it combines with several *unsaturated hydrocarbons* (*v.* Heintz, *A.* 100, 370; Guthrie, *C. J.* 12, 109).

Sulphur tetrachloride SCl_4. This compound exists only at temperatures under $-20°$. The molecular weight is probably 173·46 (SCl_4).

Preparation.—S_2Cl_2 is cooled to below $-20°$ (c. $-22°$) and a slow stream of dry Cl is passed in until absorption of Cl ceases. Michaelis a. Schifferdecker (*B.* 6, 993) found that 67·5 g. S_2Cl_2, kept at $-20°$ to $-22°$, absorbed 106 g. Cl in 10 hours, that absorption of Cl then ceased, and that the liquid had the composition SCl_4.

Properties.—A mobile, yellowish-brown liquid; when removed from the freezing mixture used in the preparation, the liquid gives off Cl, and boils with an absorption of much heat. M. a. S. give the following data showing the dissociation of SCl_4 to SCl_2 and Cl:—

Temp.	P.c. SCl_4	P.c. SCl_2
− 22°	100·0	0·0
− 15	41·95	58·05
− 10	27·62	72·38
− 7	21·97	78·03
− 2	11·93	88·07
+0·7	8·87	91·13
+6·2	2·43	97·57

Reactions.—1. *Water* causes rapid decomposition to HClAq and SO_2Aq, with more or less S according to the mass and temperature of the water.—2. With *sulphur trioxide*, in the ratio $SCl_4:SO_3$ the products are $SOCl_2$ and $S_2O_5Cl_2$, in the ratio $SCl_4:2SO_3$ the products are $SOCl_2$, SO_2, and Cl (M. a. S., *l.c.*; also *B.* 5, 924). *Sulphur dioxide* does not react.—3. *Chlorosulphonic acid* reacts at a low temperature to form $S_2O_3Cl_4$ and HCl (M. a. S., *B.* 6, 996).—4. With some *hydroxylic organic compounds*, *e.g.* $C_2H_5.OH$ and $C_6H_5.CO.OH$, OH is replaced by Cl and $SOCl_2$ is formed.

Combinations.—1. Compounds of SCl_4 with several *metallic chlorides* are produced by warming the chlorides with S_2Cl_2 and passing in Cl; the compounds $2AlCl_3.SCl_4$, $AuCl_3.SCl_4$, and $2TiCl_4.SCl_4$ are formed thus (Weber, *P.* 104, 421; Rose, *P.* 42, 517; Casselmann, *A.* 83, 267). The compound with $AlCl_3$ may be distilled in a closed ⋀ shaped tube; the other two compounds give off Cl when heated. The compounds $SbCl_5.3SCl_4$ and $SnCl_4.2SCl_4$ are produced by passing Cl over SnS_2 and Sb_2S_3 respectively (R., *l.c.*; C., *l.c.*).—2. With *iodine trichloride* forms $ICl_3.SCl_4$ (Weber, *P.* 128, 459; *cf.* Jaillard, *A. Ch.* [3] 59, 454, who gives the composition $SCl_2.2ICl_3$). Prepared by passing Cl into I dissolved in CS_2 till the liquid is wine-red, cooling, and drying the red-yellow, prismatic, very deliquescent, crystals, in a tube in a stream of dry Cl. Also formed by passing Cl into a mixture of 2 pts. S and 1 pt. I. Melts to a brown liquid when heated in a closed tube; heated in an open tube forms Cl, ICl, and S_2Cl_2; decomposed by water or dilute HNO_3Aq.

Sulphur, chloro-iodide of, $SCl_7I(=SCl_4.ICl_3)$; *v. supra*, Sulphur tetrachloride, *Combinations*, No. 2.

Sulphur, chloronitride of, S_2ClN; *v.* Nitrogen sulphochloride, vol. iii. p. 571.

Sulphur, cyanides of, *v.* Cyanogen, sulphides, vol. ii. p. 358.

Sulphur, fluoride of. According to Gore (*Pr.* 20, 70 [1871]) the heavy colourless gas produced by fusing AgF with S is a fluoride of S. This gas is not liquefied at 0°, at the ordinary pressure; it fumes in the air, and attacks glass; no analyses are given by G.

Sulphur, haloid compounds of. The most stable of these compounds belong to the forms S_2X_2; where X = Cl, Br, or I. The chloride S_2Cl_2, may be distilled unchanged; the bromide, S_2Br_2, is exceedingly easily decomposed if, indeed, it has been isolated; the iodide, S_2I_2, has been very slightly examined. The compounds SCl_2 and SCl_4 also exists; the former at temperatures below c. 10°, and the latter below c. $-20°$. The compound SI_6 perhaps exists; it gives up I at the ordinary temperature. The only haloid compound of S that has been gasified unchanged is S_2Cl_2.

Sulphur, hydrides of, SH_2 and (?) S_5H_2; *v.* Hydrogen sulphides, vol. ii. p. 725.

Sulphur, nitride of, SN; *v.* Nitrogen sulphide, vol. iii. p. 570.

Sulphur, iodides of. S and I probably combine when heated together, but no definite compound has been isolated by this method (*cf.* Gay-Lussac, *G. A.* 48, 372; H. Rose, *P.* 27, 115; Lamers, *J. pr.* 84, 349; Sestini, *J.* 1868. 153; Wheeler a. Lüdeking, *Fr.* 26, 602).

Sulphur mono-iodide S_2I_2. Guthrie (*C. J.* 14, 57) obtained this compound by placing 2½ parts EtI and 1 part S_2Cl_2 in a sealed tube, opening after 12 hours, evaporating EtCl by warming with the hand and removing excess of EtI by gently warming; the S_2I_2 crystallised out in lustrous crystals resembling I. (One analysis is given, but no full description of properties.)

Ogier (*C. R.* 92, 922) gives H.F. $[S^2, I^2]$ (from gases) = 10,800.

SULPHUR HEXA-IODIDE SI_6. This compound is said to be formed by slowly evaporating, at a low temperature, a solution of I with slight excess of S in CS_2. Grey-black crystals; resembling, and isomorphous with, I; I evaporates on exposure to air and eventually only S remains; alcohol, conc. KOHAq, or KIAq, also withdraws all I (G. vom Rath, *P.* 110, 116; Lamers, *J. pr.* 84, 349). It is very doubtful whether the crystals examined by vom Rath were a compound or only I retaining a little S.

By passing H_2S into a dilute solution of $KCl.ICl_3$, Lamers (*l.c.*) obtained an orange-red pp. which dried in an exsiccator to a brown amorphous mass containing S and I in the ratio S_3I_2.

By subliming SnS_2 with I, Schneider (*J.* 1860. 186) obtained a compound to which he gave the composition $SnSI_2.SI_2$.

Sulphur, iodochloride of, $SICl_7$ $(= SCl_4.ICl_3)$ *v.* SULPHUR TETRACHLORIDE, *Combinations* No. 2.

Sulphur, oxides of. Four compounds have been isolated; S_2O_3, SO_2, SO_3, and S_2O_7. S and O combine directly to form SO_2 and SO_3; S dissolves in SO_3 to form S_2O_3; S_2O_7 is formed by the action of an electric discharge on a mixture of SO_2 and O, or SO_3 and O.

SULPHUR SESQUIOXIDE S_2O_3 (*Hyposulphurous anhydride*). The production of a blue substance, on distilling fuming H_2SO_4 and S, was noticed by Buchholz in 1804 (*Gehlen's J.* 3, 7); Vogel, in 1812, obtained the blue body by bringing together S and SO_3 (*S.* 4, 121); the substance was examined by Wach (*S.* 50, 1), Berzelius (*Lehrbuch* [5th edit.] 1, 485), and Stein (*J. pr.* [2] 6, 172). Weber, in 1875, isolated the compound and found its composition to be S_2O_3 (*P.* 156, 531).

S_2O_3 is prepared by adding well-dried flowers of sulphur, little by little, to SO_3 quite free from H_2SO_4, more S being added when the previous quantity has all combined. The process is conveniently conducted in a test tube, covered with a small porcelain crucible to exclude moisture, and plunged into water cooled to c. 12°; the S disappears in the SO_3 and blue drops are formed; the tube should be tilted so that the blue drops come into contact with the sides of the tube where they form a thin crust (if the drops solidify as they float in the SO_3, the solid S_2O_3 retains SO_3, from which it cannot be freed). When c. 1 g. S has been added, excess of SO_3 (which should be colourless) is poured off, the last traces being removed by gently and carefully warming not above 35°; the solid S_2O_3 is scraped out of the tube by a glass rod.

S_2O_3 is a blue-green solid, consisting of a mass of microscopic crystals. Insoluble pure SO_3; if a little H_2SO_4 is present the S_2O_3 dissolves to a deep-blue liquid. Melts with decomposition; decomposes slowly in dry air, quickly on heating, to SO_2 and S; deliquesces in moist air to a brown liquid from which S soon separates; reacts violently with water, giving H_2SO_4Aq, SO_2Aq, $H_2S_2O_3Aq$, polythionic acids, and S; decomposed also by alcohol and ether, with separation of S, also by ordinary H_2SO_4.

S_2O_3 may be regarded as the anhydride of $H_2S_2O_4$; although the acid has not been obtained from the oxide, nor the oxide from the acid.

For the compounds $SSeO_3$ and $STeO_3$ *v.* *Selenion thio-oxide* (p. 441) and *Tellurium thio-oxide* (under TELLURIUM OXIDES).

SULPHUR DIOXIDE SO_2. (*Sulphurous oxide. Sulphurous anhydride. Thionyl oxide.*) Mol. w. 63·9. Melts at c. −76° (Faraday, *T.* 1845. 155); c. −80° (Mitchell, *A.* 37, 356). Boils at c. −10° (Bunsen, *P.* 46, 97; Andréeff, *J.* 1859; Pictet, *C. C.* 1877. 81). S.G. (liquid) 1·4911 at −20·5°, 1·4384 at −2·08°, 1·4252 at +2·8°, 1·3769 at 20°, 1·3258 at 38·65° (Andréeff, *A. Ch.* [3] 56, 317); 1·4338 at 0°, 1·2872 at 52°, 1·1845 at 82·4°, 1·1041 at 102·4°, ·956 at 130·3°, ·7317 at 151·75°, ·52 at 156° (Cailletet a. Mathias, *C. R.* 104, 1563). S.G. (gas at 0° and 760 mm.) 2·2639 (Leduc, *C. R.* 117, 219). V.D. 32·23 (Gay-Lussac, Berzelius, Buff; Biltz, *B.* 21, 2769). S.H. (equal wt. water = 1) ·1544; (equal volume air = 1) ·3414 (Regnault, *J.* 1863. 84). Ratio of S.H. constant pressure to S.H. constant volume = 1·2562 (Müller, *W.* 18, 94). C.E. ·00423 for 1° between 0° and 10°, ·004005 10° to 20°, ·003846 at 50°, ·003757 at 100°, ·003718 at 150°, ·003695 at 200°, ·003685 at 250° (Amagat, *C. R.* 73, 183; *cf.* *C. R.* 68, 1170). Leduc (*C. R.* 117, 219) gives C.E. between 0° and 20° as ·00396. For C.E. of liquid SO_2 *v.* Drion (*A. Ch.* [3] 56, 5) and Andréeff (*A.* 110, 1). The ratio $\frac{PV}{P_1V_1} > 1$; Amagat (*l.c.*) gives these values,

1·0185 at 15°, 1·0110 at 50°, 1·0054 at 100°, 1·0032 at 150°, 1·0021 at 200°, 1·0016 at 250°. H.F. $[S,O^2] = 71,070$ from solid rhombic S; 71,720 from solid monoclinic S (*Th.* 2, 247). Heat of liquefaction of gaseous SO_2 = 5644 (Favre, *A. Ch.* [5] 1, 209). Critical temperature = 156° (Cailletet a. Mathias, *C. R.* 104, 1563); 155·4° (Sajotscheffski, *P. B.* 1879. 741); 157°–161° (Ladenburg, *B.* 11, 821). Heat of vaporisation of liquid SO_2, at 0° = 91·2, at 60° = 69 (C. a. M., *l.c.*; *cf.* Chappuis, *C. R.* 104, 897). Regnault (*C. R.* 50, 1063) gives vapour pressures as follows:

Temp.	Vap. pressure	Temp.	Vap. pressure
−25°	373·79 mm. Hg	30°	3131·80 mm. Hg
−20	479·46 "	40	4670·23 "
−10	762·49 "	50	6220·01 "
0	1165·06 "	60	8123·80 "
+10	1719·55 "	65	9221·40 "
20	2462·05 "		

Vapour-pressure at critical temp. = 78·9 atmos. (Sajotscheffski, *P. B.* 1879. 741). S. in water between 0° and 20° (gaseous SO_2) = $79·789 - 2·6077t + ·029349t^2$; 1 vol. of the saturated SO_2Aq contains $68·861 - 1·87025t + ·01225t^2$ vols. SO_2; S. (water) between 21° and 40° = $75·182 - 2·1716t + ·01903t^2$; 1 vol. of the saturated SO_2Aq contains $60·952 - 1·38898t + ·00726t^2$ vols. SO_2 (Bunsen a. Schönfeldt, *A.* 95, 2). S. in alcohol, at 760 mm. = $328·62 - 16·95t + ·3119t^2$; S.G. of solution = $1·11937 - ·014091t + ·000257t^2$ (Carius, *A.* 94, 148). Sims (*C. J.* 14, 1) gives the table on the next page, which presents both the weight of SO_2 in grams and the volume of gaseous SO_2 in c.c. dissolved by unit weight of water at the normal pressure and different temperatures:—

Temp.	Grams SO_2	c.c. SO_2
	absorbed by 1 g. water at 760 mm.	
8°	·168	58·7
12	·142	49·9
16	·121	42·2
20	·104	36·4
24	·092	32·3
28	·083	28·9
32	·073	25·7
36	·065	22·8
40	·058	20·4
44	·053	18·4
48	·047	16·4
50	·045	15·6

The quantity of SO_2 dissolved by a given weight of water varies with pressure, and only at c. 40° and upwards is the quantity proportional to the partial pressure of the gas (*v.* Sims, *C. J.* 14, 1). For S.G. and composition from ·5 to 10 p.c. of SO_2Aq *v.* Anthon (*C. C.* 1860. 744); also Giles a. Schearer (*S. C. I.* 4, 303). $[SO^2,Aq]=7,700$ (gaseous SO_2) (*Th.* 2, 249); 1500 (liquid SO_2) (Berthelot, *C. R.* 96, 142, 208; Chappuis, *A. Ch.* [2] 19, 21). H_2SO_4Aq absorbs the following quantities of gaseous SO_2 (Kolb, *D. P. J.* 209, 270; *cf.* Dunn, *C. N.* 43, 121; 45, 270):—

S.G. H_2SO_4Aq	Kilos. SO_2 per kilo. acid	Litres SO_2 per litre acid
1·841	·009	5·8
1·839	·014	8·9
1·540	·021	11·2
1·407	·032	15·9
1·227	·068	29·7

SO_2 is absorbed by charcoal; 1 c.c. charcoal = 1·57 g. was found by Favre (*A. Ch.* [5] 1, 209) to absorb 165 c.c. SO_2. Camphor absorbs c. 308 times its vol., glacial acetic acid c. 318 times, SO_2Cl_2 c. 187 times, its volume of SO_2 (Schulze, *J. pr.* [2] 24, 168; Bineau, *A. Ch.* [3] 34, 326). $\mu_{Na}=1·35$ at 15° (Bleekrode, *Pr.* 37, 359). For surface tension of liquid SO_2 *v.* Clark (*C. N.* 38, 294; 40, 8). For absorption-spectrum *v.* Liveing a. Dewar (*C. N.* 47, 121).

Occurrence.—In volcanic gases, and in river and spring water near volcanoes (*v.* Ricciardi, *G.* 18, 38).

Formation.—1. By burning S in O. Baker (*Pr.* 45, 1; *C. J.* 47, 349) found that the combustion of S in O is retarded the drier the O is; using very carefully dried O there was no flame. According to Hempel (*B.* 23, 1456) c. 2 p.c. of the gas formed when S is burnt in O at the ordinary pressure is SO_3, 98 p.c. being SO_2; at a pressure of 40°–50° atmos. c. half the S is burnt to SO_2 and half to SO_3; at higher pressures c. 70 atmos. the proportion of SO_2 increases.—2. By heating S with oxide of Pb, Mn, Hg, Zn, &c.—3. By heating various sulphates with S, also SO_3 with S, or conc. H_2SO_4 with C, Cu, Hg, or S; by heating Na_2SO_4 with charcoal and SiO_2.—4. By the decomposition, by acids, of alkali thiosulphate or polythionate solutions.—5. By burning H_2S, CS_2, and various organic compounds containing S.—6. By decomposing conc. H_2SO_4 by heat.—7. By the action of electric sparks on a mixture of sulphur with CO_2, NO, or N_2O (Chevrier, *C. R.* 69, 136).

Preparation.—1. Pure H_2SO_4, mixed with half to two-fifths its volume of water, is heated with pure Cu; the SO_2 that comes off is passed through water in a large flask, and then through a couple of bottles filled with pumice, broken into small pieces and moistened; the pumice should be twice moistened with pure H_2SO_4 and heated to redness before being used, to remove chlorides and fluorides (Stas, *Chem. Proport.* 115). The SO_2 may be dried by passing it through pure conc. H_2SO_4, and then over $CaCl_2$.—2. A mixture of 3 parts pure CuO and 1 part S in powder is heated in a tube of hard glass; the anterior part of the tube contains CuO only, to oxidise S that may sublime (Marchand, *P.* 42, 144).—3. Neumann (*B.* 20, 1584) obtains a regular stream of approximately pure SO_2 by placing a mixture of three parts $CaSO_3$ and 1 part $CaSO_4$, made into small cubes, in a Kipp's apparatus, and decomposing by ordinary oil of vitriol. The acid should be allowed to come into contact with sufficient cubes, and no more, to give the stream of gas that is required. Using c. 500 g. of the cubes, N. obtained a constant stream of SO_2 for 30 hours. The cubes are made by mixing the $CaSO_3$ and $CaSO_4$, moistening with water so that a semi-solid mass is obtained that can be worked with the fingers with some difficulty, pressing this in an iron mortar, hammering it into an iron frame c. 10–12 mm. in height, covering with oilcloth and pressing strongly, cutting into cubes while still in the frame, removing and drying at c. 20° (*v.* Winkler, *B.* 20, 184).

Properties.—A colourless gas, at ordinary temperatures and pressures, with the strong penetrating, choking odour of burning S; causes coughing and blood-spitting if inhaled in any quantity. Incombustible in air, and extinguishes flame; when mixed with O and passed over heated spongy Pt it is oxidised to SO_3. Dry SO_2 is said not to redden litmus paper (Wilson, *C. J.* 1, 332). Bleaches many vegetable colours; the colours are generally restored by alkalis. Bad conductor of electricity (*v.* Bleekrode, *P. M.* [5] 5, 375, 439). Is not decomposed by passing through a red-hot tube. Condensed at c. −10° under the ordinary pressure—by passing the dry gas into a tube surrounded by a mixture of snow and salt; may also be condensed at the ordinary temperature by evolving the gas (by warming charcoal saturated with SO_2, or a mixture of 1 part S and 5 parts SO_3) in one limb of a closed tube, the other limb being placed in cold water. Convenient apparatus for liquefying SO_2 is described by Wöhler (*A.* 137, 371) and Hofmann (*B.* 2, 262).

Liquid SO_2 is a colourless, mobile liquid. Exposed to air it evaporates very rapidly, with disappearance of much heat; an air thermometer placed in liquid SO_2 at 10°, in an open vessel, falls to −57°. Liquid SO_2 dissolves P, S, I, Br, and many gums. It is miscible in all proportions with liquid SO_3; partially miscible with CS_2, Et_2O, $CHCl_3$, and C_6H_6 on warming; but immiscible with conc. H_2SO_4 (Sestini, *Bl.* [2] 10, 226). Liquid SO_2 is a non-conductor of electricity (Magnus, *P.* 104, 553).

By evaporating liquid SO_2 rapidly in an air-pump, part of it solidifies to a white, woolly mass; the liquid may also be solidified by placing it in a mixture of solid CO_2 and ether.

Reactions and Combinations.—1. SO_2 is not decomposed by passing through a red-hot tube. But by *heating* to c. 1200° it is changed to SO_3 and S ($3SO_2 = 2SO_3 + S$); the action stops when the SO_3 attains a certain vapour pressure, but if the SO_3 is removed (by conc. H_2SO_4) the whole of the SO_2 is decomposed (Deville, *C. R.* 60, 317). *Induction sparks* effect the decomposition of SO_2 to SO_3 and S (*v.* Buff a. Hofmann, *A.* 113, 129); *light* acts similarly (Morren, *C. R.* 69, 397).—2. H_2O and S are produced by passing SO_2 mixed with *hydrogen* through a red-hot tube.—3. *Chlorine* combines with SO_2, in sunlight, to form SO_2Cl_2 (*v.* Sulphuryl chloride). SO_2Cl_2 is also formed by passing SO_2 and Cl into glacial acetic acid, even in the dark; also by passing SO_2 over charcoal saturated with Cl (Melsens, *C. R.* 76, 92).—4. *Ozone* produces SO_3; the same compound is formed by passing SO_2 mixed with *oxygen* over heated spongy Pt, or by burning SO_2 in O under a pressure of several atmos. (*v. supra; Formation,* No. 1). According to Berthelot (*A. Ch.* [5] 12, 463), S_2O_7 is formed by the action of the *silent discharge* on SO_2 mixed with *oxygen*. The compound $S_2O_9N_2$ is said to be formed by passing *electric sparks* through a mixture of SO_2 and *air*. This compound is probably $S_2O_5(NO_2)_2$ (*v.* Nitrosulphonic anhydride, p. 601).—5. Passed over red-hot *carbon* the products are CO, CO_2, and S; COS and CS_2 are also sometimes formed, probably by secondary reactions (Scheurer-Kestner, *C. R.* 114, 296; *cf.* Berthelot, *Bl.* [2] 40, 362; Eilsart, *J.* 1885. 457).—6. *Potassium* burns when heated in SO_2, giving K_2SO_4, $K_2S_2O_3$, and polysulphides.—7. Many other *metals*, especially when in fine powder, burn in SO_2; Sb and Sn form oxides and sulphides; Fe, sulphide and sulphate; Pd and Pt, sulphides and SO_3; Au, S and SO_3; Mg, sulphate, sulphite, and sulphide; Al, Co, Ni, and Zn also burn; Bi and Hg do not react (Schiff, *A.* 67, 94; 117, 92; Uhl, *B.* 23, 2151).—8. *Water* dissolves SO_2, forming H_2SO_3Aq (*v.* Sulphurous acid, p. 614). 9. Several *metallic peroxides* combine readily with SO_2, forming sulphates; *e.g.* $PbO_2 + SO_2 = PbSO_4$; in this reaction much heat is produced.—10. *Nitrogen dioxide* is said to react with liquid SO_2 to form *nitrosulphonic anhydride* $S_2O_5(NO_2)_2$ (*v.* p. 601). With *nitric oxide* or *dioxide, in presence of water, nitrosulphonic acid* $NO_2(SO_2.OH)$ (*q.v.*, p. 601) is formed. *Nitric oxide in presence of alkali* produces salts of $SO_2.OH(NO)_2.H$ (*v.* Nitrososulphates, p. 581).—11. *Selenion dioxide* does not react with SO_2 (Schulze, *J. pr.* [2] 32, 390).—12. Dry *hydrogen sulphide* does not react; moist H_2S, at the ordinary temperature, produces $H_2S_5O_6$, S, and H_2O (Cluzel a. Schmid, *Chem. Zeitung,* 11, 50); there is said to be no reaction in presence of water above 400° (Mulder, *J.* 1858. 84).—13. *Phosphoretted hydrogen* reacts at the ordinary temperature to form H_2O and P_2S_5 (C. a. S., *l.c.*).—14. *Ammonia* combines with SO_2 probably producing $SO_2.NH_3$ ($= SO.OH.NH_2$) and $SO_2.2NH_3$ ($= SO.ONH_4.NH_2$) (*v.* Thionamic acid).—15. *Hydrochloric* or *hydriodic acid* produces H_2O, S, and Cl or I.—16. Many *oxy-salts, e.g.* nitrates and chlorates, react with SO_2, when heated, to form sulphates and N oxides; at higher temperatures SO_3 is sometimes produced (*v.* Hodgkinson a. Young, *C. N.* 66, 199).—17. *Alkali nitrites* yield salts of *nitrilosulphonic acid* $N(SO_2.OH)_3$ (*q.v.*, p. 601), and salts of *oxy-imidosulphonic acid* $N(OH)(SO_2.OH)_2$ (*q.v.*, p. 602).—18. Combines with *aluminium chloride* at 50°–60°, forming $AlCl_3.SO_2$, which gives off SO_2 at a higher temperature (Adrianoffski, *B.* 12, 688).—19. *Phosphorus pentachloride* produces $POCl_3$ and $SOCl_2$ (Kremers, *A.* 70, 297; Schiff, *A.* 102, 111).

Sulphur trioxide SO_3. (*Sulphuric oxide. Sulphuric anhydride.*) Mol. w. 79·86. Melts at 14·8° (Weber, *B.* 19, 3189; Rebs, *A.* 246, 356). Some other observers have given m.p. as high as 29·5° (*v.* Buff, *A. Suppl.* 4, 129; Bussy, *A. Ch.* [2] 26, 411; Fischer, *P.* 16, 119; Marignac, *A.* 88, 230). Boils at 46·2° (Weber, *l.c.*; *v.* also Buff, *l.c.*; Fischer, *l.c.*; Schultz-Sellack, *P.* 139, 480). S.G. 1·94 at 16° (Weber, *l.c.*); 1·97 at 20° (Bussy, *l.c.*); 1·9086 at 25° (Buff, *l.c.*). V.D. 39·78 (Schultz-Sellack, *P.* 139, 480; Perman, *Pr.* 48, 45). H.F. $[S,O^3] = 103,240$ (liquid SO_3 from solid S; *Th.* 2, 254); $[SO^2, O] = 32,160$ (liquid SO_3 from gaseous SO_2; *Th., l.c.*); $[SO^3, Aq] = 39,170$ (liquid SO_3; *Th., l.c.*). For heat of vaporisation *v.* Berthelot (*C. R.* 90, 1510). Schultz-Sellack gives vapour-pressure at 20° as 152 mm. Hg (*P.* 139, 480).

Formation.—1. By the interaction of ozone and SO_2. Also by the action of an induction current on a mixture of SO_2 and O_2 (Buff a. Hofmann, *A.* 113, 129; Deville, *Bl.* [2] 3, 366); Berthelot (*C. R.* 86, 20) says that the product is S_2O_7.—2. By burning S in O under a pressure of several atmos. (*v.* Sulphur dioxide, *Formation* No. 1). Also by heating pyrites (Scheurer-Kestner, *C. R.* 99, 917; Lunge, *B.* 10, 1824).—3. By passing a mixture of SO_2 and O over heated Pt (Phillips a. Magnus, *P.* 24, 610), spongy Pt (Hodgkinson a. Lowndes, *C. N.* 57, 193), or certain oxides, *e.g.* Fe_2O_3, CuO, Cr_2O_3 (Mahla a. Wöhler, *A.* 81, 255).—4. By heating certain sulphates or bisulphates, *e.g.* $Fe_2(SO_4)_3$, $Bi_2(SO_4)_3$, Ag_2SO_4, or $NaHSO_4$.—5. By distilling Nordhausen sulphuric acid (*v.* Osann, *D. P. J.* 151, 158); also by heating conc. H_2SO_4 with P_2O_5 (Barreswil, *C. R.* 25, 30; Evans, *Ph.* 8, 127).

Preparation.—1. Fuming sulphuric acid is heated at as low a temperature as possible; the impure SO_3 is collected in a dry retort and redistilled once or twice, the most volatile portion being collected each time. The partially purified SO_3 is then distilled into a small tube, c. 8–10 mm. wide and about the length of a finger, containing some dry P_2O_5; this tube is narrowed at one end and fused on to a thick-walled tube c. 1–1·5 mm. wide, which is bent round and fused to a receiving tube c. 12–15 mm. wide and 300 mm. long; the tube containing the SO_3 and P_2O_5 is heated in a water-bath to 90°–100° for 6 or 8 hours, the receiving tube projecting upwards, so that the distillate flows back again into the distilling-tube. The position of the apparatus is then changed, so that the receiving tube is lower than the distilling tube, and the SO_3 is distilled from the P_2O_5 on a water-bath. When sufficient SO_3 has been collected, the narrow connecting tube is fused off, and the SO_3 is kept in the sealed receiving tube (Weber, *B.* 19, 3189).—

2. A mixture of SO_2 and O, in the ratio SO_2:O, is passed over platinised asbestos heated nearly to redness; the SO_3 is condensed in a small dry tube, in which it is sealed up. The mixture of SO_2 and O is obtained by strongly heating conc. H_2SO_4 and removing H_2O ($H_2SO_4 = H_2O + SO_2 + O$) by cooling and passing through coke moistened with 60 p.c. H_2SO_4Aq (Winkler, *D. P. J.* 218, 128). The asbestos is platinised by soaking in $PtCl_4$Aq made alkaline by soda, and mixed with sufficient HCO_2Na to reduce the Pt, drying at 100°, carefully washing out the salts with water, and drying (Thomsen, *B.* 3, 496). The SO_3 thus obtained is not quite pure. It may be purified by distillation with P_2O_5 (*v. supra*).

Properties.—A colourless, mobile liquid, solidifying at c. 15° to long, prismatic, transparent crystals, which melt at 14·8°. According to some observers (*v.* Marignac, *Ar. Ph.* 22, 225; 58, 228; Schultz-Sellack, *P.* 139, 480) the crystals of SO_3 slowly change to a mass of tough, opaque, lustrous needles, which melt above 50°, and constitute a distinct modification of SO_3; but the experiments of Weber (*P.* 139, 480; *B.* 19, 3187; *cf.* Rebs, *A.* 246, 356) have shown that pure SO_3 exists only in one form, and that the substance with higher m.p. is formed by the action of traces of H_2SO_4 in the SO_3; a small trace of moisture suffices to cause the gradual change. SO_3 is very acrid and poisonous; it chars paper, wood, and organic matter generally. SO_3 is extremely hygroscopic; it dissolves in water with a hissing sound and production of much heat ([SO^3,Aq] = 39, 170), forming H_2SO_4Aq. Non-conductor of electricity (Magnus, *P.* 104, 553); not decomposed by electric sparks, but by passing through a red-hot tube gives SO_2 and O. SO_3 does not redden dry litmus. It is a strongly acid-forming oxide (*v.* Sulphuric acid).

Reactions and Combinations.—1. *Heated to redness* (by passing through red-hot tube) gives $SO_2 + O$.—2. Not decomposed by *electric sparks* (Magnus, *P.* 104, 553); *electrolysis* of SO_3 in H_2SO_4 causes separation of S and O, and the solution becomes blue (Geuther, *A.* 109, 129).—3. *Water* reacts violently with SO_3 forming H_2SO_4Aq (*v.* Sulphuric acid).—4. *Hydrogen sulphide* produces H_2SO_4 and S.—5. A mixture of SO_3 and *oxygen*, in the ratio $2SO_3$:O, forms S_2O_7 when submitted to the *silent electric discharge* (Berthelot, *A. Ch.* [5] 14, 345).—6. *Sulphur* dissolves in SO_3 forming S_2O_3; *selenion* and *tellurium* react similarly (*v.* Sulphur thio-oxide, Selenion thio-oxide, and tellurium thio-oxide).—7. *Phosphorus* ignites in vapour of SO_3, forming P_2O_5 and S.—8. *Iodine* dissolves in SO_3, apparently forming several compounds (*v.* Wach, *S.* 50, 37; Schultz-Sellack, *B.* 4, 109), Weber (*J. pr.* [2] 25, 224) describes the compounds $I(SO_3)_3$, $I(SO_3)$, and $I_2(SO_3)$.—9. *Iron* and *zinc* react at red heat to give sulphides and oxides; *mercury* produces sulphate and SO_2 (d'Heureuse, *P.* 75, 255).—10. Several *metallic sulphides*—*e.g.* of Sb, Pb, K—form sulphates and SO_2 when heated with SO_3 (Weber, *P.* 130, 329).—11. Dry *sulphur dioxide* is absorbed by SO_3 at 0°, forming a thin, fuming liquid, approximately $SO_3.2SO_2$ (H. Rose, *P.* 89, 173). According to Schultz-Sellack, liquid SO_2 and SO_3 are miscible in all proportions (*P.* 139, 480). 12. *Selenion dioxide* combines to form $SO_3.SeO_2$ (*v.* Selenion dioxide, *Combinations*, No. 4, p. 441).—13. *Nitric oxide*, in absence of moisture and O, forms $S_2O_9N_2$, which is generally called *nitrosulphonic anhydride* (*q. v.*, p. 601) and written $S_2O_5(NO_2)_2$. *Nitrogen dioxide* (made by heating $Pb(NO_3)_2$) seems to form $SO_3.NO_2$, and on heating this and passing in more NO_2, O is given off and the compound $S_2O_9N_2$ remains (*v.* Weber, *P.* 123, 337; Brüning, *A.* 98, 377). The formula of the first of these compounds is generally doubled, and the compound regarded as $S_2O_5.O.(NO_2)_2$ = *oxynitrosulphonic anhydride* (*q. v.*, p. 601); the second is described in some books as $S_2O_7(NO)_2$ and is called *nitrosyl pyrosulphate*, but from the descriptions of Weber and Brüning it is evidently the same as the compound $S_2O_9N_2$ formed from NO and SO_3, *i.e.* it is *nitrosulphonic anhydride.*—14. SO_3 combines with *iodine pentoxide* to form $3SO_3.I_2O_5$ and $SO_3.5I_2O_5$ (Weber, *B.* 20, 86; Kämmerer, *J. pr.* 83, 72). With *phosphorus pentoxide* $3SO_3.P_2O_5$, decomposing at 30°, is formed (Weber, *B.* 19, 3185; 20, 86). *Arsenious oxide* forms various unstable compounds (Adie, *C. J.* 55, 157; *cf.* Weber, *B.* 19, 3185; Schultz-Sellack, *B.* 4, 109; Reich, *J. pr.* 90, 176; Schafhaütl, *B. J.* 22, 113; and Pearce, *Z. K.* 20, 632). According to Baker (*C. J. Proc.* 1893. 130), dry SO_3 does not react with *dry oxides of barium, calcium, or copper.*—15. The compound $SO_3.N_2O_5.5H_2SO_4$ is said to be formed by passing SO_3 into pure, well-cooled, *nitric acid* (Weber, *P.* 123, 233; 142, 602).—16. *Boric acid* forms $BH_3O_3.3SO_3$ [$= B(HSO_4)_3$] (D'Arcy, *C. J.* 55, 155; *cf.* Merz, *J. pr.* 99, 81; Schultz-Sellack, *B.* 4, 15).—17. *Hydrobromic* and *hydriodic acids* separate Br, and I, and form H_2SO_4 and SO_2.—18. *Hydrochloric* and *hydrofluoric acids* form $Cl(SO_2.OH)$ and $F(SO_2.OH)$ (*v.* Chlorosulphonic acid, p. 599; and Fluosulphonic acid, p. 600). 19. *Conc. sulphuric acid* forms $H_2S_2O_7$ (*v.* Pyrosulphuric acid, p. 625).—20. *Ammonia* produces $NH_2(SO_2.OH)$ and salts of this acid (*v.* Sulphamic acid and salts, p. 567); and also salts of $NH(SO_2.OH)_2$ (*v.* Imidosulphonic acid and salts, p. 600).—21. *Phosphoretted hydrogen* produces SO_2 and red P (H. Rose, *P.* 24, 140; Aimé, *J. pr.* 6, 79).—22. *Phosphorus trichloride* reacts violently, forming $POCl_3$ and SO_2 (Armstrong, *B.* 3, 732; Michaelis, *J. Z.* 6, 239). *Phosphorus pentachloride* produces *pyrosulphuryl chloride* $S_2O_5Cl_2$ (*q. v.* under Sulphur oxychlorides, p. 617).—23. *Boron chloride* reacts at c. 120° to form $S_2O_5Cl_2$ (Prudhomme, *Bl.* [2] 14, 385).—24. *Nitrosyl chloride* (produced by heating *aqua regia*) produces $SO_3.NOCl$ $= NO_2(SO_2Cl)$ (*v.* Nitrosulphonic chloride, p. 601). — 25. *Pyrosulphuryl bromide* $S_2O_5Br_2$ (*q. v.*, p. 617) is perhaps formed by the reaction of *bromoform* with SO_3.—26. *Selenion tetrachloride* produces $SSeO_5Cl_4$ (*v.* Selenion thio-oxychloride, p. 441).

Sulphuric peroxide S_2O_7. (*Sulphur heptoxide. Persulphuric anhydride.*) Mol. w. not known with certainty but probably 175·68 (S_2O_7). This oxide was prepared by Berthelot in 1877 (*A. Ch.* [5] 14, 345) by passing the 'silent' electric discharge, for several hours, through a mixture of SO_3 and O in the ratio $2SO_3$:O, or of SO_2 and O in the ratio $2SO_2$:3O. (For apparatus used *v.* B., *A. Ch.* [5] 12, 463.) Oily drops formed on the sides of the tube, and on reducing the temperature nearly to 0° they solidified to long, white, crystalline, needles. S_2O_7 resembles solid SO_3 in appearance; it remains unchanged in a sealed tube for some days at 0°; when heated it gives SO_3 and O; dissolves in conc. H_2SO_4 forming a fairly stable solution; fumes in the air; in water it rapidly decomposes forming H_2SO_4Aq and giving off a brisk stream of O; with BaOAq forms $BaSO_4$ and O; and also some Ba persulphate, according to Berthelot (*l.c.*; no analyses given). By electrolysing H_2SO_4Aq, containing water and acid in the ratio $10H_2O:H_2SO_4$, B. (*C. R.* 90, 269) obtained a quantity of persulphuric acid ($H_2S_2O_8$; *v.* under SULPHURIC ACID, p. 625) equal to from 88 to 123 g. S_2O_7 per litre; using an acid of the concentration $H_2SO_4:2H_2O$ to $H_2SO_4:3H_2O$, B. (*l.c.*) says that a compound $S_2O_7.2H_2O_2$ is formed, which is decomposed by excess of conc. H_2SO_4 chiefly to $H_2S_2O_8$, and by dilution with water to $H_2S_2O_8Aq$ and H_2O_2Aq which after a time decompose to H_2SO_4Aq, H_2O, and O.

S_2O_7 is the anhydride of *persulphuric acid* $H_2S_2O_8$ (*q. v.*, p. 625). Mendeléeff (*B.* 15, 242) regards S_2O_7 as analogous in constitution to H_2O_2, and writes the formula $\left.\begin{array}{l}OSO_2\\ |\\ OSO_2\end{array}\right>O$; he looks on the corresponding acid as derived from H_2O_2 by replacing 2H by $2SO_2OH$, thus:

$$\begin{array}{l}O.(SO_2.OH)\\ |\\ O.(SO_2.OH)\end{array}$$

According to Traube (*B.* 22, 1518; 24, 1764; 25, 95), the liquid obtained by electrolysing 40 p.c. H_2SO_4Aq contains an oxide to which he gives the formula SO_4 and calls *sulphuryl hyperoxide* (or *holoxide*), $SO_2.O_2$. Traube did not isolate this compound; his argument for its existence is based on the results of indirect analyses. In the light of the criticisms of Carnegie (*C. N.* 64, 158) it may be concluded that the existence of SO_4 is extremely improbable. In a later communication (*B.* 26, 1481) Traube thinks it is probable that SO_4 does not exist.

Sulphur, oxyacids of. For compositions of these acids, and references to articles where they are described, *v.* SULPHUR, OXYACIDS OF (p. 619).

Sulphur, oxyacids of, nitrogen derivatives of. For a general statement regarding these compounds, and references to the articles where they are described, *v.* SULPHUR OXYACIDS, NITROGEN DERIVATIVES OF (p. 619).

Sulphur, oxybromides of. There is very little definite knowledge regarding the compounds of S, O, and Br. According to Michaelis (*J. Z.* 6, 239, 296) PBr_5 does not react with SO_2, and a mixture of PCl_3 and Br (in the ratio PCl_3Br_2) produces $POCl_3$ and S bromides. Rose (*P.* 44, 327) and Clausnizer (*B.* 11, 2012) could not obtain an oxybromide by the reaction of SO_3 and S bromide, nor by the action of SO_2 and HBr.

In his memoir on $S_2O_5Cl_2$ prepared by the reaction of SO_3 with $CHCl_3$, Armstrong (*B.* 2, 712) states that $CHBr_3$ reacts with SO_3 similarly to $CHCl_3$, but he does not describe the product. If the reaction of $CHBr_3$ with SO_3 is strictly similar to that of $CHCl_3$ the product would be *pyrosulphuryl bromide* $S_2O_5Br_2$.

Odling (*C. J.* 7, 2) supposed that *sulphuryl oxy-bromide* SO_2Br_2 was formed by the action of sunlight on SO_2 and Br, but Sestini (*Bl.* [2] 10, 226) and Melsens (*C. R.* 76, 92) failed to obtain an oxybromide by this method.

THIONYL BROMIDE $SOBr_2$. This compound was obtained, but not quite free from S bromides, by Hartog a. Sims (*C. J. Proc.* No. 118, 1893. 10) by the interaction of $SOCl_2$ and NaBr; it is described as a very hygroscopic, crimson liquid, S.G. 2·68 at 18°, decomposing at 150° to Br, S bromides, &c.

Sulphur, oxychlorides of. Five compounds have been isolated, $SOCl_2$, SO_2Cl_2, $S_2O_5Cl_2$, S_2OCl_4, and $S_2O_3Cl_4$.

THIONYL CHLORIDE $SOCl_2$ (*Sulphurous oxy chloride*). Mol. w. 118·62. Boils at 78·8°; S.G. $\frac{0°}{4°}$ 1·67673, S.G. at b.p. 1·52143 (Thorpe, *C. J.* 37, 354; for other data *v.* Carius, *A.* 106, 303; 111, 93; Wurtz, *C. R.* 62, 460). V.D. at c. 150° = 56, at c. 440° = 39 (Heumann a. Köchlin, *B.* 16, 1625). H.F. $[S,O,Cl^2]$ = 40,800; heat of vaporisation = 6,480 (Ogier, *C. R.* 94, 82). S.V. 78·01 (Thorpe, *l.c.*).

Formation.—1. By the reaction of PCl_5 with SO_2 (Kremers, *A.* 70, 297; Schiff, *A.* 102, 111), SO_2Cl_2, $C_6H_5.SO_2Cl$, and several other organic compounds containing S (*v.* Kekulé a. Barbaglia, *B.* 5, 875; Carius, *J. pr.* [2] 2, 262), sulphites, or thiosulphates; also by the reaction of $POCl_3$ with sulphates.—2. By the action of Cl_2O on CS_2, or on S in S_2Cl_2 at −12° (Wurtz, *C. R.* 62, 460).—3. By the interaction of SO_3 and SCl_4 (Michaelis a. Schifferdecker, *B.* 5, 924; 6, 993).—4. Along with SO_2Cl_2 by the gradual decomposition of $S_2O_3Cl_4$ (*q. v.*, p. 619).

Preparation.—1. About 100 g. dry PCl_5 are placed in a retort connected with a reversed condenser, and a stream of dry SO_2 is led in till the PCl_5 has liquefied; another 100 g. PCl_5 is added and the stream of SO_2 is continued; when sufficient PCl_5 has thus been decomposed ($PCl_5 + SO_2 = SOCl_2 + POCl_3$) the liquid is heated for some time (the reversed condenser being still attached) to get rid of SO_2, and then fractionated repeatedly ($SOCl_2$ boils at 78·8° and $POCl_3$ at 107·2°) (Carius, *A.* 106, 303; 111, 93; Wurtz, *A.* 139, 375; Michaelis, *A.* 170, 1; Thorpe, *C. J.* 37, 354).—2. S_2Cl_2 is placed in a small flask, cooled to c. −20°, a stream of dry Cl is led in till the liquid is saturated, and then SO_3 is distilled into the flask from a solution in conc. H_2SO_4; the weights of S_2Cl_2 and SO_3 used should be in the ratio $S_2Cl_2:4SO_3$ (= 1:2·37); convenient quantities to use are 22 g. S_2Cl_2 and 50 g. SO_3. ($SCl_4 + 2SO_3 = SOCl_2 + S_2O_5Cl_2$). The liquid is fractionated finally from a small quantity of SO_3 (Michaelis a. Schifferdecker, *B.* 5, 924; 6, 993).

Properties.—A colourless, very refractive liquid, fuming in the air, with a very penetrating odour; vapour attacks the eyes and respiratory organs. V.D. 56 at c. 150°, but 39 at c. 440°; the smaller value corresponds with the decomposition $4SOCl_2 = S_2Cl_2 + 2SO_2 + 3Cl_2$; these products are obtained by passing vapour of $SOCl_2$ through a red-hot tube (Heumann a. Köchlin, *B.* 16, 1625).

Reactions and Combinations.—1. *Moist air* produces HCl and SO_2.—2. *Water* also forms HClAq and SO_2, warm water forming in addition H_2SO_4Aq and S (Carius, *l.c.*).—3. *Hydrogen sulphide* produces SO_2, HCl, and S (Prinz, *A.* 223, 371).—4. *Phosphorus pentasulphide* reacts to form SO_2, $PSCl_3$, and S, and some S_2Cl_2 (Prinz, *l.c.*).—5. With *antimony trisulphide* the products are $SbCl_3$, SO_2, and S.—6. *Sulphur*, heated to 180° with $SOCl_2$, forms S_2Cl_2 and SO_2; *selenion* forms S_2Cl_2 and $SSeCl_2$ (Prinz, *l.c.*).—7. Powdered *antimony* reacts without heating, forming $SbCl_3$, Sb_2S_3, and SO_2.—8. $POCl_3$, $PSCl_3$ and PCl_5 are formed by heating $SOCl_2$ with *phosphorus trichloride* (Michaelis, *J. Z.* 6, 239).—9. Heating with *sulphur dichloride* produces S_2OCl_4 (*q. v.*, p. 619) (Ogier, *Bl.* [2] 37, 293).—10. *Ammonia* does *not* produce thionylamide $SO(NH_2)_2$, but forms NS, NH_4Cl, $(NH_4)_2SO_3$, and NH_4 polythionates (M., *l.c.*).—11. Reacts rapidly with *silver nitrate*, forming $NO_2(SO_2.Cl)$ (Thorpe, *C. J.* 41, 297).—12. $SOCl_2$ absorbs *sulphur dioxide* and *chlorine* freely (M., *l.c.*).—13. For reactions with various *organic compounds v.* Michaelis (*l.c.*); Heumann a. Köchlin (*B.* 16, 1625); Böttinger (*B.* 11, 1407).

SULPHURYL CHLORIDE SO_2Cl_2 (*Sulphuric oxychloride*). Mol. w. 134·58. Boils at 69·95° (Thorpe, *C. J.* 37, 359; for other determinations *v.* Regnault, *J. pr.* 19, 243; Clausnizer, *B.* 11, 2010; Ogier, *C. R.* 94, 82). S.G. $\frac{0^{\circ}}{4^{\circ}}$ 1·70814; at b.p. 1·56025 (Thorpe, *l.c.*). V.D. 65 at 184°; 34 at 440° (Heumann a. Köchlin, *B.* 16, 602; *cf.* Regnault, *J. pr.* 18, 97; Behrend, *J. pr.* [2] 15, 23). S.V. 86·29 (Thorpe, *l.c.*, p. 372). H.F. $[S,O^2,Cl^2]=89{,}780$; $[SO^2,Cl^2]=18{,}700$ (*Th.* 2, 310; *cf.* Ogier, *C. R.* 94, 82). S.H. (15°–63°) ·233 (Ogier, *l.c.*). Heat of vaporisation 7,060 (O., *l.c.*).

Formation.—1. By the direct combination of SO_2 and Cl in sunlight, or by reacting on a mixture of C_2H_4 and SO_2 by Cl in sunlight (Regnault, *J. pr.* 18, 93; 19, 243). Schulze (*J. pr.* [2] 23, 351; 24, 168) recommends to allow SO_2 and Cl to react in presence of camphor. Melsens (*C. R.* 76, 92) passes SO_2 and Cl into glacial acetic acid.—2. By passing SO_3 over charcoal saturated with Cl (M., *l.c.*).—3. By the interaction of PCl_5 with H_2SO_4 or SO_3 (Williamson, *P. M.* [4] 7, 365; Schiff, *A.* 102, 111); according to Michaelis (*J. Z.* 6, 233, 292), SO_3 and PCl_5 form $S_2O_5Cl_2$.—4. By heating SO_3 and BCl_3, in the ratio $2SO_3:BCl_3$, to 120° in a closed tube (Gustavson, *B.* 6, 9).—5. By heating $Cl(SO_2.OH)$ to c. 200° for some time (Behrend, *B.* 8, 1004; *cf.* Otto a. Beckurts, *B.* 11, 2058).

Preparation.—1. Cl and SO_2 are passed into camphor, and the colourless liquid is fractionated (Schulze, *l.c.*).—2. $Cl(SO_2.OH)$ (*v.* CHLOROSULPHONIC ACID, p. 509) is heated to c. 200°, in a closed tube, for some hours, when it decomposes thus, $2[Cl(SO_2.OH)]=SO_2Cl_2+H_2SO_4$; the liquid is distilled, the portion coming over at 67°–71° being collected separately and then repeatedly fractionated (Behrend, *l.c.*; *cf.* Thorpe, *l.c.*).

Properties and Reactions.—A colourless liquid, fuming slightly in air. 1. Decomposed by *heating* to dull redness into SO_2 and Cl; decomposition is complete at 440° (Heumann a. Köchlin, *B.* 16, 602); but does not begin at 250° (Beckurts a. Otto, *B.* 11, 2060).—2. *Water* produces HClAq and H_2SO_4Aq; a small quantity of water is said to form $Cl(SO_2.OH)Aq$.—3. Excess of SO_2Cl_2 added to a little *alcohol* forms $Cl(SO_2.OEt)$; with excess of alcohol $SO_2(OEt)_2$ is produced (Behrend, *B.* 9, 1334).—4. *Phosphorus pentachloride* reacts to form $POCl_3$, $SOCl_2$, and Cl (H. a. K., *B.* 15, 1736).—5. *Phosphorus*, *arsenic*, and *antimony* produce PCl_3, $AsCl_3$, and $SbCl_3$ respectively, and SO_2 (H. a. K., *l.c.*).—6. *Ammonia* forms NH_4Cl and $SO_2.NH_2.ONH_4$.—7. With many *organic compounds* SO_2Cl_2 reacts like PCl_5 or $POCl_3$, substituting Cl for H (*v.* Dubois, *Z.* [2] 2, 705; Michaelis, *A.* 170, 1).

PYROSULPHURYL CHLORIDE $S_2O_5Cl_2=Cl.SO_2.O.SO_2.Cl$. (*Disulphuryl chloride. Pyrosulphuric oxychloride. Chlorosulphonic anhydride.*) Mol. w. 214·38. Boils at 139·59° (Thorpe, *C. J.* 37, 360; for other determinations *v.* Rose, *P.* 44, 291; Michaelis, *J. Z.* 6, 235, 240, 292; Rosenstiehl, *C. R.* 53, 658; Schützenberger, *C. R.* 69, 352). S.G. $\frac{0^{\circ}}{4^{\circ}}$ 1·85846, at b.p. 1·60610 (Thorpe, *l.c.*). V.D. at slightly above b.p. = 104; between 160° and 240° = 54·8 (Heumann a. Köchlin, *B.* 16, 479; Kanowaloff, *B.* 16, 1127; *cf.* Rosenstiehl, *C. R.* 53, 658; Rose, *P.* 44, 291; Ogier, *C. R.* 94, 82, 217; 96, 648). H.F. $[S^2,O^5,Cl^2]=180{,}600$ (Kanowaloff, *l.c.*); Ogier (*l.c.*) gives 159,400. Heat of vaporisation 7,570 (K., *l.c.*); 13,160 (O., *l.c.*). S.H. ·258 (K., *l.c.*).

Formation.—1. By the interaction of PCl_5 and SO_3 or $Cl(SO_2.OH)$.—2. By heating P_2O_5 and $Cl(SO_2.OH)$ (Billitz a. Heumann, *B.* 16, 483).—3. By heating SO_3 with NaCl (R., *l.c.*), with S_2Cl_2 (Rose, *P.* 44, 291), with CCl_4 (Schützenberger, *C. R.* 69, 352; Kanowaloff, *C. R.* 95, 1284), with C_2Cl_6 (Prudhomme, *C. R.* 70, 1137), with $CHCl_3$ (Armstrong, *C. J.* [2] 1, 244), or with $SiCl_4$ (Gustavson, *B.* 5, 332).—4. By the interaction of $POCl_3$ and $SOCl_2$ (Michaelis, *J. Z.* 6, 235, 240, 292).

Preparation.—1. P_2O_5 and $Cl(SO_2.OH)$ are heated in a flask with a reversed condenser, using rather more $Cl(SO_2.OH)$ than P_2O_5; when HCl and SO_2 cease to be given off, the liquid is distilled, and the portion coming over between 135° and 145° is fractionated (B. a. H., *l.c.*).—2. S_2Cl_2 in a flask is surrounded by a freezing mixture, and saturated with SO_3; the product is fractionated; $5SO_3+S_2Cl_2=5SO_2+S_2O_5Cl_2$ (Rose, *P.* 44, 291). Thorpe (*C. J.* 37, 360) found that the product of this reaction boiled almost wholly between 135° and 138°.

Properties and Reactions.—A colourless, mobile, very refractive liquid, fuming in the air with formation of $Cl(SO_2.OH)$.—1. Decomposed by *heat* to SO_3, SO_2, and Cl (Rose, *P.* 44, 291); the V.D. determinations of Heumann a. Köchlin (*B.* 16, 479) show that at 440° the decomposition is $S_2O_5Cl_2=SO_3+SO_2+Cl_2$.—2. Sinks in *water*, and is slowly decomposed to HClAq and H_2SO_4Aq; if a very little water is used $Cl(SO_2.OH)$ is formed, thus $S_2O_5Cl_2+H_2O=2Cl(SO_2.OH)$ (*v.* B. a. H., *l.c.*)—3. Reacts with *phosphorus*, *sulphur*, *antimony*, *copper*, *iron*, *zinc*, and some other *metals*, to produce chlorides, SO_3 and SO_2 (Heumann a. Köchlin, *B.* 16, 479).—4. *Phosphorus trichloride* produces

PCl_3, $POCl_3$, and SO_2; *phosphorus pentachloride* forms $POCl_3$, Cl, and SO_2 (Geuther, *B.* 5, 925). 5. *Selenion tetrachloride* gives $SSeO_3Cl_4$ (Clausnizer, *B.* 11, 2010).—6. *Chromates* react to form CrO_2Cl_2 (Rosenstiehl, *C. R.* 53, 658).—7. *Ammonia* forms a white solid, which dissolves in water, producing NH_4Cl and a sulphamate of NH_4 (Rose, *l.c.*).

Sulphur monoxytetrachloride S_2OCl_4. By heating equal weights of S_2Cl_2 and SO_2Cl_2 to 250° in a sealed tube, Ogier (*Bl.* [2] 37, 293) obtained a deep-red liquid resembling S_2Cl_2, S.G. 1·656 at 0°, decomposing under 100° to S_2Cl_2, SO_2, and S, to which he gave the composition S_2OCl_4. Decomposed by water to H_2SO_4Aq, SO_2Aq, HClAq, thionic acids, and S.

Sulphur tri-oxytetrachloride $S_2O_3Cl_4$. Mol. w. not determined. This compound was obtained by Millon (*A. Ch.* [3] 29, 327) by the action of moist Cl on S_2Cl_2 (*cf.* Marchand, *J. pr.* 22, 507; Carius, *A.* 106, 295). It is conveniently prepared by the reaction $SCl_4 + Cl(SO_2.OH) = HCl + S_2O_3Cl_4$; a stream of dry Cl is led into a mixture, in the ratio of equal numbers of molecules, of S_2Cl_2 and $Cl(SO_2.OH)$, kept at c. −20°, until a semi-solid mass is obtained (a very wide tube must be used to lead in Cl); the temperature is then kept at c. −13° and the Cl is continued till the mass gets quite solid; the freezing mixture is then removed, and the Cl is continued till the mass is white, when the excess of Cl is removed by a stream of dry CO_2 (Michaelis a. Schifferdecker, *B.* 6, 996).

$S_2O_3Cl_4$ is a white, crystalline solid, with a most disagreeable odour; the vapour acts on the eyes. Melts at 57°, giving off SO_2 and Cl, and leaving a liquid that solidifies chiefly to $SOCl_2$ and $S_2O_5Cl_2$; a portion sublimes in fine white needles. Ice-cold water produces SO_2Aq, H_2SO_4Aq, and HClAq; water at the ordinary temperature also separates S. Deliquesces in a partially closed vessel, giving off HCl, Cl, and SO_2, and leaving a liquid that gives $SOCl_2$ and $S_2O_5Cl_2$ on distillation. Conc. H_2SO_4 reacts violently, forming HCl, SO_2, and $Cl(SO_2.OH)$; CS_2 produces very rapid decomposition to $COCl_2$, CO, SO_2, S_2Cl_2, and $SOCl_2$. On long standing in a closed tube $S_2O_3Cl_4$ separates into equal numbers of molecules of $SOCl_2$ and SO_2Cl_2 (M. a. Mathias, *B.* 6, 1452).

Sulphur, phosphides of, *v.* Phosphorus sulphides, p. 145.

Sulphur, selenides of, *v.* Selenion sulphides, p. 442.

Sulphur, silicides of, *v.* Silicon sulphides, p. 462.

Sulphur, tellurides of, *v.* Tellurium sulphides, p. 655. M. M. P. M.

SULPHUR, OXYACIDS OF. Several acids have been isolated, and salts of some others are known. The following list gives the names and compositions of the oxyacids of sulphur and their salts, with references to the articles where these compounds are described:—

Hyposulphurous acid and salts $H_2S_2O_4$ and $M_2S_2O_4$; *v. Hyposulphurous acid* under Sulphurous acid (p. 627), and *hyposulphites* under Sulphites (p. 592).

Sulphurous acid and salts H_2SO_3, $MHSO_3$, and M_2SO_3; *v.* Sulphurous acid (p. 626), and Sulphites (p. 587).

Sulphuric acid and salts H_2SO_4, $MHSO_4$, and M_2SO_4; *v.* Sulphuric acid (p. 620) and Sulphates (p. 567).

Thiosulphuric acid and salts $H_2S_2O_3$, MHS_2O_3, and $M_2S_2O_3$; *v.* Thiosulphuric acid (p. 708) and Thiosulphates (p. 705).

Thionic acids and salts $H_2S_2O_6$, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$ (and salts); *v.* Thionic acids (p. 698) and Thionates (p. 695).

Pyrosulphuric acid and salts $H_2S_2O_7$, MHS_2O_7, and $M_2S_2O_7$; *v. Pyrosulphuric acid* under Sulphuric acid (p. 625), and *Pyrosulphates* under Sulphates (p. 583).

Persulphuric acid and salts $H_2S_2O_8Aq$, $M_2S_2O_8$, and MS_2O_8; *v. Persulphuric acid* under Sulphuric acid (p. 625), and *Persulphates* under Sulphates (p. 582). M. M. P. M.

SULPHUR OXYACIDS, NITROGEN DERIVATIVES OF. In 1845 Fremy (*A. Ch.* [3] 15, 408) described the K salts of a number of acids obtained by the interaction of KNO_2Aq and K_2SO_3Aq, and by boiling the products of this interaction with slightly acidified water; he called the compounds *salts of sulphazotised acids*. The examination of these salts was prosecuted by Claus a. Koch (*A.* 152, 336 [1874], and by Claus (*A.* 158, 52, 194 [1876]); Berglund (*Bl* [2] 25, 455; *B.* 9, 252, 1896 [1875]); and Raschig (*A.* 241, 161; *B.* 20, 584 [1887]) also investigated the sulphazotised acids of Fremy; and the researches of Divers and Haga (*C. J. Trans.* 1885. 1886. 1889. 1892) have thrown much light on many classes of these compounds. The more recent investigations noted above have shown many of the formulæ given by Fremy to be inaccurate, and they have also led to a considerable revision of Claus's results. As the compounds that have been fairly thoroughly examined are noticed under the heading Sulphonic acids and derivatives (p. 509), it does not seem necessary to give an account of the other *salts of sulphazotised acids*, especially as it is very probable that the formulæ assigned to these compounds will require modification, and that some of the compounds will be found not to exist.

The chief *sulphazotised compounds* that have been investigated sufficiently to establish their composition satisfactorily are the following:—

Amidosulphonic acid and salts $NH_2(SO_2.OH)$; described as Sulphamic acid (p. 567).

Imidosulphonic acid and salts $NH(SO_2.OH)_2$ (p. 600).

Nitrilosulphonates $N(SO_2.OM)_3$ (p. 601).

Nitrosulphonic acid and salts $NO_2(SO_2.OH)$ (p. 601).

Nitrosulphonic anhydride $(NO_2)_2S_2O_5$ (p. 601).

Nitrosulphonic chloride $NO_2(SO_2.Cl)$ (p. 601).

Nitroso-oxy-amidosulphonates $N(NO.OH)(SO_2.OM)$; described as *nitrososulphates* under Sulphates (p. 581).

Oxy-amidosulphonic acid and salts (and salts derived therefrom) $NH(OH)(SO_2.OH)$ (p. 602).

Oxy-imidosulphonates (and salts derived therefrom) $N(OH)(SO_2.OM)_2$ (p. 602).

Oxy-nitrosulphonic anhydride $(NO_2)_2.O.S_2O_2$ (p. 601).

Sulphamide $(NH_2)_2SO_2$ (p. 567).

Sulphimide $NH.SO_2$ (p. 587).

Sulphimido-amide $NH(SO_2.NH_2)_2$ (p. 587).

Thionamic acid and salts $NH_2(SO.OH)$ (p. 695). M. M. P. M.

SULPHURETTED HYDROGEN *v.* HYDROGEN SULPHIDE, vol. ii. p. 725.

SULPHURIC ACID; also **PERSULPHURIC ACID** and **PYROSULPHURIC ACID.**

SULPHURIC ACID H_2SO_4 (*Oil of vitriol*). Mol. w. probably 97·76. Melts at 10·35° (Pickering, *C. J.* 57, 331); 10·5° (Thilo, *Chem. Zeitung*, 16, 1688). Boiling begins at c. 290°, SO_3 and H_2O with some $H_2SO_4.xH_2O$ passing off; b.p. rises till 338° is reached, when it becomes constant and complete dissociation to SO_3 and H_2O occurs; for b.p. of H_2SO_4Aq from 95 to 5 p.c. H_2SO_4 *v.* Lunge (*B.* 11, 370). S.G. $\frac{15°}{15°}$ 1·8884 (Perkin, *C. J.* 63, 59; *cf.* Pickering, *C. J.* 57, 73, *note*; Kohlrausch, *W.* 17, 69; Schertel, *J. pr.* [2] 26, 246; Mendeléeff, *B.* 17, 30, 2536; Lunge a. Isler, *Zeit. für anorg. Chemie*, 1890. 129). V.D. 25 at 440°, corresponding with dissociation to $SO_3 + H_2O$ (Deville a. Troost, *C. R.* 56, 891; Wanklyn a. Robinson, *Pr.* 12, 507). S.H. (22° to 80°) ·355; (22° to 170°) ·37 (Pfaundler, *B.* 3, 798); (16° to 20°) ·3315 (Marignac, *Ar. Sc.* 39, 217, 273). C.E. ·0005585 at 20° (Marignac, *l.c.*). H.F. $[H^2,S,O^4] = 192{,}920$; $[H^2O, SO^3] = 21{,}320$ (formation of liquid H_2SO_4) (*Th.* 2, 255). Heat of fusion = 860 g. units (for 98 g. H_2SO_4) (Berthelot, *C. R.* 78, 716). T. C. *v.* Beetz (*W.* 7, 435), Weber (*J.* 1885. 121). $\frac{\mu-1}{d}$. Mol. w. = 32·45 (Gladstone, *P. M.* [4] 36, 311). For further data *v. infra.*

Occurrence.— Small quantities of H_2SO_4, from ·1 to ·5 p.c., are found in some rivers and springs in volcanic districts; in a pool in Texas, Mallet (*C. N.* 26, 147) found 5·29 g. H_2SO_4 per litre of water. The acid is also found in certain animal secretions; the salivary glands of some molluscs are said to contain c. 2 p.c. (Bödeker a. Troschel, *B. B.* 1854. 486; De Luca a. Panceri, *Bl.* [2] 9, 400; Maly, *M.* 1, 205). The salts of sulphuric acid occur in large quantities (*v.* SULPHATES, p. 567).

Formation.—The formation of an oily liquid by heating alum is spoken of by Geber in the eighth century; a similar liquid was formed in the fifteenth century by burning sulphur with saltpetre. These liquids were shown to be identical towards the end of the sixteenth century. Oil of vitriol seems to have been manufactured in fair quantities by heating ferrous sulphate from about the early part of the eighteenth century; the first manufactory for making the acid from sulphur was started at Richmond by Ward about 1740. The composition of sulphuric acid was determined by Lavoisier.

1. By long exposure of flowers of sulphur in the air (John, *S.* 14, 417; Wagenmann, *P.* 24, 601).—2. By heating S with H_2O to c. 200°; by electrolysing H_2O, using Pt electrodes with pieces of S attached, the H_2SO_4 forms at the positive pole (Becquerel, *C. R.* 56, 237).—3. By the oxidation of S in presence of H_2O by Cl, HNO_3, HCl and $KClO_3$, *aqua regia*, &c.; also by certain metallic salts (*v.* Wicke, *A.* 82, 146; Parkmann, *Am. S.* [2] 33, 328).—4. By oxidising SO_2Aq or SO_2 in presence of water, by Cl, Br, H_2O_2Aq, NO_2, HNO_3, &c.; by passing moist SO_2 and air over hot Pt black (Phillips, *A.* 4, 171), through a red-hot tube containing pieces of glass (Magnus, *P.* 24, 610), or over red-hot sand (Blondeau, *C. R.* 29, 405).—5. By the oxidation of H_2S and polythionic acids (*v.* Cloëz a. Guignet, *C. R.* 46, 1110).—6. By the interaction of water and SO_3, SO_2Cl_2, $SO_2.Cl.OH$, &c.

Preparation.—Commercial oil of vitriol is diluted until the S.G. is 1·53 (= 50° Beaumé, or 106° Twaddell, = 62·5 p.c. H_2SO_4 by weight); the acid is heated to 70°–80°, and $Na_2S_2O_3$ is added in quantity sufficient to decompose the As_2O_3 present (which should be estimated beforehand), according to the equation $3Na_2S_2O_3 + As_2O_3 = 3Na_2SO_4 + As_2S_3$; the acid is stirred until the As_2S_3 separates in flocks (Thorn, *D. P. J.* 217, 495); the acid is filtered from As_2S_3 through asbestos or glass-wool, and is then concentrated by evaporation in a Pt dish till it begins to fume, and then in a retort of Pt or hard glass. The conc. acid is now heated with a little pure $(NH_4)_2SO_4$, whereby HNO_2 and HNO_3 are decomposed ($NH_4.NO_2$ and $NH_4.NO_3$ are formed, and then decomposed to N and H_2O, and N_2O and H_2O). The acid is then distilled from a glass retort, heated by a ring-burner placed around the retort at about two-thirds of the distance from the level of the acid to the bottom of the retort. The distillate is re-distilled in small quantities from a Pt retort into a Pt receiver; the condenser being formed of Pt tubes, soldered with gold and fitting closely one into the other, and the temperature being such that the acid does not boil during the distillation (*cf.* Stas, *Chem. Proport.* 112). Various other methods for removing As have been proposed; for the preparation of H_2SO_4 free from As for chemico-medical use *v.* Bloxam (*C. J.* 15, 52), also Buignet a. Bussy (*J. Ph.* [3] 44, 177; 46, 252).

Commercial oil of vitriol is prepared by passing SO_2, mixed with a little HNO_3, into large leaden chambers into which jets of steam are also sent. The SO_2 is prepared by burning S or pyrites in a stream of air; the hot gas is passed over HNO_3, or over pots containing KNO_3 and H_2SO_4, so that it sweeps into the leaden chambers a certain quantity of HNO_3. The interactions between the hot SO_2 and HNO_3 probably produce NO and N_2O_3 ($3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO$; and also $2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + N_2O_3$); the NO then combines with O in the air of the chambers to form N_2O_3 ($4NO + O_2 = 2N_2O_3$), which interacts with SO_2 and H_2O to produce H_2SO_4 and NO ($N_2O_3 + SO_2 + H_2O = H_2SO_4 + 2NO$):—if N_2O_3 is produced in the primary reaction of SO_2 with HNO_3, this N_2O_3 may take up O to form N_2O_4, which in turn may react with SO_2 and H_2O to produce H_2SO_4 and NO ($N_2O_4 + 2SO_2 + 2H_2O = 2H_2SO_4 + 2NO$). These cycles of changes proceed as long as SO_2 is sent into the chambers, and there is present a sufficiency of O, H_2O, and oxides of N. If there is not sufficient H_2O present to complete the decomposition of N_2O_3 and SO_2 (or N_2O_4 and SO_2) to H_2SO_4 and NO, nitrosulphonic acid—$NO_2(SO_2.OH)$—is formed as a solid on the sides of the chamber ($3N_2O_3 + 2SO_2 + H_2O = 2NO_2(SO_2.OH) + 4NO$; or $3N_2O_4 + 4SO_2 + 2H_2O = 4NO_2(SO_2.OH) + 2NO$);

when steam is now sent into the chamber the nitrosulphonic acid is decomposed to H_2SO_4 and N_2O_3 ($2NO_2(SO_2.OH) + H_2O = 2H_2SO_4 + N_2O_3$). It is possible that the formation of $NO_2(SO_2.OH)$ and the interaction of this with water may form normal stages in the series of reactions that occur in the chambers. Lunge (*C. J.* 47, 465) regards N_2O_3 as the chief carrier of O from the air to the SO_2; he formulates the two main interactions as

(1) $2SO_2 + N_2O_3 + O_2 + H_2O = 2NO_2(SO_2.OH)$,
(2) $2NO_2(SO_2.OH) + H_2O = 2H_2SO_4 + N_2O_3$;

moreover, he insists that the interactions take place for the most part between gases in contact with the surface of the vesicles of liquid water formed by the condensation of the steam sent into the chamber. (A fuller discussion of the reactions that occur in the leaden chambers will be found in the DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 726.)

Some portion of the oxides of N is swept through the chambers and so lost (part of this is recovered in the Gay-Lussac towers); some is lost by leakage, solution in the acid formed in the chambers, and in other mechanical ways; but some portion of the available oxides of N is also destroyed by secondary reactions that occur in the chambers, and result in the formation of N_2O and sometimes of N or NH_3 (*v.* Weber, *P.* 130, 329; Pelouze, *A. Ch.* [2] 60, 162; Lunge, *B.* 14, 2196; *cf.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 729).

Properties.—A clear, colourless, oily, hygroscopic liquid; solidifying at c. 10·5°. The liquid may be cooled much below its freezing-point without solidifying, but addition of a crystal of H_2SO_4 or a small quantity of SO_3 causes crystallisation; the presence of a trace of water lowers the freezing-point to c. 0°. H_2SO_4 is exceedingly acrid and burning, and is a violent poison. H_2SO_4 fumes very slightly in air at the ordinary temperature; at 30°-40° it fumes much, giving off SO_3; according to Colefax (*C. N.* 63, 179), H_2SO_4 is probably slightly volatilised at ordinary temperatures. The mol. w. of H_2SO_4 has not been determined directly, but from the mol. weights of such derivatives as SO_2Cl_2, $SO_2(OMe)_2$, &c., the formula H_2SO_4 is most probably molecular. H_2SO_4 is decomposed when heated, and does not show a definite b.p.; boiling begins at c. 290°, and the temperature gradually rises to 338°, at which temperature dissociation to H_2O and SO_3 is complete. The residue has the composition $H_2SO_4.\frac{1}{12}H_2O$; acid with this composition is obtained by boiling down either $H_2SO_4.xH_2O$ or $H_2SO_4.xSO_3$ (Marignac, *A. Ch.* [3] 39, 184; Dittmar, *C. J.* [2] 7, 446). The sp.gr. of the vapour given off at c. 440° corresponds with that calculated for the dissociation of H_2SO_4 into $SO_3 + H_2O$ (Deville a. Troost, *C. R.* 56, 891; Wanklyn a. Robinson, *Pr.* 12, 507). The b.p. of H_2SO_4Aq, containing from 95 p.c. H_2SO_4 (b.p. = 295°), to 5 p.c. H_2SO_4 (b.p. 101°) is given by Lunge (*B.* 11, 370). H_2SO_4 freezes at 10·352° (*v.* Pickering, *C. J.* 57, 331; where a long series of determinations is given of f.p. of H_2SO_4Aq containing from ·005 to 100 p.c. H_2SO_4). The S.H. and mol. heat (= S.H. × 98) are given by Pfaundler (*B.* 3, 798) as follows:

Temp. interval from 22° to	S.H.	Mol. heat.
80°	·355	34·790
90	·356	34·888
100	·358	35·084
110	·359	35·182
120	·360	35·280
130	·362	35·476
140	·364	35·672
150	·365	35·770
160	·367	35·966
170	·370	36·260

For S.H. of $H_2SO_4.xH_2O$ from 16° to 20°, varying from 0 to 400, *v.* Marignac (*Ar. Sc.* 3 217, 273); Bode (*Zeit. für anorg. Chemie*, 188. 244) gives S.H. of H_2SO_4Aq from S.G. 1·842 to 1·037; Pickering (*C. J.* 57, 160) gives S.H. of H_2SO_4Aq from c. ·2 to c. 12 p.c. H_2SO_4 dissolves in water in all proportions; much heat is produced, and contraction occurs; for thermal measurements *v.* Thomsen (*Th.* 3, 44), Favre a. Silbermann (*C. R.* 24, 1081), F. a. Quaillard (*C. R.* 50, 1150), Pfaundler (*J.* 1869. 122), and, especially, Pickering (*C. J.* 57, 164). According to Pickering (*C. N.* 64, 14), the maximum contraction, calculated for unit weight of solution, changes from 67 p.c. at 8°, to 70·1 p.c. at 38°; but the maximum is constant at 76 p.c., from 8° to 38°, if calculated for unit volume; for fuller data *v.* P. (*C. J.* 57, 148). The expansion of $H_2SO_4.xH_2O$, at 20°, when x varies from 0 to 400, is given by Marignac (*Ar. Sc.* 39, 217, 273). The refractive indices and dispersion of H_2SO_4Aq containing from 93·87 to ·088 p.c. H_2SO_4 are given by Pickering (*C. J.* 63, 99; *cf.* van der Willingen, *Ar. N.* 3, 122). Perkin (*C. J.* 63, 57) gives Mol. R. for H_2SO_4Aq from 99·92 to 9·18 p.c. H_2SO_4 (= from $H_2SO_4 + 53·87\ H_2O$ to $H_2SO_4 + ·004\ H_2O$).

The electrical conductivities of H_2SO_4Aq of different concentrations have been measured by Kohlrausch (*P.* 154, 215; 159; 233; *W.* 6, 1; 17, 69), also by Pickering (*C. J.* 57, 158), who gives determinations for H_2SO_4Aq containing from 1 to 100 p.c. H_2SO_4 (*v.* also Bouty, *C. R.* 108, 393; also Grotrian, *P.* 151, 378).

The S.G. and composition of H_2SO_4Aq of varying concentrations have been determined by many observers. Pickering (*C. J.* 57, 152) gives S.G. and composition of H_2SO_4Aq containing from ·5 to 100 p.c. H_2SO_4 at 0°, 2°, 4°, and each 2° up to 40°. Lunge a. Isler (*Zeit. für anorg. Chemie*, 1890. 129) give the following tables (*cf.* Mendeléeff, *Z. P. C.* 1887. 273; Pickering, *C. N.* 64, 311; Lunge, *C. N.* 65, 13):—

S.G. $\frac{15°}{4°}$ *in vacuo*	Degrees Beaumé	Degrees Twaddell	100 parts by weight contain		1 litre contains kilos.	
			P.c. SO_3	P.c. H_2SO_4	SO_3	H_2SO_4
1·000	0	0	0·07	0·09	0·001	0·001
1·005	0·7	1	0·68	0·83	0·007	0·008
1·010	1·4	2	1·28	1·57	0·013	0·016
1·015	2·1	3	1·88	2·30	0·019	0·023
1·020	2·7	4	2·47	3·03	0·025	0·031
1·025	3·4	5	3·07	3·76	0·032	0·039
1·030	4·1	6	3·67	4·49	0·038	0·046
1·035	4·7	7	4·27	5·23	0·044	0·054
1·040	5·4	8	4·87	5·96	0·051	0·062

S.G. $\frac{15°}{4°}$ *in vacuo*	Degrees Beaumé	Degrees Twaddell	100 parts by weight contain		1 litre contains kilos.	
			P.c. SO_3	P.c. H_2SO_4	SO_3	H_2SO_4
1·045	6·0	9	5·45	6·67	0·057	0·071
1·050	6·7	10	6·02	7·37	0·063	0·077
1·055	7·4	11	6·59	8·07	0·070	0·085
1·060	8·0	12	7·16	8·77	0·076	0·093
1·065	8·7	13	7·73	9·47	0·082	0·102
1·070	9·4	14	8·32	10·19	0·089	0·109
1·075	10·0	15	8·90	10·90	0·096	0·117
1·080	10·6	16	9·47	11·60	0·103	0·125
1·085	11·2	17	10·04	12·30	0·109	0·133
1·090	11·9	18	10·60	12·99	0·116	0·142
1·095	12·4	19	11·16	13·67	0·122	0·150
1·100	13·0	20	11·71	14·35	0·129	0·158
1·105	13·6	21	12·27	15·03	0·136	0·166
1·110	14·2	22	12·82	15·71	0·143	0·175
1·115	14·9	23	13·36	16·36	0·149	0·183
1·120	15·4	24	13·89	17·01	0·156	0·191
1·125	16·0	25	14·42	17·66	0·162	0·199
1·130	16·5	26	14·95	18·31	0·169	0·207
1·135	17·1	27	15·48	18·96	0·176	0·215
1·140	17·7	28	16·01	19·61	0·183	0·223
1·145	18·3	29	16·54	20·26	0·189	0·231
1·150	18·8	30	17·07	20·91	0·196	0·239
1·155	19·3	31	17·59	21·55	0·203	0·248
1·160	19·8	32	18·11	22·19	0·210	0·257
1·165	20·3	33	18·64	22·83	0·217	0·266
1·170	20·9	34	19·16	23·47	0·224	0·275
1·175	21·4	35	19·69	24·12	0·231	0·283
1·180	22·0	36	20·21	24·76	0·238	0·292
1·185	22·5	37	20·73	25·40	0·246	0·301
1·190	23·0	38	21·26	26·04	0·253	0·310
1·195	23·5	39	21·78	26·68	0·260	0·319
1·200	24·0	40	22·30	27·32	0·268	0·328
1·205	24·5	41	22·82	27·95	0·275	0·337
1·210	25·0	42	23·33	28·58	0·282	0·346
1·215	25·5	43	23·84	29·21	0·290	0·355
1·220	26·0	44	24·36	29·84	0·297	0·364
1·225	26·4	45	24·88	30·48	0·305	0·373
1·230	26·9	46	25·39	31·11	0·312	0·382
1·235	27·4	47	25·88	31·70	0·320	0·391
1·240	27·9	48	26·35	32·28	0·327	0·400
1·245	28·4	49	26·83	32·86	0·334	0·409
1·250	28·8	50	27·29	33·43	0·341	0·418
1·255	29·3	51	27·76	34·00	0·348	0·426
1·260	29·7	52	28·22	34·57	0·356	0·435
1·265	30·2	53	28·69	35·14	0·363	0·444
1·270	30·6	54	29·15	35·71	0·370	0·454
1·275	31·1	55	29·62	36·29	0·377	0·462
1·280	31·5	56	30·10	36·87	0·385	0·472
1·285	32·0	57	30·57	37·45	0·393	0·481
1 290	32·4	58	31·04	38·03	0·400	0·490
1·295	32·8	59	31·52	38·61	0·408	0·500
1·300	33·3	60	31·99	39·19	0·416	0·510
1·305	33·7	61	32·46	39·77	0·424	0·519
1·310	34·2	62	32·94	40·35	0·432	0·529
1·315	34·6	63	33·41	40·93	0·439	0·538
1·320	35·0	64	33·88	41·50	0·447	0·548
1·325	35·4	65	34·35	42·08	0·455	0·557
1·330	35·8	66	34·80	42·66	0·462	0·567
1·335	36·2	67	35·27	43·20	0·471	0·577
1·340	36·6	68	35·71	43·74	0·479	0·586
1·345	37·0	69	36·14	44·28	0·486	0·596
1·350	37·4	70	36·58	44·82	0·494	0·605
1·355	37·8	71	37·02	45·37	0·502	0·614
1·360	38·2	72	37·45	45·88	0·509	0·624
1·365	38·6	73	37·89	46·41	0·517	0·633
1·370	39·0	74	38·32	46·94	0·525	0·643
1·375	39·4	75	38·75	47·47	0·533	0·653
1·380	39·8	76	39·18	48·00	0·541	0·662
1·385	40·1	77	39·62	48·53	0·549	0·672
1·390	40·5	78	40·05	49·06	0·557	0·682
1·395	40·8	79	40·48	49·59	0·564	0·692
1·400	41·2	80	40·91	50·11	0·573	0·702
1·405	41·6	81	41·33	50·63	0·581	0·711
1·410	42·0	82	41·76	51·15	0·589	0·721
1·415	42·3	83	42·17	51·66	0·597	0·730
1·420	42·7	84	42·57	52·15	0·604	0·740
1·425	43·1	85	42·96	52·63	0·612	0·750
1·430	43·4	86	43·36	53·11	0·620	0·759
1·435	43·8	87	43·75	53·59	0·628	0·769
1·440	44·1	88	44·14	54·07	0·636	0·779
1·445	44·4	89	44·53	54·55	0·643	0·789
1·450	44·8	90	44·92	55·03	0·651	0·798
1·455	45·1	91	45·31	55·50	0·659	0·808
1·460	45·4	92	45·69	55·97	0·667	0·811
1·465	45·8	93	46·07	56·43	0·675	0·827
1·470	46·1	94	46·45	56·90	0·683	0·837
1·475	46·4	95	46·83	57·37	0·691	0·846
1·480	46·8	96	47·21	57·83	0·699	0·856
1·485	47·1	97	47·57	58·28	0·707	0·865
1·490	47·4	98	47·95	58·74	0·715	0·876
1·495	47·8	99	48·34	59·22	0·723	0·885
1·500	48·1	100	48·73	59·70	0·731	0·896
1·505	48·4	101	49·12	60·18	0·739	0·906
1·510	48·7	102	49·51	60·65	0·748	0·916
1·515	49·0	103	49·89	61·12	0·756	0·926
1·520	49·4	104	50·28	61·59	0·764	0·936
1·525	49·7	105	50·66	62·06	0·773	0·946
1·530	50·0	106	51·04	62·53	0·781	0·957
1·535	50·3	107	51·43	63·00	0·789	0·967
1·540	50·6	108	51·78	63·43	0·797	0·977
1·545	50·9	109	52·12	63·85	0·805	0·987
1·550	51·2	110	52·46	64·26	0·813	0·996
1·555	51·5	111	52·79	64·67	0·821	1·006
1·560	51·8	112	53·12	65·08	0·829	1·015
1·565	52·1	113	53·46	65·49	0·837	1·025
1·570	52·4	114	53·80	65·90	0·845	1·035
1·575	52·7	115	54·13	66·30	0·853	1·044
1·580	53·0	116	54·46	66·71	0·861	1·054
1·585	53·3	117	54·80	67·13	0·869	1·064
1·590	53·6	118	55·18	67·59	0·877	1·075
1·595	53·9	119	55·55	68·05	0·886	1·085
1·600	54·1	120	55·93	68·51	0·895	1·096
1·605	54·4	121	56·30	68·97	0·904	1·107
1·610	54·7	122	56·68	69·43	0·913	1·118
1·615	55·0	123	57·05	69·89	0·921	1·128
1·620	55·2	124	57·40	70·32	0·930	1·139
1·625	55·5	125	57·75	70·74	0·938	1·150
1·630	55·8	126	58·09	71·16	0·947	1·160
1·635	56·0	127	58·43	71·57	0·955	1·170
1·640	56·3	128	58·77	71·99	0·964	1·181
1·645	56·6	129	59·10	72·40	0·972	1·192
1·650	56·9	130	59·45	72·82	0·981	1·202
1·655	57·1	131	59·78	73·23	0·989	1·212
1·660	57·4	132	60·11	73·64	0·998	1·222
1·665	57·6	133	60·46	74·07	1·007	1·233
1·670	57·9	134	60·82	74·51	1·016	1·244
1·675	58·2	135	61·20	74·97	1·025	1·256
1·680	58·4	136	61·57	75·42	1·034	1·267

S.G. $\frac{15^\circ}{4^\circ}$ *in vacuo*	Degrees Beaumé	Degrees Twaddell	100 parts by weight contain		1 litre contains kilos.	
			P.c. SO_3	P.c. H_2SO_4	SO_3	H_2SO_4
1·685	58·7	137	61·93	75·86	1·043	1·278
1·690	58·9	138	62·29	76·30	1·053	1·289
1·695	59·2	139	62·64	76·73	1·062	1·301
1·700	59·5	140	63·00	77·17	1·071	1·312
1·705	59·7	141	63·35	77·60	1·080	1·323
1·710	60·0	142	63·70	78·04	1·089	1·334
1·715	60·2	143	64·07	78·48	1·099	1·346
1·720	60·4	144	64·43	78·92	1·108	1·357
1·725	60·6	145	64·78	79·36	1·118	1·369
1·730	60·9	146	65·14	79·80	1·127	1·381
1·735	61·1	147	65·50	80·24	1·136	1·392
1·740	61·4	148	65·86	80·68	1·146	1·404
1·745	61·6	149	66·22	81·12	1·156	1·416
1·750	61·8	150	66·58	81·56	1·165	1·427
1·755	62·1	151	66·94	82·00	1·175	1·439
1·760	62·3	152	67·30	82·44	1·185	1·451
1·765	62·5	153	67·65	82·88	1·194	1·463
1·770	62·8	154	68·02	83·32	1·204	1·475
1·775	63·0	155	68·49	83·90	1·216	1·489
1·780	63·2	156	68·98	84·50	1·228	1·504
1·785	63·5	157	69·47	85·10	1·240	1·519
1·790	63·7	158	69·96	85·70	1·252	1·534
1·795	64·0	159	70·45	86·30	1·265	1·549
1·800	64·2	160	70·94	86·90	1·277	1·564
1·805	64·4	161	71·50	87·60	1·291	1·581
1·810	64·6	162	72·08	88·30	1·305	1·598
1·815	64·8	163	72·69	89·05	1·319	1·621
1·820	65·0	164	73·51	90·05	1·338	1·639
1·821	—	—	73·63	90·20	1·341	1·643
1·822	65·1	—	73·80	90·40	1·345	1·647
1·823	—	—	73·98	90·60	1·348	1·651
1·824	65·2	—	74·12	90·80	1·352	1·656
1·825	—	165	74·29	91·00	1·356	1·661
1·826	65·3	—	74·49	91·25	1·360	1·666
1·827	—	—	74·69	91·50	1·364	1·671
1·828	65·4	—	74·86	91·70	1·368	1·676
1·829	—	—	75·03	91·90	1·372	1·681
1·830	—	166	75·19	92·10	1·376	1·685
1·831	65·5	—	75·35	92·30	1·380	1·690
1·832	—	—	75·53	92·52	1·384	1·695
1·833	65·6	—	75·72	92·75	1·388	1·700
1·834	—	—	75·96	93·05	1·393	1·706
1·835	65·7	167	76·27	93·43	1·400	1·713
1·836	—	—	76·57	93·80	1·406	1·722
1·837	—	—	76·90	94·20	1·412	1·730
1·838	65·8	—	77·23	94·60	1·419	1·739
1·839	—	—	77·55	95·00	1·426	1·748
1·840	65·9	168	78·04	95·60	1·436	1·759
1·8405	—	—	78·33	95·95	1·441	1·765
1·8415	—	—	79·19	97·00	1·458	1·786
1·8410	—	—	79·76	97·70	1·469	1·799
1·8415	—	—	80·16	98·20	1·476	1·808
1·8400	—	—	80·57	98·70	1·483	1·816
1·8400	—	—	80·98	99·20	1·490	1·825
1·8395	—	—	81·18	99·45	1·494	1·830
1·8390	—	—	81·39	99·70	1·497	1·834
1·8385	—	—	81·59	99·95	1·500	1·838

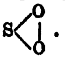
For the properties of fuming H_2SO_4 *v.* PYROSULPHURIC ACID, p. 625.

For a test for small quantities of free H_2SO_4 *v.* Carey Lea (*Am. S.* [3] 45, 478; abstract in *C. J.* 64 (ii.), 566).

Reactions.—1. Conc. H_2SO_4 is decomposed by *heat*; at c. 440° the products are SO_2 and H_2O, and by passing through a red-hot tube SO_2, O, and H_2O are formed (Deville a. Troost, *C. R.* 56, 891; Wanklyn a. Robinson, *Pr.* 12, 507; Redwood, *Ph.* [2] 5, 601; Deville a. Debray, *A. Ch.* [3] 61, 125).—2. Decomposed by the *electric current*; with conc. H_2SO_4 and a raised temperature O separates at the positive pole, and H and S at the negative; at 0° only H and O are given off (Faraday, *T.* 1834; Warburg, *P.* 135, 114; Luckow, *Fr.* 1880. 1; Berthelot, *C. R.* 86, 71; 90, 269). Gladstone a. Tribe (*C. J.* 35, 176; 43, 345) found that a little SO_2 was formed when the electrolysis of 98·2 p.c. H_2SO_4 was very slow. According to the concentration of the H_2SO_4Aq electrolysed, the strength of the current, and the current density, ozone, H_2O_2, and S_2O_7 are formed, besides H and O. For an examination of the conditions favourable to the production of ozone *v.* McLeod (*C. J.* 49, 591, where references are given to earlier memoirs). According to Bouty (*C. R.* 108, 393), acid of the concentration $H_2SO_4 + H_2O$ always gives H_2O_2 on electrolysis; Richarz (*A. Ch.* [2] 24, 183) says that the maximum production of H_2O_2 is obtained with acid of the concentration $H_2SO_4 + 1·347H_2O$; with acid more dilute than 60 p.c. H_2SO_4 very little H_2O_2 is obtained, but considerable quantities of S_2O_7 and ozone (Bouty, *l.c.*; *cf.* Kuriloff, *J. R.* 23, 235). In connection with the electrolysis of H_2SO_4Aq, and the conditions of production of H and O only, or of H_2O_2, ozone, and S_2O_7 also, *v.* Armstrong (*C. J. Proc.* 1893–4. 188 [No. 127]).—3. By passing a mixture of the vapour of H_2SO_4 mixed with *hydrogen* through a red-hot tube, H_2O is obtained along with SO_2, S, or H_2S, according to the quantity of H (*v.* Warner, *C. N.* 28, 13). *Hydrogen occluded by palladium or platinum* partially reduces 98·2 p.c. H_2SO_4, giving SO_2 (G. a. T., *l.c.* p. 177).—4. SO_2, CO_2, and H_2O are formed by heating conc. H_2SO_4 with *carbon*; and SO_2 and H_2O by heating with *sulphur*.—5. *Phosphorus* takes fire in boiling H_2SO_4 with separation of S; *red phosphorus* reacts with the conc. acid when hot, forming SO_2 and H_3PO_4.—6. *Chlorine* reacts with conc. H_2SO_4 to form $Cl(SO_2.OH)$ (*v.* CHLOROSULPHONIC ACID, p. 509).—7. Most *metals* interact; K and Na give off H, Zn and Fe and several other metals also give off H with more or less dilute H_2SO_4Aq at ordinary temperatures; on raising the temperature SO_2 and H_2S are generally evolved and S is often separated. Some metals, such as Sb, Bi, Cu, Hg, react only with warm fairly conc. H_2SO_4, giving off SO_2, and often also H_2S. Au, Ir, Pt, Rh, and W do not interact with H_2SO_4. Regarding the conditions of the interaction of H_2SO_4Aq with metals—concentration, temperature, and products—*v.* Ditte (*A. Ch.* [6] 19, 68). Pattison Muir a. Adie (*C. J.* 53, 47) found that the only products of the interaction of *approximately pure zinc* and dilute H_2SO_4Aq (c. $H_2SO_4.12H_2O$ to c. $H_2SO_4.15H_2O$) were $ZnSO_4Aq$ and H; that with conc. acid (c. $H_2SO_4.H_2O$ to c. H_2SO_4) SO_2 was the chief gaseous product, and that H_2S was also produced at higher temperatures; and that with acid of intermediate concentration (c. $H_2SO_4.2H_2O$) both SO_2 and H_2S were formed in considerable quantities at c. 160°. For experiments on the rate of action of H_2SO_4Aq on different specimens of zinc *v.* Divers a. Shimidzu (*C. J.* 47, 598), who have also examined the production of NH_2OH by the interaction of zinc with H_2SO_4Aq and HNO_3Aq together (*cf.* HYDROXYLAMINE, vol. ii. p. 734). For qualitative experiments on the interaction of H_2SO_4 and *tin*, *v.* Pattison Muir a. Robbs (*C. N.* 45, 69, where references to other memoirs are given). Pullinger (*C. J.* 59, 815) found that *pure zinc* was not acted on by H_2SO_4Aq (1 part conc. acid + 3 parts water by weight) provided the acid had been boiled for a long time before use and the surface of the zinc was quite smooth; if the surface was rough some of the zinc was dissolved. P. also found that oxidisers increased the rate of solution of zinc, and reducers, if not containing S, almost stopped the solution. P. concluded that when the surface of the zinc was rough S_2O_7 was probably formed, and then the action proceeded. Weeren (*B.* 24, 1785) noticed that there was scarcely any reaction between pure zinc and H_2SO_4Aq (c. 20 parts water); he supposed that a layer of H was condensed on the surface of the metal. W. thought that with impure zinc the H is given off from the surface of the more negative metal present, and so the surface of the zinc is left exposed to the action of the acid. W. found that the evolution of H proceeded more rapidly *in vacuo*, and that it was hastened by brushing the surface of the metal. The weight of pure zinc dissolved in 30 mins. was 2·1 mgm. at 0°, 9·3 mgm. at 98°, and 122·1 mgm. at the b.p. of the acid used. W. obtained similar results with Al, Cd, Co, and Fe. *Sodium amalgam* or *zinc amalgam*, with conc. H_2SO_4, gives off H, then quantities of H_2S, then SO_2 and S, and finally only SO_2 (Walz, *C. N.* 23, 245). The interaction of H_2SO_4 and *copper* has been fully examined by Pickering (*C. J.* [2] 18, 112; *cf.* COPPER, vol. ii. p. 253).—8. H_2SO_4 reacts with the *oxides of nitrogen* (not with N_2O) to form $NO_2(SO_2.OH)$ (*v.* NITROSULPHONIC ACID, p. 601).—9. *Phosphoretted hydrogen* reacts slowly with H_2SO_4 at the ordinary temperature, giving SO_2, S, and H_3PO_4 (Rose, *P.* 24, 139).—10. With *sulphuretted hydrogen*, H_2O, S, and SO_2 are formed.—11. *Phosphorus pentoxide* withdraws H_2O from hot conc. H_2SO_4, producing $P_2O_5.H_2O$ and SO_3 (Barreswil, *C. R.* 25, 30; Evans, *Ph.* 8, 127); *phosphorus pentachloride* or *trichloride* forms SO_3 and $POCl_3$, also SO_2Cl_2 when PCl_5 is used (Williamson, *P. M.* [4] 7, 365; Schiff, *A.* 202, 111; *cf.* Michaelis, *J. Z.* 6, 233, 292), and also $Cl(SO_2.OH)$ (Müller, *B.* 6, 277; Geuther, *B.* 5, 925; Thorpe, *C. J.* 37, 358).—12. H_2SO_4 reacts with most *salts* to form sulphates, and set free the acid of the salt if that acid is more volatile than H_2SO_4. In several cases secondary reactions occur between the acid set free and the H_2SO_4; thus, with bromides and iodides, Br and I, and SO_2 or H_2S, are produced. The interaction of H_2SO_4Aq and KBr has been examined by Addyman (*C. J.* 61, 94), who found that the percentage of HBr decomposed varied almost directly with the quantity of H_2SO_4 used, and that when so much H_2SO_4 was present that the water produced in the reaction $2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$ caused no sensible dilution of the H_2SO_4, all the HBr was decomposed; with dilute acid, c. 30 p.c. H_2SO_4, using excess of acid, scarcely a trace of HBr was decomposed (*cf.* Feit a. Kubierschki, *J. Ph.* [5] 24, 159). Jackson (*C. J.* 43, 339) finds that the interaction of conc. H_2SO_4 and KI varies according as the acid is present in large excess, or in quantity just sufficient for the KI used. In the first case all the I of the KI is set free along with an equivalent quantity of SO_2; in the second case all the I is liberated with the equivalent quantity of H_2S. Many *salts of acids containing much oxygen, e.g.* dichromates and permanganates, are decomposed by hot conc. H_2SO_4 with evolution of O. The reaction of H_2SO_4Aq with $KMnO_4Aq$ has been examined by Gooch a. Danner (*Am. S.* [3] 44, 301), who found that the quantity of O given off increased with (1) concentration of H_2SO_4Aq, (2) time, (3) temperature; no O was given off after a few hours with 20 p.c. acid at the ordinary temperature, but a considerable quantity of O was produced after five days' action, and c. the same result was obtained by heating to 80° for one and a half hours (*cf.* Jones, *C. J.* 33, 95).—13. Conc. H_2SO_4 reacts with many oxygenated *organic compounds*, withdrawing H_2O; with benzenoid hydrocarbons it forms sulpho- acids; many organic compounds, such as sugar, starch, &c., are charred by warm H_2SO_4.—14. Pictet (*C. R.* 115, 708, 814) has examined the *reactions of sulphuric acid at low temperatures*, using acid of 89 p.c. H_2SO_4; no action occurred below −125° with such bodies as NaOH, NaCl, NH_3, Na_2CO_3, Na, K; in most cases action began suddenly at temperatures varying from −120° to −60°.—15. H_2SO_4 combines with *water*; the hydrates $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, and $H_2SO_4.3H_2O$ have been isolated as solids (*v. infra*).—16. Conc. H_2SO_4 combines with *sulphur trioxide* to form $H_2SO_4.SO_3$ and other compounds (*v.* PYROSULPHURIC ACID).

For the reactions of fuming H_2SO_4 *v.* PYROSULPHURIC ACID (p. 625). The salts of H_2SO_4 are described under SULPHATES (p. 567). Both amides of H_2SO_4, viz. $SO_2.OH.NH_2$ and $SO_2(NH_2)_2$, have been isolated (*v.* SULPHAMIC ACID, p. 567, and SULPHAMIDE, p. 567); the imide $SO_2.NH$ is also known, *v.* SULPHIMIDE, p. 587; *cf.* also SULPHIMIDO-AMIDE $NH(SO_2.NH_2)_2$, p. 587, and IMIDOSULPHONIC ACID $NH(SO_2.OH)_2$, p. 600.

Constitution of sulphuric acid.—The reactions of H_2SO_4 with Cl and with PCl_5, and the reactions of the products with water, also the formation of $SO_2.OH.NH_2$, $SO_2(NH_2)_2$, and $SO_2.NH$, show that H_2SO_4 contains two OH groups. The fact that only one compound, $SO_2.OEt.OMe$, can be formed from H_2SO_4 shows that the two OH groups in $SO_2(OH)_2$ are related to the rest of the molecule in the same way; hence the formula for the acid is to be written $S{<}\begin{smallmatrix}O.OH\\O.OH\end{smallmatrix}$ or $O_2S{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$. Inasmuch as SO_2Cl_2 is formed from $SO_2(OH)_2$ by the reaction of PCl_5, as certain hydrocarbons interact with SO_2Cl_2 to form SO_2R_2 (where R = Me, Ph, &c.), and as these compounds SO_2R_2 are reduced to SR_2, where the radicles R are certainly in direct union with S, it is extremely probable that the OH groups in $SO_2(OH)_2$ are in direct union with S, and hence the formula $O_2S{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$ is to be preferred to $S{<}\begin{smallmatrix}O.OH\\O.OH\end{smallmatrix}$ for sulphuric acid. It is

undecided whether the group SO_2 in $O_2S.OH.OH$ has the constitution O.S.O or  **.**

Hydrates of sulphuric acid. Two solid hydrates have been isolated; a liquid hydrate has probably also been isolated.

Monohydrate $H_2SO_4.H_2O$ (*Tetrahydroxysulphuric acid* $SO(OH)_4$). Large, colourless, six-sided tablets; formed by mixing 1 part conc. H_2SO_4 with rather less than one-fifth part water (by weight), and surrounding with a freezing mixture. The crystals melt at 7·5° (Pierre a. Puchot, *A. Ch.* [5] 2, 164). The hydrate readily remains liquid considerably below its m.p. S.G. $\frac{0^\circ}{4^\circ}=1{\cdot}7943$ (for the liquid) (Mendeléeff, *B.* 19, 380); 1·77806 at 15°, 1·77423 at 20°, 1·77071 at 25° (Perkin, *C. J.* 49, 777; determinations made with liquid, and referred to water at same temperatures). Thomsen gives H.F. from liquid H_2SO_4 and H_2O $[H^2SO^4,H^2O]=6,379$ (*Th.* 3, 54); Berthelot gives 6,120 (*C. R.* 78, 716). Heat of fusion = 3680 g. units (for 116 g.) $H_2SO_4.H_2O$ (Berthelot, *C. R.* 78, 716). For vapour pressures from 143° to 204° *v.* Tate (*P. M.* [4] 26. 502).

Dihydrate $H_2SO_4.2H_2O$ (*Perhydroxysulphuric acid* $S(OH)_6$). Formed by adding ·368 parts H_2O to 1 part pure H_2SO_4, by weight. This hydrate has not been obtained as a solid; the S.G. of the liquid at $\frac{0^\circ}{4^\circ}$ is given by Mendeléeff (*B.* 19, 380) as 1·6655 (*cf.* Perkin, *C. J.* 49, 777).

It is stated (*v.* Mendeléeff, *B.* 19, 388) that the maximum contraction when H_2SO_4 and H_2O are mixed occurs when the compounds are present in the ratio $H_2SO_4{:}2H_2O$, but Pickering (*C. J.* 57, 84) says that the maximum does not correspond with the composition of any hydrate the existence of which is indicated in other ways.

Tetrahydrate $H_2SO_4.4H_2O$. Obtained by Pickering (*C. J.* 57, 339) as a crystalline solid, melting at −25°, by cooling H_2SO_4Aq containing 57·6 p.c. H_2SO_4 ($H_2SO_4.2H_2O$ corresponds with 57·66 p.c. H_2SO_4). The crystals are large and well defined, and resemble $H_2SO_4.H_2O$; the compound may be kept liquid at 20° to 25° below its freezing point.

Hydrates of sulphuric acid in aqueous solution.—According to Mendeléeff (*B.* 19, 380; *cf.* his *Principles of Chemistry*, vol. ii. p. 234), an examination of the connections between the concentration of H_2SO_4Aq and the S.G. indicates the existence of hydrates that have not yet been isolated. Pickering (*C. J.* 57, 64) comes to the same general conclusion from an extended examination of the connections between the changes of composition of H_2SO_4Aq and the changes of S.G., heat capacity, electrical conductivity, heat of solution, and expansion by heat of the solution. Pickering's reasoning is a special case of that explained in the article Solutions (part ii. p. 492); for the detailed argument, and criticisms of it, *v.* Pickering, *C. J.* 57, 64; Rücker, *P. M.* [5] 32, 304; 33, 204; P., *P. M.* [5] 33, 132, 463; *cf.* Mendeléeff, *Z. P. C.* 1, 275; and Crompton, *C. J.* 53, 116.

PERSULPHURIC ACID $H_2S_2O_8Aq$. This acid is present in the solution obtained by electrolysing H_2SO_4Aq of certain concentrations; Berthelot (*C. R.* 90, 269; 112, 1481) obtained a quantity of the acid equal to from 88 to 123 g. S_2O_7 per litre by electrolysing H_2SO_4Aq containing water and acid in the ratio $10H_2O{:}H_2SO_4$ (*cf.* Sulphuric peroxide, p. 616; and Sulphuric acid, *Reactions*, No. 2, p. 623). According to Traube (*B.* 22, 1518, 1528) a solution of $H_2S_2O_8$ in H_2SO_4 does not oxidise $H_2C_2O_4$, HNO_2, CO, or $Cr_2(SO_4)_3$; Richarz, however (*B.* 21, 1670), says that oxalic and nitrous acids are oxidised. The acid has not been isolated; by electrolysing at temperatures below 0°, and then adding BaOAq or KOHAq, the Ba or K salt is obtained. The formula $H_2S_2O_8$ is given rather than HSO_4, because of the results of Bredig's measurements of the conductivities of solutions of the K salt. For salts of this acid *v.* Persulphates, p. 582.

PYROSULPHURIC ACID $H_2S_2O_7$ (*Disulphuric acid*). A solution of this acid in H_2SO_4 is known as *fuming sulphuric acid*, or *Nordhausen acid*. This acid is obtained by adding rather more SO_3 to H_2SO_4 than the proportion $SO_3{:}H_2SO_4$, cooling, and spreading out the crystals that form over nearly conc. H_2SO_4 under a bell-jar till the excess of SO_3 is removed (Schultz-Sellack, *B.* 4, 109). Forms large crystals, melting at 35°. Easily decomposed by heat to H_2SO_4 and SO_3. $H_2S_2O_7$ is dibasic, forming salts MHS_2O_7 and $M_2S_2O_7$ (*v.* Pyrosulphates, p. 583). *Fuming sulphuric acid* is a solution of $H_2S_2O_7$ in H_2SO_4; it is prepared by heating dry $FeSO_4$ in fireclay vessels and collecting the oily, fuming liquid that distils over. The acid fumes strongly in the air, and gives off SO_3 when warmed. But few of the reactions described for *pyrosulphuric acid*, or for *fuming sulphuric acid*, can be set down as belonging to a definite compound, but rather to solutions of $H_2S_2O_7$ (and perhaps other compounds of H_2SO_4 and SO_3) in H_2SO_4. Finely-divided *silver* dissolves easily; the solution poured into water gives Ag_2SO_4 and SO_2; *mercury* reacts similarly; spongy *copper* has a slight reaction, giving Cu_2S and $CuSO_4$ (Divers a. Shimidzu, *C. J.* 47, 636). Distilled with *phosphorus pentoxide in a stream of hydrogen chloride*, $Cl(SO_2.OH)$ is formed; the same acid is formed by heating with PCl_5, and also by heating 'crystallised fuming sulphuric acid' with HCl (*v.* Chlorosulphonic acid, p. 509). *Nitrogen dioxide* passed into well-cooled pyrosulphuric acid gives $NO_2(SO_2.OH)$ (*v.* Nitrosulphonic acid, p. 601). By saturating ordinary conc. H_2SO_4 with SO_3 (Jacquelain, *A. Ch.* [3] 30, 343), or by cooling fuming H_2SO_4 to −10° (Wackenroder, *Ar. Ph.* [2] 87, 267), the compound $H_2S_2O_7.2H_2SO_4$ ($=3H_2SO_4.SO_3$) is said to be obtained in transparent crystals. Schultz-Sellack (*B.* 4, 109) failed to obtain any compound of H_2SO_4 and SO_3, except $H_2S_2O_7$. Crystals of the composition $H_2SO_4.3SO_3$ ($=H_2S_4O_{13}$) melting at 8°–10° are said by Weber (*P.* 159, 313) to be formed by adding cooled conc. H_2SO_4, little by little, to SO_3.

M. M. P. M.

SULPHURIC ANHYDRIDE SO_3 *v.* Sulphur trioxide, p. 615.

Persulphuric anhydride S_2O_7 *v.* Sulphuric peroxide, p. 616.

SULPHURIC-NITROSYL CHLORIDE $SO_3.NOCl$ *v.* Nitrosulphonic chloride, p. 601.

SULPHURIC OXIDE SO_3 *v.* Sulphur trioxide, p. 615.

SULPHURIC PEROXIDE S_2O_7 *v.* p. 616.

SULPHUROSAMIC ACID $SO.OH.NH_2$ *v.* Thionamic acid, p. 695.

SULPHUROUS ACID and HYPOSULPHUROUS ACID.

SULPHUROUS ACID H_2SO_3Aq. The acid has not been isolated; a solution of SO_2 in water reacts as a weak dibasic acid, forming salts of the types M^IHSO_3, $M^I_2SO_3$, and $M^{II}SO_3$ (*v.* Sulphites, p. 587). H.F. $[H^2,S,O^3,Aq] = 147,130$; $[H^2O,S,O^2,Aq] = 78,780$ (from rhombic S; *Th.* 2, 251).

The methods of formation and preparation of H_2SO_3Aq are sufficiently detailed under Sulphur dioxide (p. 613); it is only necessary to add water to the SO_2 obtained.

Properties.—An aqueous solution of H_2SO_3 readily decomposes, giving off SO_2; on standing for some time in the air, and more quickly by warming, H_2SO_4Aq is formed with production of much heat; $[H^2SO^3Aq,O] = 63,634$ (*Th.* 2, 253). H_2SO_3Aq is altered by the action of light, so that after exposure to light for some time the solution ppts. Ag_2S from $AgNO_3Aq$, and reduces silver haloid compounds, forming some Ag_2S; the solution after exposure to light behaves like a dilute solution of a polythionic acid (Stas, *Chem. Proport.* 64). Löw (*L'Institut*, 1873. 67) says that dilute H_2SO_3Aq is changed to H_2SO_4Aq and S by long exposure to light.

Reactions.—1. *Heated in a closed tube* to 170°–180°, H_2SO_4Aq and S are formed, and after a time also H_2S (Geitner, *A.* 129, 350).—2. Decomposed by an *electric current*, giving H_2SO_4Aq at the positive pole and S at the negative; with a weak current $H_2S_2O_4Aq$ is probably formed at first at the negative pole (Guéroult, *C. R.* 85, 225).—3. *Phosphorus pentachloride* produces $SOCl_2$ and $POCl_3$ (Kremers, *A.* 70, 297; Schiff, *A.* 102, 111).—4. *Sulphurous chloride* with H_2SO_3Aq produces polythionic acids (*v.* Debus, *C. J.* 53, 345).—5. Vapour obtained by heating H_2SO_3Aq reacts with *chlorine*, when passed over red-hot Pt, to form $Cl(SO_2.OH)$ (*v.* Chlorosulphonic acid, p. 599).—6. $NO_2(SO_2.OH)$ (*v.* Nitrosulphonic acid, p. 601) is formed by the interaction of moist SO_2, *i.e.* H_2SO_3Aq, with *nitric oxide* or *nitrogen dioxide.*—7. H_2SO_3Aq is oxidised to H_2SO_4Aq by *oxygen*, the *halogens*, and many other *oxidisers.*—8. Heated with *phosphorus* in a closed tube to 200°, H_2S is produced (Oppenheim, *Bl.* [2] 1, 163).—9. Reduced by *zinc* and *dilute sulphuric acid* to H_2S (*v.* Reinsch, *D. P. J.* 163, 286; 181, 332); with *zinc* alone, H_2SO_3Aq is partly reduced, probably giving $H_2S_2O_4Aq$ (*v.* Hyposulphurous acid, p. 627).—10. Many *metals* which evolve H from H_2SO_4Aq or HClAq react with H_2SO_3Aq to form sulphites and sulphides, with evolution of little or no H (*v.* Federoff, *Chem. Zeitung*, 5, 15). For a fairly full qualitative examination of the interaction of Al, Cd, Mg, Ni, and Zn with H_2SO_3Aq, *v.* Schweitzer (*C. N.* 23, 293).—11. Many of the *oxyacids of the halogens* are reduced to hydracids by H_2SO_3Aq.—12. *Phosphorous acid* gives H_3PO_4Aq and H_2S; then S, and thionic acids (Wöhler, *A.* 39, 252; Maquenne, *Chem. Zeitung.* 1890 [1] 511).—13. *Phosphoretted hydrogen* produces H_3PO_4Aq, and S (Cavazzi, *G.* 16, 169). 14. *Hydrogen sulphide* passed into H_2SO_3Aq forms a solution containing H_2SO_4, $H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$, probably $H_2S_6O_6$, S in suspension, and a colloidal form of S in solution; if the passage of H_2S is continued until reaction ceases the final products are S and H_2O (Debus, *C. J.* 53, 282; *cf.* Thionic acids, p. 698).—15. Many *metallic salts* are reduced, in aqueous solutions, by H_2SO_3Aq; salts of Ag and Hg to the metals, ferric to ferrous salts, &c. According to Divers a. Shimidzu (*C. J.* 49, 575), the reduction does not consist in the withdrawal of O by H_2SO_3Aq and the oxidation of that acid thereby to H_2SO_4Aq. The first step is looked on by D. a. S. as probably the formation of a sulphite of the metal of the salt, and this is followed by either the decomposition of this sulphite by water to metal and H_2SO_4Aq, or the reaction of the sulphite with some of the original, unchanged, salt to form metal and a persulphite (or -ic sulphite) of the metal.—16. With *potassium thiosulphate* H_2SO_3Aq forms K tri- tetra- and penta-thionates, and S (Debus, *C. J.* 53, 343).—17. H_2SO_3Aq dissolves many freshly ppd. *metallic sulphides*, *e.g.* MnS, FeS, ZnS, forming thiosulphates (Schönbein, *P.* 104, 300; Heldt, *J. pr.* 83, 20).—18. *Alkali nitrites* give salts of nitrilosulphonic acid $N(SO_2.OH)_3$ (*q. v.*, p. 601), and also salts of oxy-imidosulphonic acid $N(OH)(SO_2.OH)_2$ (*q. v.*, p. 602). Using a dilute, ice-cold solution of H_2SO_3 (= 5 p.c. SO_2), and adding 40 g. KNO_2 in 1,000 c.c. water to 3 litres of this H_2SO_3Aq, Raschig (*A.* 241, 234) obtained $NH_2(SO_2.OK)$ (*cf.* Sulphamic acid, p. 567). Under certain conditions of concentration and temperature NO and N_2O, also NH_3 and sometimes NH_2OH, are produced. With *nitrous acid* the final products are NH_3, NO, N_2O, and H_2SO_4Aq; according to Raschig (*l.c.*), $NH_2(SO_2.OH)$ is always formed, and the gaseous products are to be looked on as resulting from secondary reactions between nitrous acid and $NH_2(SO_2.OH)$ or other nitrogenised sulphonic acids formed in the primary reaction between the nitrous and sulphurous acids. With *silver* and *mercurous nitrites* Divers a. Haga (*C. J.* 51, 659) found that sulphites were produced, along with some NO and H_2SO_4, and more or less NH_2OH.—19. For the reaction of H_2SO_3Aq with *potassium platinochloride* *v.* Platino-sulphonates, this vol., p. 285.

Neither the amide $SO(NH_2)_2$ (*v.* the heading Thionamide), nor the imide SO.NH, of H_2SO_3 has been isolated; and it is doubtful whether the acid $SO.OH.NH_2$ or $SO_2.NH_2.H$ is known. *v.* Thionamic acid.

Constitution of sulphurous acid. The fact that many haloid derivatives of hydrocarbons interact with $NaHSO_3$ to form sulphonic acids—*e.g.* $EtI + NaHSO_3 = EtSO_3H + NaI$—makes it probable that the Na in $NaHSO_3$ is in direct union with the S, because the S in sulphonic acids is almost certainly in direct union with the hydrocarbon radicle; hence it is likely that one H atom in H_2SO_3 is directly combined with the S atom, and hence the formula for H_2SO_3 is probably $H.SO_2.OH$. This view of the constitution of H_2SO_3 is insisted on, and illustrated, by Divers (*C. J.* 47, 205).

Hydrates of sulphurous acid. Colourless, ice-like crystals are obtained by passing SO_2 into water surrounded by ice, by cooling saturated SO_2Aq, or by passing moist SO_2 through a tube kept at a low temperature. After filtering quickly in a covered filter, and pressing between filter paper at 8°, the crystals have the composition $H_2SO_3.xH_2O$; Dopping (*Petersburg Acad. Bull.*, 7, 100) found $x = 10$, Pierre (*A. Ch.* [3] 23, 416) found $x = 8$, Schönfeld (*A.* 95, 22) found $x = 14$, Roozeboom (*R. T. C.* 3, 29, 59, 75, 84; 4, 65) found $x = 6$, and this was confirmed by Geuther (*A.* 224, 218). Roozeboom (*l.c.*) gives S.G. of the crystals as 1·21 (referred to water at 4°); Geuther (*l.c.*) gives 1·147 as the S.G. after melting at 14°, and 14° as the m.p. with separation of some liquid SO_2 under the layer of SO_2Aq. R. (*l.c.*) gives the following dissociation-pressures, which are independent of the quantity of the hydrate: 303 mm. at 0°, 754 mm. at 7·05°, 1177 mm. at 10°, 1773 mm. at 12·1°. According to R. the critical temperature of decomposition is 7·1° in an open vessel and 12·1° in a closed vessel.

HYPOSULPHUROUS ACID $H_2S_2O_4Aq$. This acid has not been isolated. An aqueous solution is probably formed by decomposing the Na salt by dilute H_2SO_4Aq or $H_2C_2O_4Aq$, and also perhaps by digesting H_2SO_3Aq with zinc clippings till the liquid is brownish red; but neither the aqueous solution of the acid, nor any of its salts, has been obtained free from impurities. For preparation of the sodium salt, and for references, *v.* HYPOSULPHITES (p. 592).

M. M. P. M.

SULPHUROUS ANHYDRIDE *v.* SULPHUR DIOXIDE, p. 613.

SULPHUROUS OXIDE *v.* SULPHUR DIOXIDE, p. 613.

SULPHURYLAMIDE *v.* SULPHAMIDE, p. 567.

SULPHURYL BROMIDE *v.* SULPHUR OXYBROMIDES, p. 617.

Pyrosulphuryl bromide *v.* SULPHUR OXYBROMIDES, p. 617.

SULPHURYL CHLORIDE *v.* SULPHUR OXYCHLORIDES, p. 618.

Nitrosulphuryl chloride *v.* NITROSULPHONIC CHLORIDE, p. 601.

Pyrosulphuryl chloride *v.* SULPHUR OXYCHLORIDES, p. 618.

SULPHURYL HYDROXYLCHLORIDE *v.* CHLOROSULPHONIC ACID, p. 599.

SULPHURYL HYDROXYLFLUORIDE *v.* FLUOSULPHONIC ACID, p. 600.

SULPHURYLIMIDE *v.* SULPHIMIDE, p. 587.

SULPHURYL IMIDO-AMIDE *v.* SULPHIMIDO-AMIDE, p. 587.

SULPHYDRATES *v.* HYDROSULPHIDES, vol. ii. p. 733.

SULPHYDRIC ACID *v.* HYDROGEN SULPHIDE, vol. ii. p. 725.

SULPHUVINURIC ACID $C_4H_4N_2SO_2$, *i.e.* $\begin{matrix}S-C(NH_2)\\CH:C(CO_2H)\end{matrix}\!>\!N$ (Strende, *A.* 261, 26). Formed from di-bromo-pyruvic acid and a conc. solution of thio-urea (Nencki a. Sieber, *J. pr.* [2] 25, 74). Crystals (containing 2aq), sl. sol. cold water. Reduces Fehling's solution in the cold. $FeCl_3$ gives a deep violet colour.—**Salts:** MgA'_2.—ZnA'_2: minute needles.—$HA'HCl$.—$HA'HBr$.—$HA'HNO_3aq$: needles, sl. sol. water.

SULPHYDRO-ACETIC ACID *v.* THIOGLYCOLLIC ACID.

SULPHYDRO-ACETONE $CH_3.CO.CH_2.SH$.

Ethyl derivative $EtS.CH_2Ac$. (171°). Formed from chloro-acetone and NaSEt (Autenrieth, *B.* 24, 165). Yields a phenyl hydrazide [57°].

Phenyl derivative $PhS.CH_2Ac$. [36°]. (266°). Formed from $CH_3.CO.CH_2Cl$ and NaSPh in alcohol in the cold. Crystals. Yields a phenyl-hydrazide [87°] (A., *cf.* Delisle, *A.* 260, 250). Combines with $KHSO_3$ and $NaHSO_3$.

SULPHYDRO-ACETOPHENONE. *Phenyl derivative* $C_{14}H_{12}SO$, *i.e.* $C_6H_5.S.CH_2.CO.C_6H_5$. [53°]. Formed from ω-bromo-acetophenone and NaOPh (Delisle, *B.* 22, 309). Needles (from alcohol), v. sol. ether and acetone.

SULPHYDRO-ACETYL-PROPIONIC ETHER. *Phenyl derivative* $C_{13}H_{16}SO_3$, *i.e.* $C_6H_5.S.CH_2.CO.CH_2.CH_2.CO_2Et$. (197° at 15 mm.). Formed from bromo-acetyl-propionic ether and NaSPh (Delisle, *B.* 22, 309).

SULPHYDRO-ALLYL-QUINAZOLINE. *Dihydride* $C_6H_4\!<\!\begin{matrix}CH_2.N.C_3H_5\\NH.CS\end{matrix}$. [91°]. Formed from ω-oxy-tolyl-allyl-thio-urea and HClAq at 100° (Söderbaum a. Widman, *B.* 22, 1670). Needles, v. e. sol. alcohol and benzene.

Reference. — OXY-SULPHYDRO-ALLYL-QUINAZOLINE.

DISULPHYDRO-DI-ALLYL-TRIAZOLE $NH\!<\!\begin{matrix}CS.N.C_3H_5\\CS.N.C_3H_5\end{matrix}$. Formed from allyl-thio-urea and HNO_2 (Hector, *J. pr.* [2] 44, 505). Oil.—$B'_2H_2PtCl_6$: crystalline pp.

o-**SULPHYDRO-BENZOIC ACID** $C_6H_4(SH).CO_2H$. *Thio-salicylic acid.* Formed by reducing *o*-sulpho-benzoic chloride with zinc-dust and H_2SO_4 (Delisle, *B.* 22, 2206). Amorphous powder, sl. sol. hot water, v. sol. alcohol. Not volatile with steam.—AgA'.

Thio-amide $C_6H_4(SH).CS.NH_2$. Formed by heating *o*-oxy-benzamide with P_2S_5 (Spilker, *B.* 22, 2771). Minute dark-red crystals.

Phenyl derivative $C_6H_5S.C_6H_4.CO_2H$. [166°]. Formed from *o*-diazobenzoic acid, phenyl mercaptan, and NaOHAq at 50° (Graebe a. Schultess, *A.* 263, 4). Plates (from alcohol) or needles (from HOAc); sl. sol. water.—NH_4A'.—KA': needles, v. sol. water.—EtA'. [151°].

m-Sulphydro-benzoic acid $C_6H_4(SH).CO_2H$. [147°]. Formed by the action of tin and HClAq on $C_6H_4(SO_2Cl).COCl$ (Frerichs, *B.* 7, 793). Colourless plates, m. sol. water.—$BaA'_2\,2\frac{1}{2}aq$.—HgA'_2.—$PbC_7H_4SO_2\,3aq$.—$Cu(OH)A'$.—AgA'.

α-**SULPHYDRO-BUTYRIC ACID** $CHEt(SH).CO_2H$. Formed from α-bromo-butyric acid and alcoholic KSH (Duvillier, *Bl.* [2] 30, 507). Sol. water, alcohol, and ether.

Sulphydro-isobutyric acid $HS.CMe_2.CO_2H$. Formed from α-bromo-isobutyric ether by successive treatment with alcoholic K_2S and alcoholic KOH (Lovén, *J. pr.* [2] 33, 109). Oil.

α-**SULPHYDRO-CINNAMIC ACID** $C_6H_5.CH:C(SH).CO_2H$. [119°]. Formed, together with sulphocyanic acid, by heating benzylidene-rhodanic acid $C_6H_5:CH:C(SH).CO.S.CN$ with baryta-water (Ginsburg a. Bondzynski, *B.* 19, 128; *M.* 8, 350). Yellowish crystals. V. sol.

alcohol, ether, benzene, and CS_2, nearly insol. water. By treatment with iodine in alcoholic solution it is oxidised to di-sulphido-di-cinnamic acid $S_2(C_2HPh.CO_2H)_2$.

Reference.—NITRO-SULPHYDRO-CINNAMIC ACID.

β-SULPHYDRO-CROTONIC ACID. *Ethyl derivative* $CH_3.C(SEt){:}CH.CO_2H$. [113°]. Formed from β-chloro-crotonic acid [94·5°], mercaptan, and Na (Autenrieth, *A.* 254, 235; *B.* 20, 3189). Crystals, insol. water, v. sol. ether and alcohol. Gives a dark-green colour on warming with isatin and H_2SO_4. Yields $CH_3.C(SEt){:}CH_2$ (110°) on heating above its melting-point.—BaA'_2 aq.—AgA′: silky needles, not decomposed by hot water. Ac_2O forms the compound $CH_3.C(SEt){:}CH.CO.OAc$, a brownish oil.

Isomeride of the ethyl derivative $CH_3.C(SEt){:}CH.CO_2H$. [92°]. S. (alcohol) 20. Formed in like manner from the isomeric β-chloro-crotonic acid (A.). Crystals, nearly insol. water. Forms a dark-green liquid on warming with isatin and H_2SO_4. When heated alone it yields the same ethyl-sulphydro-propylene (110°) as its isomeride.—BaA'_2 aq: thin plates (from Aq).

Phenyl derivative v. PHENYL-SULPHYDRO-CROTONIC ACID.

SULPHYDRO-ETHYL ALCOHOL $HO.C_2H_4.SH$. Formed from glycolic chlorhydrin and alcoholic KSH (Carius, *A.* 124, 258). Oil, v. e. sol. alcohol. Oxidised by HNO_3 to isethionic acid.—$Hg(C_2H_5OS)_2$. Needles (from warm alcohol).

SULPHYDRO - ETHYL - QUINAZOLINE. *Dihydride* $C_6H_4<\substack{CH_2.NEt\\NH.CS}$. [103°]. Formed by warming ω-tolyl-ethyl-thio-urea with HCl (Söderbaum a. Widman, *B.* 22, 2936). Needles. —$B'HAuCl_4$. [118°].—$B'_2H_2PtCl_6$. [208°].

SULPHYDRO - METHANE DISULPHONIC ACID $HS.CH(SO_3H)_2$. Formed by boiling the tri-sulphonic acid with HOAc (Albrecht, *A.* 161, 134). Gives a blue colour with $FeCl_3$.—$K_2A''\frac{1}{2}$aq. —$Pb_3(CHS_2O_6)_2$ 8aq. Small needles.

Sulphydro-methane trisulphonic acid $HS.C(SO_3H)_3$. Formed by boiling CS_2 or $CSCl_2$ with K_2SO_3Aq.—K_3A''' 2aq: triclinic crystals. S. 2 at 12°. Gives a blue colour with $FeCl_3$.—$(NH_4)_3A'''$ aq. Thin plates.

SULPHYDRO-METHENYL-AMIDO-CRESOL $\left[4\ \substack{1\\2}\right]$ $C_6H_3Me<\substack{O\\N}>C.SH$. [217°]. Formed by heating benzene-azo-*p*-cresol with CS_2 at 200° (Jacobsen a. Schenke, *B.* 22, 3235). Needles.

SULPHYDRO - METHENYL - AMIDO - (α) - NAPHTHOL $C_{10}H_6<\substack{N\\O}>C.SH$. [above 220°]. Formed by heating an alcoholic solution of $S_2(C_{10}H_6.NH_2[1{:}2])_2$ with CS_2 (Jacobson, *B.* 21, 2624). Needles. Oxidised by K_3FeCy_6 to a crystalline disulphide.

Sulphydro - methenyl - amido - (β) - naphthol. [249°]. Formed by heating benzene-azo-(β)-naphthol with CS_2 at 250° (Jacobson, *B.* 21, 414). Needles, sl. sol. benzene. HClAq at 170° yields amido-(β)-naphthol. An alcoholic solution of iodine forms crystalline $(C_{10}H_6<\substack{N\\O}>C)_2S_2$.

SULPHYDRO - METHENYL - α - AMIDO-NAPHTHYL MERCAPTAN $C_{10}H_6<\substack{N\\S}>C.SH$. [above 240°]. Formed by heating α-naphthyl thiocarbimide with S at 225°, and got also by the action of CS_2 on di-amido-di-naphthyl di-sulphide (Jacobson, *B.* 21, 2625; 24, 1406). Minute rosettes, sol. alcohol. Oxidised by K_3FeCy_6 to $(C_{10}H_6<\substack{N\\S}>C)_2S_2$.—$B'HgCl_2$. [210°].

Sulphydro - methenyl - amido - (β) - naphthyl mercaptan [232°]. Formed by heating (β)-naphthyl thiocarbimide with S. Minute needles. Yields a methyl ether [74°], crystallising in needles.

SULPHYDRO - METHENYL - *o* - AMIDO-PHENOL $C_6H_4<\substack{N\\O}>C.SH$. *Thiocarbamido-phenol.* [196°]. Formed by boiling an alcoholic solution of *o*-amido-phenol for several days with CS_2 in a current of H as long as H_2S is given off (Dünner, *B.* 9, 465). Formed also by heating oxy-phenyl-thio-urea, and by heating *o*-oxy-phenyl-allyl-thio-urea with HCl at 130° (Von Chelmicki, *J. pr.* [2] 42, 442; *B.* 20, 177). Obtained also by adding dilute alcohol to a mixture of potassium xanthogenate and amido-phenol hydrochloride (Kalckhoff, *B*, 16, 1825). Needles (from water), sl. sol. cold water. Sol. NH_3Aq, crystallising therefrom unaltered.

Reactions.—1. Converted in *o*-amido-phenol by HClAq at 170°, and by NH_3Aq at 200°.—2. Ac_2O yields $C_6H_4<\substack{N\\O}>C.SAc$ [120°].—3. BzCl forms benzenyl - amido - phenol and $C_6H_4(NHBz).OBz$.—4. An alcoholic solution of iodine, added to its solution in NaOHAq, forms $(C_6H_4<\substack{N\\O}>C)_2S_2$ [110°], which is re-converted by hot dilute NaOHAq into sulphydro-methenyl-amido-phenol. — 5. Boiling methyl-aniline forms a base (? $C_6H_4<\substack{N\\O}>C.NPhMe$) which yields $B'_2H_2PtCl_6$.

Salt.—AgC_7H_4NSO. Amorphous.

Ethyl ether EtC_7H_4NSO. (c. 267°). Solid, melting below 35°; volatile with steam.

SULPHYDRO-METHENYL-AMIDO-PHENYL-MERCAPTAN $C_6H_4<\substack{N\\S}>C.SH$. [179°] (H.); [174°] (J. a. F.).

Formation.—1. By digesting *o*-amido-phenol with CS_2 (Hofmann, *B.* 20, 1789).—2. By heating $C_6H_5.N_2.C_6H_5$ with CS_2 at 265° (Jacobson a. Frankenbacher, *B.* 24, 1403).—3. By heating phenyl thiocarbimide with sulphur.

Properties.—Needles or plates, v. sol. alcohol and ether. Forms $B'HgCl_2$. Oxidised by $K_2Cr_2O_7$ to $(C_6H_4<\substack{N\\S}>C)_2S_2$, which yields $B'K_2Cr_2O_7$ [180°]. MeI yields $C_6H_4<\substack{N\\S}>C.SMe$ [52°], which forms $B'_2H_2PtCl_6$, crystallising in plates.

SULPHYDRO - METHENYL - BENZENYL - THIO-AMIDOXIM $C_6H_5.C<\substack{N.S\\N}>C.SH$. [162°]. Formed by the action of CS_2 on an alkaline alcoholic solution of benzenyl-amidoxim (Crayen, *B.* 24, 388). Needles, nearly insol. water and cold alcohol. Conc. HClAq at 150° decomposes it into benzoic acid, CO_2, NH_3, H_2S, and S. NaOEt and EtI yield $C_6H_5.C<\substack{N.S\\N}>CEt$ [49°].

while benzyl chloride forms, in like manner, $C_4H_3.C<\begin{matrix}N.S\\N\end{matrix}>C.CH_2Ph$ [79°].

SULPHYDRO - METHENYL - *p* - TOLYL - METHENYL-THIO-AMIDOXIM $C_9H_8N_2S_2$ *i.e.* $C_6H_4Me.C<\begin{matrix}N.S\\N\end{matrix}>C.SH$. [166°]. Formed from CS_2 and tolyl-methenyl-amidoxim (Crayen, *B.* 24, 391). Crystals (from alcohol acidulated with HOAc), insol. water, sl. sol. ether. Forms salts with bases. *p*-Tolyl-methenyl-amidine forms the salt $C_6H_4Me.C(NH_2):NHHA'$ [172°]. Boiling EtI and NaOEt yield $C_6H_4Me.C<\begin{matrix}N.S\\N\end{matrix}>C.SEt$ [37°].

SULPHYDRO - METHYL - GLYOXALINE $C_4H_6SN_2$ *i.e.* $\begin{matrix}CH.NMe\\CH-N\end{matrix}>C.SH$. [142°]. (c. 280°). Formed by boiling $CH(OEt)_2.CH_2.NH_2$ with methyl thiocarbimide, alcohol, and dilute (30 p.c.) H_2SO_4 (Wohl a. Marckwald, *B.* 22, 1354). Plates, v. sol. water, sol. alcohol.—B'_2PtCl_4.—$B'AuCl_3$.—$C_4H_5AgSN_2$.—B'MeI. [148°]. Needles.

Methyl derivative $\begin{matrix}CH.NMe\\CH-N\end{matrix}>C.SMe$. *Methylimidazolyl methyl sulphide.* (225° uncor.). Formed by treatment with MeI and alkalis. Liquid, miscible with water, alcohol, and ether. Boiling dilute HNO_3 forms $C_5H_7(NO_2)SN_2$ [85°], which yields $B'_2H_2PtCl_6$ [197°]. $C_5H_8SN_2MeI$. [173°]. Needles, v. sol. Aq.

Reference. — OXY-SULPHYDRO-DI-METHYL-GLYOXALINE.

SULPHYDRO-DI-METHYL-PYRIDINE $CS<\begin{matrix}CH:CMe\\CH:CMe\end{matrix}>NH$. [210°-215°]. Formed by heating oxy-di-methyl-pyridine with P_2S_5 at about 160° (Guthzeit a. Epstein, *B.* 20, 2113). Needles, v. sol. hot water and alcohol.

SULPHYDRO - METHYL - QUINAZOLINE. *Dihydride* $C_6H_4<\begin{matrix}CH_2.NMe\\NH.CS\end{matrix}$. [139°]. Formed by warming ω-oxy-tolyl-methyl-thio-urea with HClAq (Söderbaum a. Widman, *B.* 22, 2935). Needles.—$B'_2H_2PtCl_6$. [195°].—$B'HAuCl_4$. [153°]. Minute needles.

SULPHYDRO-METHYL-QUINOLINE $C_{10}H_9NS$ *i.e.* $C_6H_4<\begin{matrix}CMe:CH\\N=C.SH\end{matrix}$. [253°]. Formed by heating (*Py.* 3,1)-oxy-methyl-quinoline with P_2S_5 (Roos, *B.* 21, 625). Small brown needles (from alcohol). Tastes bitter. Insol. cold water. Does not react with hydroxylamine and phenyl-hydrazine. H_2O_2 forms $C_{20}H_{16}N_2S_2$ [167°] crystallising from benzene in plates. EtI and alcohol at 100° form $C_6H_4<\begin{matrix}CMe:CH\\N=C.SEt\end{matrix}$, which is oily and yields B'HI [240°] and $B'_2H_2PtCl_6\frac{1}{2}aq$ crystallising in reddish prisms.

Sulphydro-methyl-quinoline $C_6H_4<\begin{matrix}C(SH):CH\\N=CMe\end{matrix}$. [187°]. Got by heating (*Py.* 1,3)-oxy-methyl-quinoline with P_2S_5 at 150° (Roos, *B.* 21, 629). Yellow prisms (from water). EtI and NaOEt yield $C_{10}H_8EtNS$ [56°].—B'HCl. [205°-210°] (Conrad a. Limpach, *B.* 21, 1972).

SULPHYDRO-METHYL-THIAZOLE. *Dihydride* $\begin{matrix}CHMe.S\\CH_2-N\end{matrix}>C.SH$. [82°]. Formed from β-bromo-propyl-amine hydrobromide, NaOHAq, and CS_2 (Hirsch, *B.* 28, 968). White needles, v. sol. hot water. Yields $C_3H_3MeNS(SMe)$ (217°), $C_3H_3MeNS(SEt)$ (229°), and the propyl ether $C_3H_3MeNS(SC_3H_7)$ (247°).

ψ-SULPHYDRO-(α)-NAPHTHYL-METHYL-BIAZOLE $O<\begin{matrix}CMe:N\\CS-NC_{10}H_7\end{matrix}$. [86°]. Formed from acetyl (α)-naphthyl-hydrazine and $CSCl_2$ in $CHCl_3$ (Preund, *B.* 24, 4184). Yellow needles, v. e. sol. alcohol. The isomeride from (β)-naphthyl-hydrazine melts at 109°.

SULPHYDRO-PENTHIAZOLE. *Dihydride* $CH_2<\begin{matrix}CH_2.S\\CH_2.N\end{matrix}>C.SH$. [132°]. Formed by shaking γ-bromo-ethylamine hydrobromide with NaOHAq and CS_2 in the cold (Gabriel a. Lauer, *B.* 23, 92). Crystals, v. sol. hot water and alcohol, insol. acids, sol. NaOHAq. Bromine-water at 100° produces $CH_2(NH_2).CH_2.CH_2.SO_3H$.

ψ - SULPHYDRO - PHENYL - AMIDO - (α) - NAPHTHYL-THIOBIAZOLE $C_{18}H_{13}N_3S_2$ *i.e.* $S<\begin{matrix}C(NHPh):N\\CS.N(C_{10}H_7)\end{matrix}>$. [255°]. Formed by mixing $NHPh.CS.NH.NHC_{10}H_7$ with $CSCl_2$ in benzene (Preund, *B.* 24, 4192). Colourless crystals, v. sol. acetone, sl. sol. alcohol.

ψ - SULPHYDRO - PHENYL - METHYL - BIAZOLE $O<\begin{matrix}CS.NPh\\CMe:N\end{matrix}$. [72°]. Formed from dichloro-phenyl-methyl-biazole dihydride and alcoholic ammonium sulphide (Freund a. Kuh, *B.* 23, 2837). Formed also from NHAc.NHPh and $CSCl_2$ (Freund a. Goldschmidt, *B.* 21, 2456). Prisms (from alcohol). Yields phenyl thiocarbimide on distilling with P_2S_5.

SULPHYDRO-PHENYL-GLYOXALINE $C_9H_8N_2S$ *i.e.* $\begin{matrix}CH:CH\\N:C(SH)\end{matrix}>NPh$. [181°]. Formed by boiling $NHPh.CS.NH.CH_2.CH(OEt)_2$ with dilute H_2SO_4 (Wohl a. Marckwald, *B.* 22, 569, 1353). Needles (from hot water), v. sol. NaOHAq, insol. NH_3Aq.—Salts: $C_9H_7AgN_2S$.—$B'_2H_2PtCl_6$: deep-red crystals.—B'MeI. [152°].

Methyl derivative $\begin{matrix}CH:CH\\N=C(SMe)\end{matrix}>NPh$. [54°]. Formed by treatment with alcoholic NaOH and MeI. White needles (from alcohol), insol. water.—$B'C_6H_3N_3O_7$.—$B'HNO_3$. Needles, v. e. sol. water.—B'MeI. [177°]. Crystalline rosettes (from water). Oxidised by dilute HNO_3 to a nitro- compound [116°].

ψ - SULPHYDRO - PHENYL - DI - METHYL - PYRIDINE DICARBOXYLIC ETHER $CS<\begin{matrix}CMe:C(CO_2Et)\\CMe:C(CO_2Et)\end{matrix}>NPh$. [245°]. Formed by heating $CS<\begin{matrix}CMe:C(CO_2Et)\\CMe:C(CO_2Et)\end{matrix}>O$ with aniline and HOAc (Guthzeit a. Epstein, *B.* 20, 2112). Sulphur-yellow crystals (from alcohol).

ψ - SULPHYDRO - PHENYL - NAPHTHYL - BIAZOLE $O<\begin{matrix}CS.NC_{10}H_7\\CPh:N\end{matrix}$. [164°]. Formed from $NHBz.NHC_{10}H_7$ and $CSCl_2$ in $CHCl_3$ (Preund, *B.* 24, 4186). Needles, v. sol. alcohol.

SULPHYDRO - PHENYL - QUINAZOLINE. *Dihydride* $C_6H_4<\begin{matrix}CH_2.NPh\\NH.CS\end{matrix}$. [197°]. Formed by warming ω-oxy-tolyl-phenyl-thio-urea with conc. HClAq (Söderbaum a. Widman, *B.* 22, 1671). Needles. — $B'_2H_2PtCl_6$. [219°]. — $B'HAuCl_4$. [197°]. Needles.

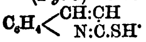
Reference.—OXY-SULPHYDRO-PHENYL-QUINAZOLINE.

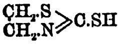
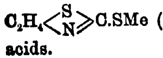
DI-SULPHYDRO-DI-PHENYL-THIO-UREA. *Di-methyl derivative* $CS(NH.C_6H_4.SMe)_2$. [162°]. Formed by boiling [1:2] $NH_2.C_6H_4.SMe$ with CS_2 and solid KOH (Hofmann, *B.* 20, 1794). Prisms, v. sl. sol. alcohol. Forms, when heated, $SCN.C_6H_4.SMe$ (c. 270°).

β-SULPHYDRO-PROPIONIC ACID $CH_2(SH).CH_2.CO_2H$. Formed from β-iodopropionic acid and KSH. Got also by reducing sulphido-dipropionic acid (Lovén, *J. pr.* [2] 29, 376). Liquid, miscible with water, alcohol, and ether. Easily oxidised by air. $CuSO_4$ gives a pale-violet pp., but if not in excess it forms a yellow pp. of $CH_2(SCu).CH_2.CO_2H$ while $S(C_2H_4.CO_2H)_2$ remains dissolved. —$Hg(S.C_2H_4.CO_2H)_2$. Scales. —$Bi(S.C_2H_4.CO_2H)_3$.

Isomeride.—Thiolactic acid.

SULPHYDRO - PROPYL - PHTHALIMIDE $C_8H_4O_2:N.CH_2.CH_2.CH_2SH$. [48°]. Formed by heating γ-bromo-propyl-phthalimide with KSHAq at 100° (Gabriel a. Lauer, *B.* 23, 88). Needles (from hot ligroïn). Fuming HClAq at 180° forms phthalic acid and γ-amido-propyl mercaptan.

(*Py.* 3)-**SULPHYDRO-QUINOLINE**  $C_6H_4\left\langle\begin{array}{l}CH:CH\\N:C.SH\end{array}\right.$ [174°]. Formed by heating (*Py.* 3)-oxy-quinoline with P_2S_5 at 140° (Roos, *B.* 21, 620). Yellow plates (from dilute alcohol), insol. cold water, sol. acids and alkalis. Oxidised by H_2O_2 to $C_{18}H_{12}N_2S_2$ [137°]. EtI and alcohol at 100° form $C_9H_6(SEt)NHI$ [154°], which yields $(C_9H_6(SEt)N)_2H_2PtCl_6aq$, melting, when anhydrous, at 190°.

SULPHYDRO - THIAZOLE. *Dihydride*  $\left.\begin{array}{l}CH_2.S\\CH_2.N\end{array}\right\rangle C.SH$. [107°]. Formed from bromo-ethyl-amine, NaOH, CS_2, and alcohol (Gabriel, *B.* 22, 1152). Needles, sol. alcohol and hot water. Sol. alkalis. Bromine-water yields taurine. Alcohol, KOH and MeI form oily  $C_2H_4\left\langle\begin{array}{c}S\\N\end{array}\right\rangle C.SMe$ (217°), insol. alkalis but sol. acids.

Reference.—Oxy-sulphydro-thiazole.

SULPHYDRO-ACETONE. The compound $CH_3.C(SEt)_2.CH_2SEt$ (170°) is formed by passing gaseous HCl into $CH_3.CO.CH_2SEt$ mixed with mercaptan (Autenrieth, *B.* 24, 167).

ω-SULPHYDRO-*o*-TOLUIC ACID. *Methyl derivative* $CH_2(SMe).C_6H_4.CO_2H$. [138°]. Formed by the action of conc. HClAq at 100° on the nitrile $CH_2(SMe).C_6H_4CN$ (278°), which is got by dissolving thio-phthalimidine in alcoholic KOH and adding MeI (Day a. Gabriel, *B.* 23, 2484). Light oil.

SULPHYDRO-ISOVALERIC ACID $CHPr(SH).CO_2H$. Formed from α-bromo-isovaleric acid and alcoholic KSH (Duvillier, *Bl.* [2] 30, 507).

SUPER. *Use of this prefix applied to inorganic compounds.* The prefix *super* is sometimes employed to denote the presence in compounds of relatively more of the characteristic negative element, or elements, than is found in the normal compounds of the same form. The prefix *per* is, however, much oftener used than *super.* It has been proposed by Mendeléeff to designate the oxides that belong to the same type as H_2O_2 *superoxides*, to distinguish them from other peroxides (*v.* Oxides, vol. iii. p. 660).

M. M. P. M.

SUPERBIN. A poisonous substance contained in the root of *Gloriosa superba* (Warden, *Ph.* [3] 11, 495).

SYCOCERYL ALCOHOL $C_{32}H_{54}O$. *[114°]. Occurs as acetyl derivative in the resin of Ficus rubiginosa* (De la Rue a. Müller, *C. J.* 5, 62; Rennie a. Goyder, *C. J.* 61, 916). Thin crystals (from alcohol), insol. water and alkalis. BzCl yields a crystalline benzoyl derivative.

Acetyl derivative $C_{34}H_{56}O_2$. [121°]. Flat six-sided tablets, v. sol. hot alcohol, ether, and chloroform.

SYLVANE C_5H_6O. (63°). S.G. ·887. Got by distilling pine-wood (Atterberg, *B.* 13, 879). Liquid, readily resinified. Oxidised by $KMnO_4$ to acetic acid. Not attacked by Na, alkalis, or Ac_2O. HCl passed into its ethereal solution forms a small quantity of $C_{15}H_{22}O$, a liquid boiling at 240°.

SYLVANE-ACETIC ACID *v.* Methyl-furfuryl-acetic acid.

SYLVANE - CARBOXY-ACETIC ACID *v.* Methyl-carboxy-furfuryl-acetic acid and Methronic acid.

SYLVESTRENE *v.* Terpenes.

SYLVIC ACID C = 78·7 p.c. H = 9·7 p.c. [c. 162°]. $[\alpha]_D = -53°$. This acid is obtained from colophony by repeated crystallisation from dilute alcohol, and is perhaps identical with abietic acid (Liebermann, *B.* 17, 1884; Haller, *B.* 18, 2166). By heating with HI and P it is converted into a terpene $C_{10}H_{16}$. Sylvic acid appears also to be formed by the action of gaseous HCl on an ethereal solution of dextro-pimaric acid (Vesterberg, *B.* 19, 2173). A sylvic acid $C_{20}H_{30}O_2$ is described by Maly (*Sitz. W.* 44, 121) as formed by adding dilute H_2SO_4 or gaseous HCl to a solution of abietic acid. Duvernoy (*A.* 148, 147) obtained a sylvic acid [129°] by distilling pimaric acid *in vacuo*.

Isosylvic anhydride $C_{40}H_{58}O_3$. (250° at 30 mm.). $\alpha_D = +63°$. Got by distilling rosin *in vacuo* (Bischoff, *B.* 23, 1921). Colourless, brittle, microcrystalline substance, insol. water, v. sol. alcohol and ether. Isosylvic acid [62°] is ppd. on adding dilute HOAc to its solution in potash.

SYLVINOLIC ACID $C_{25}H_{38}O_4$? [130°]. Formed, together with sylvic acid, by saturating an alcoholic solution of abietic acid with HCl (Maly, *Sitz. W.* [2] 44, 121). Amorphous powder, v. sol. alcohol and ether.—CaA″.—Ag_2A'': pulverulent pp., insol. NH_3Aq.

SYMBOLS. Symbols are employed to express the composition, and, as far as possible, the interactions, of compounds; *v.* Equations, chemical (vol. ii. p. 433), Formulæ (vol. ii. p. 572), Isomerism (vol. iii. p. 79), and *cf.* Optical methods (this vol. p. 253). M. M. P. M.

SYNANTHRENE $C_{14}H_{10}$. *Phosene.* Occurs in crude anthracene (Zeidler, *A.* 191, 298; *cf.* Barbier, *A. Ch.* [5] 7, 526). Yellowish-white plates. Yields a di-bromo- derivative $C_{14}H_8Br_2$ [175°], crystallising in minute yellow needles, sol. alcohol (difference from di-bromo-anthracene). Di-bromo-synanthrene is oxidised by CrO_3 and HOAc to a quinone (?) [240°-250°].

SYNANTHRIN *v.* Inulin.

SYNTHESIS. The building up of compounds from their elements, or from groups of elements.

SYNTONIN *v.* PROTEÏDS.

SYRINGIN $C_{17}H_{24}O_9$. [191°]. *Dimethoxy-coniferin.* Occurs in the bark of the lilac (*Syringa vulgaris*) and of the privet (*Ligustrum vulgare*) (Bernays, *J. pr.* 25, 121; Kromayer, *Ar. Ph.* [2] 108, 7; 109, 18, 216; 113, 19; Körner, *G.* 18, 215). White needles (containing aq), v. sl. sol. cold water, v. sol. alcohol, insol. ether. Its aqueous solution is slightly bitter, is lævorotatory, and does not ppt. metallic salts. Conc. HNO_3 gives a blood-red solution. Conc. HClAq forms a colourless solution, turning blue, and finally giving a blue pp. Conc. H_2SO_4 gives a yellowish-green colour, changing to violet-brown and, on pouring into water, giving a bright-blue solution, which soon deposits an azure powder. Does not reduce Fehling's solution. Decomposed by emulsin into glucose and syringenin. $KMnO_4$ yields glucosyringic acid. CrO_3 forms glucosyringic aldehyde.

Syringenin $C_{11}H_{14}O_4$ *i.e.* [5:3:4:1]? $C_6H_2(OMe)_2(OH).C_3H_4.OH$. Formed as above. Resembles coniferyl alcohol.

Glucosyringic acid $C_{15}H_{20}O_{10}$. [206°]. Formed as above. Needles or prisms (containing 2aq), sl. sol. cold water. Decomposed by dilute H_2SO_4 into syringic acid and glucose.

Syringic acid $C_6H_2(OH)(OMe)_2.CO_2H$. *Di-methyl derivative of gallic acid.* [202°]. Decomposes at 230° into CO_2 and the di-methyl derivative of pyrogallol.—$BaA'_2$3aq: four-sided tables.—MeA'aq. [83·5°]. Crystals, sol. Aq.

Methyl derivative $C_6H_2(OMe)_3.CO_2H$. [168°]. Needles. Yields $C_6H_3(OMe)_3$ when distilled with lime. Identical with the tri-methyl derivative of gallic acid.—MeA'. [82·5°]. Needles.

Glycosyringic aldehyde $C_{15}H_{20}O_9$. [162°]. Colourless, silky needles. Decomposed by emulsin or dilute H_2SO_4 into glucose and syringic aldehyde. Yields a phenyl-hydrazide [156°] and a crystalline oxim.

Syringic aldehyde $C_9H_{10}O_4$ *i.e.* $C_6H_2(OH)(OMe)_2.CHO$. [111·5°]. Small needles, smelling like vanillin. Turns brown in air. Reacts with phenyl-hydrazine, and combines with $NaHSO_3$.

T

TAIGUIC ACID *v.* Lapachic acid.

TALOMUCIC ACID $C_6H_{10}O_8$. [158°]. $[\alpha]_D = +29.4°$ at 20°. Formed from talonic acid and HNO_3 (S.G. 1·15) (Fischer, *B.* 24, 3625). Minute plates, v. e. sol. cold water and warm alcohol; v. sl. sol. ether. Converted by HCl and HBr at 150° into dehydromucic acid. Yields a phenyl-hydrazide [185°–190°]. Pyridine at 150° forms mucic acid.—CaA″: crystalline powder.

TALONIC ACID $C_6H_{12}O_7$. Formed by heating galactonic acid with pyridine at 150° (Fischer, *B.* 24, 3622). Purified by means of its brucine salt. Syrup, very soluble hot alcohol. Lævorotatory. Yields a phenyl-hydrazide $C_6H_{11}O_6(N_2H_2Ph)$ [c. 155°].—CaA′$_2$aq. Needles (from alcohol), v. e. sol. water.—Brucine salt. [130°–133°]. Crystals, v. sol. water.

TAMPICIN $C_{34}H_{54}O_{14}$. [130°]. A neutral substance resembling convolvulin, occurring in *Tampica Jalap* (Spirgatis, *N. R. P.* 19, 452). Resin, v. sol. alcohol and ether. Converted by hot baryta-water into amorphous tampicic acid $C_{34}H_{60}O_{17}$. Boiling dilute acids resolve tampicin into glucose (3 mols.) and tampicolic acid $C_{16}H_{32}O_3$, which crystallises from dilute alcohol in minute needles and forms NaA′ and EtA′, both being crystalline.

TANACETIN $C_{11}H_{16}O_4$. A bitter substance obtained from the leaves and flowers of the tansy (*Tanacetum vulgare*) (Leroy, *J. Chim. Med.* 21, 357; Leppig, *J.* 1882, 1175). Amorphous, sol. water and alcohol.

TANACETOGENIC ACID $C_9H_{14}O_2$. (114° at 15 mm.). Formed by the action of Br and (4 p.c.) NaOHAq on tanacetone (Semmler, *B.* 25, 3346). Oil, solidified below 0°.—AgA′.

TANACETONE $C_{10}H_{16}O$. (84·5° at 13 mm.). Occurs in oil of absinthe, thuja, and sage, constituting the chief part of absinthol, salviol, and (β)-thujol (Semmler, *B.* 25, 3343, 3350). Got from ethereal oil of *Tanacetum vulgare* by shaking with $NaHSO_3$, decomposing the crystalline product with Na_2CO_3, and distilling with steam. Oil, v. sol. alcohol and ether. Does not reduce ammoniacal $AgNO_3$. Dextrorotatory; $\alpha = 38\frac{1}{2}°$ in a 20 c.m. tube. S.G. ^{22} ·913. $\mu_D = 1·450$.

Reactions.—1. Br and KOHAq yield bromoform, hence it probably contains $CO.CH_3$.—2. Reduced in alcoholic solution by Na to tanacetyl alcohol $C_{10}H_{18}O$, (93° at 13 mm.), S.G. ^{22} ·925, $\mu_D = 1·4635$. This body does not combine with Br. With PCl_5 it yields tanacetyl chloride (72° at 10 mm.).—3. Oxidised by $KMnO_4$ to Tanacetketocarboxylic acid $C_{10}H_{16}O_3$. Needles [78°] (from ligroin) or plates [74·5°] (from water). Yields AgA′. Hydroxylamine yields $C_{10}H_{16}O_2(NOH)$ [103] when prepared from the needles and [169°] when got from the plates. The ketonic acid is oxidised by Br and NaOH to tanacetogen dicarboxylic acid $C_9H_{14}O_4$ [142°]. Plates (from water). This acid yields Ag_2A'' while Ac_2O yields the anhydride $C_9H_{12}O_3$ [55°], which gives isopropyl succinic acid [114°] when fused with potash.

Oxim $C_{10}H_{16}$:NOH. [52°]. (136° at 20 mm.). Reduced in alcoholic solution by Na to tanacetylamine $C_{10}H_{17}NH_2$ (80·5 at 14 mm.), S.G. ^{22} ·874, μ_D 1·462, which yields B′HCl, which when heated gives tanacetene $C_{10}H_{16}$ (65° at 14 mm.), S.G. ^{22} ·841, μ_D 1·476. Tanacetone oxim may be converted by warming with alcohol and dilute sulphuric acid into the cymidine $C_6H_2(C_3H_7)(NH_2)Me$ [1:3:4], whence nitrous acid forms carvacrol.

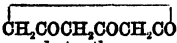
TANACETOPHORONE $C_9H_{14}O$. (90° at 13 mm.). S.G. ^{19} ·938. μ_D 1·482. Got by distilling tanacetogen dicarboxylic acid with soda-lime

(Semmler, *B.* 25, 3350). An oil, smelling like camphor-phorone. Reacts with hydroxyl-amine.

TANGHININ $C_{27}H_{40}O_8 2aq.$ [182°]. $[\alpha]_D = -67°$. Obtained from the kernels of *Tanghinia venenifera* of Madagascar (Arnaud, *C. R.* 108, 1255; 109, 701). Crystals (from alcohol), v. sl. sol. water, sl. sol. ether. Cardiac poison. Resinified by dilute acids. Baryta-water at 180° forms $C_{27}H_{44}O_{10}$.

TANNIN. TANNIC ACIDS. Under the above names are included a large series of compounds, occurring in the vegetable kingdom, of different constitutions, many of which have been very imperfectly studied. Their chief characteristics are their astringent taste and property of giving a dark-blue or green colouration with iron salts and a precipitate with a solution of gelatin. They all reduce solutions of the noble metals, and absorb oxygen in presence of alkalis. They are all aromatic derivatives, and yield on fusion with potash either pyrogallol or pyrocatechin. In some cases they have been synthetically prepared from these phenols and their derivatives, but in many cases the tannin appears to exist in the plant as a glucoside and attempts at a synthetical production have proved futile. Schiff (*B.* 15, 2590) prepared some of the tannins synthetically, and concluded that they were anhydro- compounds of gallic and protocatechuic acids respectively. Etti (*A.* 186, 332) and others have also, for example, synthetically prepared catechutannic acid by heating pyrocatechin with water or alkalis. Gallotannic acid was formerly believed to be a glucoside, but subsequent investigation showed that the amount of sugar present was variable, and Schiff (*A.* 170, 43) finally proved that, although existing in the plant as a very unstable glucoside, when it was isolated it had the constitution of an anhydro- acid formed by the removal of one molecule of water from two molecules of a trioxy-benzoic acid. He considered that in gallotannic acid the anhydride was formed thus:— $C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH$, whilst C. Etti, who has similarly investigated the tannins of the formulæ $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$ has proved that they also are not glucosides, and regards them as derivatives of a ketonic acid of the formula $C_6H_2(OH)_3.CO.C_6H(OH)_3COOH$. It would appear, then, possible to define the tannic acids as mono-carboxyl acids formed by condensation from two molecules of poly-oxy-benzoic acids and which exist as unstable glucosides in plants. The ease with which gallotannic acid is hydrolysed renders it probable that the difference in constitution between Schiff's and Etti's formulæ does actually exist, and renders it possible to subdivide the tannins into these two groups so soon as the different tannins have been re-examined from this point of view. The ketonic character of the tannins was established by Etti through noting that they reacted with phenyl-hydrazine and hydroxylamine.

The origin of tannin in plants has given rise to much debate. According to Waage (*Ph.* 1890; *Phar. Centr.* 1891, 247) its formation is similar to that of the conversion of glucose into starch. The plant removes one molecule H_2O from glucose for reserve purposes, and if under favourable circumstances three molecules H_2O can be removed, a body having the composition of a triketohexamethylene would be produced


$CH_2COCH_2COCH_2CO$. This constitution corresponds to the secondary form of phloroglucin. It is probable that the phloroglucin combines with the CO_2 in the nascent state produced by the respiration of the plant, and is thus converted into a carboxylic acid (gallic acid); two molecules of this acid by the removal of another molecule of water would then form tannin. Light and chlorophyll are necessary for the production of tannin.

Westermaier (*B. B.* 1887, 127–143) showed that with experiments made with *Quercus pedunculata* the tannin migrates downwards through the bark and the pith. Starch is always present, and it is probable that the starch only migrates in the form of tannin. The leaves of *Rumex patentia* and *Rheum rhaponticum* give both the starch and the tannin reactions. Schultze (*A. a.* 14, 525–526; *B. C.* 18, 137), by microchemical observations, also supports the view of Sachs and Heberland that the leaves of evergreens contain tannin as a winter reserve material. Tannin and starch only rarely occur simultaneously in the same cells. When the cells are rich in starch they contain a smaller amount of tannin, and *vice versâ*.

In the case of leaves containing fatty oils and tannin, the cells which contain the oil are free from tannin, and cells containing no oil are free from starch. Kraus (*B. C.* 330–334) also notes that the formation of tannin in leaves depends on the presence of light and CO_2, but believes that it acts more as a protecting agent either to prevent the plant from being eaten or rotting than as a reserve material. He points out that as fallen leaves contain as much tannin as they did during their best time of growth, the leaf tannin is of no value to the plant. Heckel a. Schlagdenhauffen (*Ph.* July 1892) note that the protecting leaf buds of certain species of gardenia contain a resinous substance which on analysis gives figures resembling cinchotannic acid. Both the gardenias and the cinchonas belong to the same order of plants (*cf.* Cross a. Bevan, *C. J.* 41, 106; Gardiner, *Ph.* [3] 14, 588; Braemer, *Les Tannoïdes*, Toulouse, 1890; Büsgen, *C. C.* 1890, 397).

Classification.—No satisfactory classification of these bodies exists. Wagner (*Fr.* 5, 1) divides them into pathological and physiological tannins. The former are chiefly glucosides, and precipitate gelatin, yield gallic acid when hydrolysed with dense sulphuric acid, and when heated alone form pyrogallol. The physiological tannins, on the other hand, form leather, and on distillation yield pyrocatechin. The old classification into iron-blueing and iron-greening tannins is found now to be untenable, as the presence of acids and salts modifies the colour which the tannins produce with $FeCl_3$, and the purity of many of the tannins examined by the earlier investigators cannot be guaranteed.

Reactions.—The oxidation of gallic and tannin acids by nitric acid of moderate dilution yields oxalic acid and two acids, probably trioxy-glutaric and trioxy-butyric. The acetyl *o*-quercitannic acid yields the same acids on oxidation (Böttinger, *A.* 257, 248–252). Metallic Na does not reduce gallic acid in absolute alcohol, but tannic acid similarly treated undergoes simple hydrolysis, the yield of gallic acid amounting to 60 p.c. of the weight of tannin. No reduction products could be prepared (Böttinger, *A.* 258, 252–260). Ammonia and zinc-dust at 60° convert both acids into benzoic acid. Dilute H_2SO_4 and Zn also form benzoic from gallic acid (Guignet, *C. R.* 113, 200–201).

The action of heat. Most tannins begin to blacken at 120°, and at 160° decomposition into metagallic acid, and either pyrogallol or pyrocatechin, takes place. Those which yield pyrogallol usually also form a 'bloom' on leather, and give a blue colour with $FeCl_3$. This class includes galls, sumac, chestnut, and oak bark. The pyrocatechin-yielding tannins do not form a 'bloom' on leather, give green compounds with $FeCl_3$, and include hemlock, catechu, rhatany, and mangrove (Trimble, *The Tannins*, 1892).

The products of the action of heat on the tannins are best obtained by allowing the heating to take place on the material suspended in glycerin (1 g. in 5 c.c. glycerin). After heating to 200° for 30 minutes, dilute with water, and extract with ether. The ethereal extract contains either pyrogallol or pyrocatechin. The tannin must be freed from gallic acid and catechin before subjecting it to this test by previous ether extraction of the aqueous solution.

The action of dilute acids. 2 p.c. absolute HCl at 100° in sealed tubes decomposes the tannins; insoluble ellagic acid, anhydrides, or phlobaphenes separate, and the filtrate contains gallic acid, glucose, and unaltered tannin. Glucose should be removed from the tannin by repeated lead acetate precipitation before this treatment, or the amount of glucose before and after hydrolysis may be determined by Fehling's solution (Wehmer a. Tollens, *A.* 243, 327).

The action of alkalis. The pyrocatechin-yielding tannins on heating with alkali yield protocatechuic acid, and either phloroglucin or acetic acid. The pyrogallol-yielding tannins form gallic and ellagic acids (20 g. with 150 c.c. of KHO solution, sp.gr. 1·2 for 3 hours are convenient quantities (Trimble, *The Tannins*).

The tannins in the bark of oak, chestnut, horsechestnut, fir, &c., are precipitated in brominated condition by bromine water; tannin, sumach tannin, and oak wood tannin are not so precipitated (Böttinger, *A.* 240, 330). From oak tannin, Böttinger, by treating with acetic anhydride, has formed an acetyl-*o*-compound of the formula $C_{15}H_7Ac_5O_9$, and from it two bromo-derivatives $C_{15}H_{10}BrAcO_9$ and $C_{15}H_7Br_4AcO_9$ (*B.* 20, 761–766). A benzoyl-*o*-derivative has also been obtained from tannin by treatment with conc. NaOHAq and benzoyl chloride (Böttinger, *A.* 254, 370). The same author has attempted to prepare cyanhydrins, but without success. Well-dried tannic acid heated with anhydrous HCN in sealed tubes yielded only an amide of gallic acid. Treated with hydroxylamine no oxim was formed, but only gallic acid (*A.* 259, 132–136). With pure tannin phenyl-hydrazine, however, forms derivatives which do not crystallise, CO_2 and N being evolved at the same time. The tannins experimented upon were extracts of sumach, divi divi, oak wood, oak bark and pine bark; the dry precipitates contained phenyl-hydrazine derivatives of tannic and gallic acids, osazones of dextrose and lævulose, and caramel (*A.* 259, 125–132; *A.* 256, 342).

Tannin solutions are very unstable, undergoing hydrolysis into gallic acid on standing. The hydrolysis into gallic acid is almost quantitative when the acid is dissolved in conc. H_2SO_4 and then water added (Böttinger, *A.* 254, 378). When heated with $KHSO_4$ and glycerin to 119°–200° and the melt extracted with water, a residue is left soluble in absolute alcohol which contains two new acids of the composition $C_{14}H_{14}O_7$Aq and called hydrotannic and isotannic acids respectively. The former, which is the less soluble in alcohol, forms with Ac_2O a tetra-acetyl- compound while the iso- acid forms a brown tri-acetyl- compound (*C. J.* 1892, 181).

Preparation of tannic acid for pharmaceutical purposes. Pelouze in 1834 first suggested the extraction of tannic acid from galls by percolation with ether, and this method is still in use. The powdered galls are placed in a closed percolator with commercial ether containing alcohol and water. The ethereal layer contains gallic and ellagic acids, together with resins and fats and a small portion of the tannic acid; the lower aqueous solution contains nearly pure tannic acid. The percolation is stopped when the lower layer ceases to increase in volume. The B. P. method consists in taking the damp galls, macerating with commercial ether, and expressing through muslin (Leconnet a. Dominé). The purest acid is obtained when 10 pts. powdered galls are allowed to stand two days covered in a percolator with a mixture of 12 pts. ether and 3 pts. alcohol. At the end of this time the percolation is commenced until 10 pts. are obtained. One-third its volume of water is then added, and the mixture well agitated. The aqueous layer contains nearly pure tannic acid, and is evaporated rapidly *in vacuo*. The commercial acid is known under the names of ether-tannin, alcohol-tannin, or water-tannin, according to the method of extraction adopted on a large scale.

Purification.—Petroleum ether percolation removes fat, wax, and some of the colouring matter. Solution in water removes resin, and, after decantation, sodium chloride precipitates the acid. Trimble adds lead acetate to the aqueous solution to precipitate colouring matter, filters, and extracts with acetic ether. The acid is re-dissolved in water, and extracted with ether to remove the last traces of gallic acid, and the aqueous solution finally dried *in vacuo*.

Detection.—1. Dilute H_2SO_4 or HCl precipitates conc. solutions.—2. $FeCl_3$, a blue or green precipitate destroyed by long boiling, sol. weak mineral acids.—3. Lime-water precipitates the Ca salt. 4. Cinchonine sulphate precipitates white cinchonine tannate.—5. Gelatin forms leather and albumen also gives a precipitate. Alum and NH_4Cl render the precipitation more complete. 6. An alcoholic solution of thymol, followed by conc. H_2SO_4, yields a rose-coloured turbid solution (pyrogallol violet; gallic acid gives no colour: Saul, *Ph.* [3] 17, 387).—7. Iodine in presence of neutral salts gives a purple colouration (Nasser). 8. Acetate of lead acidulated with acetic acid ppts. tannic and not gallic acid (Guyard, *Bl.* 2, 41, 336).—9. NH_4Cl and NH_3 give a white precipitate rapidly becoming red, gallic acid a red colour-tion only.—10. Cl water and NH_3 give a red colouration both with gallic and tannic acids.—11. K_4FeCy_6 gives a similar reaction (Rawson, *C. N.* 59, 52-53).—12. In plants, Moll (*A. a.* 12, 496) detects tannins micro-chemically by treatment with 7 p.c. copper acetate for some days, then cuts sections, treats with a drop of 0·05 p.c. ferric acetate, washes with water and then alcohol to remove chlorophyll, and mounts in glycerin and looks for blue or green stain.—13. KCN gives a green colouration with tannin and none with gallic acid.—14. $K_2Cr_2O_7$ gives a brown pp. with most tannins.—15. Saturated solutions of NaCl, $CaCl_2$, KOAc, and a number of other salts ppt. tannins from solution. —16. Conc. H_2SO_4 dissolves the dry tannins with a yellow colour, and on heating forms dark-red rufigallic acid and then black metagallic acid.—17. HNO_3 forms a yellow colour, and finally oxidises them to oxalic acid.—18. As_2O_5 heated with the dry tannins converts most into ellagic acid.—19. Most tannins are ppd. by the alkaloids.

Estimation of tannic acid. The methods devised for the estimation of tannic acid in vegetable extracts are very numerous, and may be grouped under the following heads:—

1. Gelatin or hide-powder absorption.
2. Titration with permanganate.
3. Precipitation with metallic salts.
4. Methods not included in the above.

For details of these various processes, *vide* Proctor, *Textbook of Tanning*; Trimble, *The Tannins*; Thorpe's DICTIONARY OF APPLIED CHEMISTRY, and Rideal, *Chemical Notes on Modern Tanning*; *The Assay of Tanning Materials*; *Industries*, vol. xi. pp. 19, 139, 451. The two methods most generally employed are the hide-powder method and Löwenthal's permanganate process.

The hide-powder method is conducted as follows. A weighed quantity of the material is extracted with water and made up to a known volume. 100 c.c. of this solution is then evaporated, dried, and weighed to give the total solids present in the extract. Another portion of the same solution is agitated with, aspirated, or filtered through hide powder, and the total solids left in 100 c.c. of the solution again determined. The difference gives the quantity of tannic acid or matter which combines with gelatin per 100 c.c. of the solution (*Fr.* 24, 271).

The modified Löwenthal's process, which is now official in Germany, requires a standard solution of permanganate whose indigo value is known. A measured volume of the tannin solution, together with a known volume of indigo solution, is then titrated with the permanganate solution. Another equal volume of the tannin solution is then agitated with hide powder or shaken with a gelatin and alum solution and filtered, and the filtrate, after indigo solution of known amount has been added, is titrated with the permanganate solution. The difference in the quantity of permanganate consumed is a measure of the tannic acid present. The various tannins of commerce have different permanganate values; it is, therefore, necessary to standardise the permanganate for different tannin materials (Löwenthal, *Fr.* 16, 33; Kathreiner, *Fr.* 18, 118; Simaud, *Fr.* 22, 595; Schroeder, *Fr.* 25, 121).

Gallotannic acid $C_{14}H_{10}O_9$. Occurs in gall nuts and sumach.

Constitution.—$C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.COOH$ (Schiff, *A.* 170, 43; Paul a. Kingzett, *C. J.* 33, 217).

Solubility.—Sol. acetone, glycerin, and oils; insol. CS_2, $CHCl_3$, petroleum, and C_6H_6.

Compounds.—With gelatin contains 16·5 p.c. nitrogen = 34 p.c. tannin (Böttinger, *A.* 244, 227). (For other nitrogen values of gelatin-tannin compounds in leather, *v.* Rideal a. Trotter, *S. C. I.* 1891.) Penta-acetyl-compound $C_6H_2(OAcO)_3CO.O.C_6H_2(OAcO)_2COOH$ [137°]. (Böttinger, *B.* 17, 1504).

Action of heat.—At 215° it forms pyrogallol, CO_2, and a trace of metagallic acid $C_6H_4O_2$. Strong heating at 240°–250° forms chiefly metagallic acid (Pelouze, *A.* 10, 159). Cold HNO_3 forms oxalic, trioxyglutaric, and trioxybutyric acids (Böttinger, *A.* 257, 248). Boiling with KHO forms tannomelanic acid $C_6H_4O_3$; cold KHO and air form tannoxylic acid $C_7H_6O_6$ (Büchner, *A.* 53, 373). Hydrolysed by dil. H_2SO_4 to gallic acid. Ferments also form gallic acid (van Tieghem, *C. R.* 65, 1092).

Oak bark. Tannic acid $C_{17}H_{16}O_9$.

Preparation.—The bark is extracted with alcohol, and the extract agitated with acetic ether and ether. Evaporate off ether, separate the precipitate of ellagic acid, and from residue separate gallic acid from the tannic acid by acetic ether and ether.

Properties.—Reddish-white powder. Sol. alcohol and acetic ether. Sl. sol. ether and water. Heated to 130°–140°C. it forms an anhydride $C_{34}H_{30}O_{17}$ which is sl. sol. water; sol. alcohol and alkalis, and with conc. H_2SO_4 gives a second anhydride $C_{34}H_{25}O_{16}$. Heated with conc. HCl it evolves CH_3Cl, gives also the iodoform reaction. On dry distillation it forms pyrocatechin. Fused with KOH yields protocatechuic acid, pyrocatechol, and traces of phloroglucin (Etti, *M.* 1880, 262–278). When boiled with ether the above anhydrides form a third anhydride $C_{34}H_{26}O_{15}$ (*M.* 1883, 512). Other anhydrides analysed by Etti are $C_{40}H_{38}O_{17}$, $C_{40}H_{36}O_{16}$, $C_{40}H_{34}O_{15}$, and $C_{40}H_{32}O_{14}$. Forms two hydrates (Löwe, *C. J.* 40, 901).

Salts. With Ca, Ba, and Pb; analysed by Etti and Löwe (*l.c.*).

Derivatives.—Oak-red $C_{14}H_{10}O_8\frac{1}{2}aq$ (Grabowski, *A.* 145, 2); $C_{38}H_{28}O_{17}$ (Böttinger, *A.* 240, 341). Böttinger has prepared various bromo-, acetyl-, and benzoyl-derivatives (*l.c.*) (Rochleder, *A.* 63, 205; Böttinger, *A.* 202, 270; *B.* 14, 1598; Löwe, *Fr.* 20, 210; Etti, *M.* 4, 514; Grabowski, *A.* 145, 2).

Fraxitannic acid $C_{26}H_{32}O_{14}$. In ash-leaves. Forms an anhydride $C_{26}H_{30}O_{15}$, a benzoyl-compound $C_{26}H_{26}O_{13}(OB_3)_4$, an acetyl-compound $C_{26}H_{28}(OAc)_4O_{10}$, a bromacetyl-compound $C_{26}H_{25}(OAc)_4Br_3O_{10}2aq$, and a similar nitro-compound. On heating with $Ba(OH)_2$ it forms protocatechuic acid and other products. On heating to 100° it loses 1 mol. H_2O, forming an anhydride $C_{26}H_{30}O_{13}$ (Gintl a. Reinitzer, *M.* 3, 745 *et seq.*).

The following table gives the source of the principal tannins which have been investigated, and references to the papers in which a description will be found.

Plant	Part	Name	Formula	Per cent.	References
Æsculus Hippocastanum	Nearly all parts	Horsechestnut tannin	$C_{26}H_{24}O_{12}$	—	Rochleder, *Sitz. B.* 53 [2] 478; 54 [2] 609
Æsculus Hippocastanum	Juice of berries	Rhamnotannic acid	$C_{26}H_{24}O_{13}.H_2O$	—	Rochleder, *Z.* 1867, 84
Algarobilla	Pods	Ellagotannic acid	$C_{14}H_{10}O_{10}$ *i.e.* $C_6H_2(OH)_3.CO.O.OC_6H_2(OH)_2.COOH$?	68·38	Godeffroy, *C. N.* 40, 144; Löwe, *Fr.* 14, 35; Zölffel, *Ar. Ph.* 229, 123; Hurst, *D. P. J.* 262, 288; Eitner, *D. P. J.* 244, 80
Alnus glutinosa	Wood	Alder tannin	$C_{27}H_{28}O_{11}$	—	Dreykorn a. Reichard, *D. P. J.* 195, 157
Anacahuita	Wood and bark	—	—	—	Buchner, *J.* 1861, 771
Asperula odorata	—	Aspertannic acid	$C_{14}H_{16}O_9$	—	Schwartz, *Sitz. B.* 6, 446
Aspidium Filix-mas	Root	Filitannic acid	—	—	Malin, *A. Ch.* 63, 276
Atherosperma Moschatum	Bark	Atherosperma tannin	$C_{10}H_{16}O_3$	—	Zeyer, *J.* 1861, 769
Bablak (acacia)	Fruit	—	—	19·0	Wagner, *Fr.* 5, 10
Betula rubra	Bark	Beech tannin	$C_{20}H_{22}O_9$	—	Hofstetter, *A.* 51, 78; Etti, *M.* 10, 650
Caffea arabica	Berry	Caffetannic acid	$C_{15}H_{18}O_8$	—	Rochleder, *A.* 59, 300; *A.* 66, 39; Rochleder a. Hlasiwetz, *Sitz. B.* 9, 286
Calandra granaria (corn weevil)	—	Fracticornitannin	—	—	Villon, *C. N.* 56, 175
Calluna vulgaris	Plant without root	Callutannic acid	$C_{14}H_{14}O_9$	—	Rochleder, *A.* 84, 354; *Sitz. B.* 9, 286
Canaigre	Bark	Canaigre tannin	C 58·10 per cent. H 5·33 „ O 36·57 „ (same group as mangrove tannin)	—	*D. P. J.* July 1893
Castanea vesca	Bark	Chestnut bark tannin or gallotannic acid?	$C_{14}H_{10}O_9$? $C_6H_2(OH)_3COOC_5H_2(OH)_2COOH$	—	Trimble, *C. N.* Jan. 6, 1898
Catechu	—	Catechutannic acid	$C_{17}H_{17}O_9$?	—	Guignet, *C. R.* 113, 200
Cephalis Ipecacuanha	Root	Ipecacuanhic acid	$C_{14}H_{18}O_7$	—	Willigt, *A.* 76, 342
Cerasus acida	Bark	Cherry bark tannin	$C_{21}H_{20}O_{10}+\frac{1}{2}H_2O$	—	Rochleder, *Sitz. B.* 59, 819
Chirococca racemosa	Root	Caffetannic acid	$C_{15}H_{18}O_8$	—	Rochleder, *A.* 84, 354; *Sitz. B.* 9, 286
Cinchona	Bark	Quinotannic or cinchonatannic acid	$C_{14}H_{16}O_9$	—	Schwartz, *Sitz. B.* 7, 250; Rembold, *A.* 143, 270; Berzelius, *Lehr.* 3 *Aufl.* 6, 246; Pelletier a. Caventou, *A. Ch* 15, 337

Plant	Part	Name	Formula	Per cent.	References
Cinchona nova	Bark	Quinovatannic acid	$C_{14}H_{18}O_8$	—	Hlasiwetz, *A.* 79, 129; Rembold, *A.* 143, 278
Divi-divi	—	Ellagotannic acid	$C_{14}H_{10}O_{10}$ *i.e.* $C_6H_2(OH)_3.CO.O.O.C_6H_2(OH)_2COOH$?	—	Zölffel, *Ar. Ph.* 229, 213; Löwe, *Fr.* 14, 35; Hurst, *D. P. J.* 262, 288
Elm	Leaves in autumn	Xanthotannic acid	$C_{28}H_{36}O_{41}.3H_2O$?	—	Ferrian, *J.* 1858, 463
Erythroxylon Coca	Leaves	Cocatannic acid	$C_{17}H_{22}O_{10} + 2H_2O$?	—	Niemann, *J.* 1860, 368; Warden, *Ph.* 18, 985
Euphrasia officinalis	Green parts	—	$C_{32}H_{26}O_{20}$	—	Enz, *Vierteljahrsch. Ph.* 8, 175
Filix-mas	—	Filitannic acid	—	—	—
Fraxinus excelsior	Leaves	Fraxitannic acid	$C_{26}H_{32}O_{14}$	—	Gintl and Reinitzer, *M.* 3, 745
Galium verum	Bark	Galitannic acid	$C_{14}H_{16}O_{10} + H_2O$	—	Schwartz, *A.* 83, 57
Hemlock	Bark	Hemlock tannin	$C_{20}H_{18}O_{10}$	—	Böttinger, *B.* 17, 1041
Hops	—	Hop tannin	$C_{22}H_{26}O_9$	—	Bissell, *C. J.* 34, 328; *Ph.* [3] 8, 508; Etti, *M.* 10, 651
Ilex paraguayensis	—	Caffetannic acid ?	$C_{15}H_{18}O_8$?	—	Rochleder, *A.* 66, 39; *J.* 1856, 815; Arata, *J.* 1877, 938
Krameria triandra	Bark of root	Rhatany tannin	$C_{20}H_{20}O_9$	—	Wittstein, *J.* 1854, 656; Raabe, *J.* 1880, 1060
Larch	Bark	Larch tannin	—	—	Stenhouse, *P. M.* 23, 336
Laurus caustica	—	—	$C_{17}H_{17}O_9$?	—	*C. J.* 34, 986; *C. J.* 40, 602; Arata, *An. Soc. Cient. Argent.* 10, 193
Mangrove	Bark	—	$C_{26}H_{24}O_{12}$	—	Trimble, *Ph.* Feb. 4, 1893; *S. C. I.* 1893, 364; Stenhouse, *Pr.* 11, 405
Myrobalans	—	Ellagotannic acid	$C_{14}H_{10}O_{10}$	—	Löwe, *Fr.* 14, 44; Zölffel, *Ar. Ph.* 229, 123
Nux vomica	—	Igasuric acid	—	—	Ludwig, *Ar. Ph.* [3] ii. 187
Pinus sylvestris	Bark	Cortepinitannic or pinicortannic acid	$C_{32}H_{34}O_{17}$ $(=2C_{16}H_{14}O_7 + 3H_2O)$	—	Kwalier, *Sitz. B.* 11, 363
Pinus sylvestris	Needles	Tannopinic acid Pinitannic acid Oxypinitannic acid	$C_{28}H_{30}O_{18}$? $C_{14}H_{16}O_8$ $C_{14}H_{16}O_9$	—	Kwalier, *Sitz. B.* 11, 356
Potentilla Tormentilla	Root	—	$C_{26}H_{22}O_{11}$	—	Rembold, *A.* 145, 5
Punica Granatum	Root bark	Pomegranate tannin	$C_{20}H_{16}O_{13}$	—	Rembold, *A.* 143, 285
Quebracho Colorado	Gum or wood	Quebrachitannic acid	C 52·52 per cent. H 5·11 " O 42·37 "	—	Jean, Arata, *An. Soc. Cient. Argent.* Feb. 1879; *Bl.* 28, 16

Quercus	Bark, wood, and leaves	Quercitannic acid	$C_{15}H_{12}O_9 + 2H_2O$ (from wood) $C_{19}H_{16}O_{10}$ $C_{14}H_{14}O_7$	—	Etti, *M.* 10, 650; *M.* 1, 264; Stenhouse, *P. M.* 22, 425; Böttinger, *A.* 202, 270: Löwe, *Fr.* 20, 210
Quercus	Bark and gall-nuts	Gallotannic acid	$C_{14}H_{10}O_9$ *i.e.* $C_6H_2(OH)_3COOC_6H_2(OH)_2COOH$	—	Berzelius, *Lehrb.* 3 *Aufl.* 6, 213; Löwe, *Fr.* 11, 378; Schiff, *A.* 170, 43
Quercus Ægilops	—	—	—	19-26·7	Wagner, *Fr.* 5, 10; Stenhouse, *P. M.* 22, 424
Quercus pubescens	—	Quercitannic acid	$C_{20}H_{20}O_9$	—	Etti, *B.* 17, 1823; *M.* 1, 262
Quercus robur	—	Quercitannic acid	$C_{17}H_{16}O_9$	—	Etti, *B.* 17, 1823; *M.* 1, 262
Red wine	—	Œnotannin	—	—	Gautier, *Bl.* 27, 496
Rhododendron ferrugineum	Leaves	Rhodotannic acid	$4C_{14}H_{12}O_7 + 3H_2O$	—	Schwartz, *Sitz. B.* 9, 298
Rhubarb	Root	Rheotannic acid	$C_{20}H_{26}O_{14}$	—	Kubly, *Z.* 1869, 308
Rhus	Leaves and twigs	Gallotannic acid	$C_{14}H_{10}O_9$	—	Berzelius, *Lehrb.* 3 *Aufl.* 6, 213; Schiff, *A.* 170, 43
Rhus Coriaria	Leaves	—	—	3·4	Lidoff, *J. R.* 20, 607
Rhus Cotinus	Leaves and stalks	—	—	13·26	Lidoff, *J. R.* 20, 607
Rubia tinctoria	Leaves	Rubitannic acid	$2C_{14}H_{22}O_{12} + H_2O$	—	Willigt, *A.* 82, 340
St. Ignatius beans	Beans	Igasuric acid	—	—	Ludwig, *Ar. Ph.* [3] ii. 137
Salix triandra and S. undulata	Leaf, stems, and green twigs	—	—	—	Johanson, *Ar. Ph.* [3] 13, 103; Stenhouse, *Pr.* 11, 403
Sorbus aucuparia	Juice of ripe berries	Sorbitannic acid	—	—	Vincent a. Delachanal, *Bl.* 47, 492
Spruce	Bark	Spruce bark tannin	$C_{21}H_{20}O_{10}$?	—	Böttinger, *B.* 17, 1127
Strawberry	Root	Fragarianin	—	—	Physson, *C. N.* 38, 135
Thea	—	Quercitannic acid	$C_{17}H_{16}O_9$	10	Stenhouse, *P. M.* 23, 332; Rochleder, *A.* 63, 205; Etti, *B.* 17, 1823; *M.* 1, 262; Hlasiwetz a. Malin, *J. Pk.* 101, 109
Thuja occidentalis	Green parts	Pinitannic acid	$C_{14}H_{16}O_9$	—	Rochleder, *Sitz. B.* 29, 20
Unacaria Gambier	Leaves	—	Resembles spruce bark tannin	—	Böttinger, *B.* 17, 1129
Walnut	Episperm	Micitannic acid	—	—	Phipson, *C. N.* 20, 116

S. R.

TANSY OIL. The essential oil, obtained by distillation of the tansy (*Tanacetum vulgare*), contains 1 p.c. of a terpene $C_{10}H_{16}$ (155°–160°), 26 p.c. of an alcohol $C_{10}H_{18}O$, and 70 p.c. of 'tanacetyl hydride' $C_{10}H_{16}O$ (Bruylants, *J. Ph.* [4] 26, 393; *B.* 11, 449; *cf.* Persoz, *C. R.* 8, 433). Tanacetyl hydride $C_{10}H_{16}O$ (195°–196°), S.G. ·918, V.D. 5·1, is converted by H_2SO_4 into cymene. It reduces ammoniacal $AgNO_3$, forming a mirror. $NaHSO_3$ forms crystalline $C_{10}H_{15}NaSO_3$. Split up by water into the parent substances.

TANTALATES *v.* Tantalum, acids of, and their salts, p. 639.

TANTALUM. Ta. At. w. c. 182 (exact value not known). Mol. w. not known. Ta has not been isolated.

Occurrence.—Tantalates occur in a few rare minerals, generally associated with niobates; *tantalite* contains from 35 to 75 p.c. Ta_2O_5, *columbite* from 13 to 36 p.c., *yttrotantalite* from 6 to 47 p.c., and a mineral from Western Australia, recently analysed and called *stibio-tantalite*, c. 52 p.c., Ta_2O_5 (Goyder, *C. J.* 63, 1076).

History.—A short account of the researches that led to the identification of two distinct oxides in *tantalite* is given in the article Niobium (vol. iii. p. 505). Marignac (*C. R.* 60, 234, 1355) gave the formula Ta_2O_5 to oxide of Ta, which had been represented by Rose as TaO_2. Deville determined the V.D. of the chloride, and deduced the molecular formula $TaCl_5$ (*C. R.* 56, 891). By heating Na_2TaF_7 with Na, H. Rose (*P.* 99, 69) obtained a black powder, probably a mixture of Ta and oxides of Ta. Berzelius (*P.* 4, 6) also obtained very impure Ta; Marignac (*Ar. Sc.* 1868) failed to isolate approximately pure metal.

Preparation of impure Ta.—Very finely-powdered *tantalite* is fused with three times its weight of $KHSO_4$, in an iron or platinum crucible, until completely dissolved. After cooling, the fused substance is powdered and treated with boiling water, whereby sulphates of K, Fe, and Mn are dissolved out; the insoluble portion is washed, and then digested with yellow ammonium sulphide, whereby sulphides of Sn and W are dissolved, and FeS remains mixed with Ta_2O_5 and Nb_2O_5. The residue is washed thoroughly, and digested with HClAq to remove FeS, and the portion insoluble in HClAq is thoroughly washed with boiling water until it is white. The mixture of Ta_2O_5 and Nb_2O_5 thus obtained is dissolved in HFAq in a platinum dish, the solution is heated to boiling, and a quantity of KHF_2 is added equal to one-fourth of the weight of mixed Ta_2O_5 and Nb_2O_5 used; the liquid is evaporated until 1 g. of the mixed oxides is present in about 7 c.c. and allowed to cool; the prismatic crystals of K_2TaF_7 that separate are washed with cold water until the washings give a yellow pp., without any shade of red, after standing for two hours with tincture of galls. The K_2TaF_7 thus obtained is heated, in a platinum dish, with rather more than its weight of pure conc. H_2SO_4, whereby $KHSO_4$, HF, and Ta_2O_5 are formed; the HF is removed by heat, and the $KHSO_4$ by repeated washing with water (Berzelius, *P.* 4, 6; *cf.* H. Rose, *P.* 144, 64, 72).

Lawrence Smith (*Am.* 5, 44) recommends to warm 5 g. of very finely powdered *tantalite*, dried at 150°, in a platinum basin with a little water and 8 to 10 c.c. very conc. HFAq, to filter when reaction is completed, add a little water to the filtrate and evaporate nearly to dryness, to warm with excess of conc. pure H_2SO_4, and, after the acid has been almost wholly removed by heating, to place the residue in c. 500 c.c. dilute HNO_3Aq (L. M., *C. N.* 51, 289, 304), and boil until Ta_2O_5 and Nb_2O_5 are ppd. By dissolving in HFAq, adding KHF_2, and proceeding as described above, Ta_2O_5 is obtained free from Nb_2O_5.

The pure Ta_2O_5 obtained by one of the preceding methods is dissolved in HFAq, in a platinum vessel, the solution is heated to boiling, and 70·3 pts. by weight of KHF_2 are added for 100 pts. Ta_2O_5 used. The solution is evaporated and allowed to cool; the crystals of K_2TaF_7 are washed with a little cold water, dried, mixed with c. half their weight of potassium, and heated in an iron crucible, the mixture of K_2TaF_7 and K being covered with KCl. The contents of the crucible, after cooling, are added, little by little, to water; the black powder that separates is washed with water, and then with dilute alcohol and dried (Berzelius, *P.* 4, 6). The black powder is probably a mixture of Ta and oxides of the metal. Berzelius found that 100 pts. took up 17 pts. O when heated in air, 100 pts. pure Ta require 22 pts. O to form Ta_2O_5. H. Rose (*P.* 99, 69) obtained a black powder—probably Ta mixed with oxides—by reducing Na_2TaF_7 by heating with sodium.

Properties and Reactions.—The black powder obtained by Rose was a good conductor of electricity; it glowed when heated in the air, and slowly formed Ta_2O_5; it was insoluble in acids, except in HFAq, by which it was slowly dissolved; heated in a stream of Cl it burnt to $TaCl_5$. Oxidation was effected by molten alkalis or alkali carbonates. The S.G. of a specimen containing c. 40 p.c. acid sodium tantalate was c. 10·8.

The at. w. of Ta was determined by Marignac (*A.* 140, 153; *Suppl.* 4, 351 [1865]) by decomposing K_2TaF_7 and $(NH_4)_2TaF_7$ by H_2SO_4, and determining the quantities of Ta_2O_5 and K_2SO_4 produced. The values obtained varied from 180·1 to 185·2. H. Rose in 1856 (*P.* 99, 80) analysed $TaCl_5$ by decomposing by water, ppg. $Ta_2O_5.xH_2O$ by NH_3Aq, and estimating Cl in the filtrate. His results showed marked discrepancies.

Ta is metallic in its physical properties, so far as may be judged from the impure specimens that have been prepared. Ta_2O_5 dissolves in HFAq, probably forming TaF_5. No salts are known to be formed by replacing the H of an oxyacid by Ta. In all the salts of Ta that have been isolated, other than the haloid compounds, Ta forms part of the negative radicle. Ta is the fifth member of the even-series family of Group V.; it is closely related to Nb, and less closely to N, P, V, As, Sb, Di, Er, and Bi. The only compound of Ta whose V.D. has been determined is $TaCl_5$; in this molecule the atom of Ta is pentavalent (*v.* Nitrogen group of elements, vol. iii. p. 571).

Detection and Estimation.—Tantalum com-

pounds form potassium tantalate when fused with KOH, and the fused mass dissolves in water. The product obtained by fusion with NaOH dissolves in water to a clear liquid only after NaOH has been removed by washing, as sodium tantalate is insoluble in much NaOHAq. Addition of acid to an aqueous solution of an alkali tantalate, followed by boiling, ppts $Ta_2O_5.xH_2O$ more or less completely. By adding HClAq to a solution of an alkali tantalate, and placing zinc in the solution, no blue colour is produced (*cf.* NIOBIUM, DETECTION OF, vol. iii. p. 506). According to Levy (*C. R.* 103, 1074), an amethyst colour is produced by adding a very small quantity of Ta_2O_5 to a solution of resorcin in H_2SO_4Aq. Ta is estimated as Ta_2O_5; the process is sufficiently indicated under *Preparation*.

Tantalum, acids of, and their Salts. Ta_2O_5 reacts with molten alkalis, and alkali carbonates, to form salts which may be regarded as derived from various hydrates of Ta_2O_5. Two hydrates are obtained, $Ta_2O_5.2H_2O$ and $2Ta_2O_5.3H_2O$, by decomposing $TaCl_5$ by a little water, and by fusing Ta_2O_5 with $KHSO_4$ and washing with water (*v.* TANTALUM, OXIDES AND HYDRATED OXIDES OF, p. 640). The first of these hydrates may be called *pyrotantalic acid* $H_4Ta_2O_7$, corresponding with $H_4P_2O_7$; and the second may be formulated $H_6Ta_4O_{13}$. The tantalates that have been examined do not seem to be derived from either of these compounds, but from the hypothetical acids $HTaO_3$, corresponding with HPO_3 and HNO_3, and $H_8Ta_6O_{19}$ ($=3Ta_2O_5.4H_2O$). Tantalates are not produced by neutralising $Ta_2O_5.xH_2O$, but by fusing Ta_2O_5 with alkalis, or by double decomposition from alkali salts.

TANTALATES. The tantalates belong to the form $xTa_2O_5.yMO$, where $M = (NH_4)_2$, Mg, Hg_2, K_2, Ag_2, or Na_2; of those that have been fairly fully examined, some correspond with the metaphosphates and meta-niobates M^IXO_3, and others belong to the more complex form $M^I_8Ta_6O_{19}$. Some of the alkali tantalates dissolve slightly in water, the other tantalates are insoluble. *Fluotantalates* and *fluoxytantalates* are also known (*v. infra*). The tantalates have been investigated chiefly by H. Rose (*P.* 100, 417) and Marignac (*Bl.* [2] 6, 111, 118).

Ammonium tantalate. A pp. is obtained by adding NH_4Cl to solution of $Na_8Ta_6O_{19}.xH_2O$, but the composition of the pp. is not known with certainty.

Magnesium tantalate. By adding $MgSO_4$Aq to solution of $Na_8Ta_6O_{19}.xH_2O$ a crystalline pp. was obtained which, after drying at 100°, had the composition $Mg_4Ta_6O_{19}.9H_2O$. A crystalline Mg tantalate was obtained by Joly (*C. R.* 81, 266, 1266) by fusing Ta_2O_5 with $MgCl_2$.

Mercurous tantalate. A brown, amorphous compound, perhaps $Hg_8Ta_6O_{19}.xH_2O$, is formed by adding $HgNO_3$Aq to solution in water of $Na_8Ta_6O_{19}.xH_2O$.

Potassium tantalates. (1) $K_8Ta_6O_{19}.16H_2O$; this salt is obtained by fusing Ta_2O_5 with KOH, dissolving in water, and crystallising. (2) $KTaO_3$: this salt, *potassium metatantalate*, is formed by heating the other tantalate, alone or with $(NH_4)_2CO_3$, and then treating with water.

Silver tantalate. **The yellowish white pp. obtained by adding solution of a salt of Ag to solution of $Na_8Ta_6O_{19}.xH_2O$, and drying at 100°, has the composition $Ag_8Ta_6O_{19}.3H_2O$.**

Sodium tantalates. The *meta-salt* $NaTaO_3$ is obtained by fusing Ta_2O_5 with Na_2CO_3, and washing with water. A salt of the composition $Na_8Ta_6O_{19}.xH_2O$ ($x = 25$ and 30) is prepared by fusing Ta_2O_5 with NaOH, dissolving in water, and crystallising.

FLUOTANTALATES. (*Tantalifluorides.*) These salts may be regarded as compounds of TaF_5 with metallic fluorides, or as metallic derivatives of the hypothetical acid H_2TaF_7; they are prepared by dissolving Ta_2O_5 in HFAq, adding metallic fluorides, and crystallising; some of them are formed by dissolving Ta_2O_5 and a metallic oxide in HFAq (Marignac, *A. Ch.* [4] 9, 276; Berzelius, *P.* 4, 6).

Ammonium fluotantalate $(NH_4)_2TaF_7$ is obtained by evaporating a solution of NH_4F in solution of TaF_5 in HFAq, and evaporating; the salt is crystalline and easily soluble in water.

Copper fluotantalate $CuTaF_7$ forms blue, deliquescent, rhombic prisms; it is prepared by dissolving CuO and Ta_2O_5 in excess of HFAq, and evaporating.

Potassium fluotantalate K_2TaF_7 forms white needles by dissolving KHF_2 in solution of Ta_2O_5 in HFAq, evaporating, and crystallising from hot water. The salt is very slightly soluble in cold water, but dissolves easily in hot water. On long boiling, K_2TaF_7Aq gives a white pp., probably having the composition $K_4Ta_4O_5F_{14}$ ($=2TaF_5.Ta_2O_5.4KF$). By dissolving K_2TaF_7 in warm 4 p.c. H_2O_2Aq with a little HFAq and allowing to cool, Piccini (*Zeit. für anorg. Chemie*, 2, 21) obtained crystals of the *fluoxytantalate* $K_2TaO_2F_5.H_2O$ ($=TaO_2F_3.2KF.H_2O$).

Sodium fluotantalate $Na_2TaF_7.H_2O$; obtained, as white crystals, by dissolving $Na_8Ta_6O_{19}$ in HFAq, evaporating, and drying at 100° the salt that separates.

Zinc fluotantalate $ZnTaF_7.7H_2O$; a deliquescent salt, obtained by dissolving ZnO and Ta_2O_5 in excess of HFAq and crystallising.

Tantalum, alloys of. By heating K_2TaF_7 with Al, and washing with HClAq, Marignac (*P.* 100, 145) obtained a grey powder, S.G. 7·02. By heating to whiteness, in a carbon crucible, a mixture of Ta_2O_5 and iron filings, an alloy of Ta and Fe was obtained resembling pig iron (Gahn, Berzelius a. Eggertz, *S.* 16, 437).

Tantalum, bromide of, $TaBr_5$. A yellowish, crystalline compound, obtained by heating a mixture of dry Ta_2O_5 and C in vapour of Br, and removing excess of Br by a long-continued stream of dry CO_2; decomposed by water to HBrAq and $Ta_2O_5.xH_2O$ (H. Rose, *P.* 90, 456; 99, 75). The conditions of preparation are similar to those in making $TaCl_5$ (*q. v.*).

Tantalum, carbide of. By heating TaN (*v.* TANTALUM NITRIDE) with C to the melting-point of steel, N is given off and the nitride is partly converted into brass-yellow coloured TaC_2 (Joly, *Bl.* [2] 25, 206).

Tantalum, carbonitride of. Joly (*Bl.* [2] 25, 206) obtained a substance, to which he gave the formula 10TaC.TaN, by very strongly heating a mixture of Ta_2O_5 with C and soda.

Tantalum, chloride of, $TaCl_5$. Mol. w. c. 359 (not determined with great accuracy, as at. w. of Ta is doubtful). V.D. 185 at 360° (Deville a. Troost, *C. R.* 64, 294). Melts at 211°, and boils at 242° at 753 mm. pressure (D. a. T., *l.c.*). Only one chloride of Ta has been isolated.

Preparation.—About 5 g. pure dry Ta_2O_5 is mixed with a considerable excess of dry sugar or starch, and the mixture is completely charred by heating in a closed crucible; the charred mass is broken into small pieces, which are heated to redness and placed, while red hot, in a rather wide tube of hard glass that is quickly heated to redness while a stream of thoroughly dried CO_2 is passed through it as long as any trace of moisture is given off from the contents of the tube; the tube is then allowed to cool, the current of dry CO_2 being maintained; when the tube is cold a stream of dry Cl is passed through it, and when every part of the apparatus is filled with Cl (but not until then) the contents of the tube are heated. $TaCl_5$ forms immediately behind the carbonaceous matter, as a pale-yellow solid; when the reaction has entirely ceased and CO is no longer evolved, the $TaCl_5$ may be sublimed into another part of the tube, a plentiful stream of dry Cl being maintained during the process. If sublimation is attempted before the whole of the Ta_2O_5 has been chlorinated, a part of the $TaCl_5$ is decomposed by the CO, with re-formation of Ta_2O_5. If there should be any air in the tube during the process a white sublimate is formed which is probably an oxychloride (H. Rose, *P.* 90, 456; 99, 75). Should the Ta_2O_5 used contain any WO_3, the sublimate obtained is reddish; by gently heating, the greater part of the red $WOCl_4$ may be removed, as it is more volatile than $TaCl_5$.

Demarçay obtained $TaCl_5$ by passing vapour of CCl_4 over Ta_2O_5 heated to redness (*C. R.* 104, 111).

Properties and Reactions.—Pale-yellow prismatic needles, melting at 211°, and boiling at 242° under the pressure of 753 mm.; begins to vaporise at 144°; V.D. 185 at 360° (Deville a. Troost, *C. R.* 64, 294). Decomposes in ordinary air, giving off HCl and becoming covered with a crust of crystalline Ta_2O_5. Decomposed entirely by water to HClAq and $Ta_2O_5.xH_2O$. Conc. H_2SO_4 causes evolution of HCl, and forms a somewhat turbid solution from which $Ta_2O_5.xH_2O$ separates on boiling; by adding water to this solution, and boiling, the whole of the Ta is precipitated as $Ta_2O_5.xH_2O$. Conc. HClAq reacts similarly to H_2SO_4, but only a portion of the $Ta_2O_5.xH_2O$ is ppd. on adding water and boiling. $TaCl_5$ is partly dissolved by heating with KOHAq. $TaCl_5$ is soluble in absolute alcohol; H_2SO_4Aq does not ppt. $Ta_2O_5.xH_2O$ from this solution.

No double compounds of $TaCl_5$ with KCl or NaCl—similar to those of TaF_5—have been obtained.

Tantalum, fluoride of. $Ta_2O_5.xH_2O$ dissolves in HFAq; neither boiling, nor adding H_2SO_4Aq to the solution, ppts. Ta_2O_5. The solution in HFAq gives off vapours on evaporation that probably contain TaF_5; by evaporating at a low temperature, Rose obtained crystals that dissolved easily in water, and were partly vaporised when heated, leaving some Ta_2O_5 (*P.* 90, 456; 99, 75). By evaporating *in vacuo* a solution of $Ta_2O_5.xH_2O$ in HFAq, Marignac obtained a white amorphous mass—probably an oxyfluoride—and then small crystals that were likely TaF_5.

TaF_5 combines with some metallic fluorides, forming *fluotantalates* (*q.v.*, p. 639).

Tantalum, haloid compounds of. The only haloid compounds of Ta that have been isolated are $TaCl_5$ and $TaBr_5$. The former has been gasified, and the formula is molecular. TaF_5 also probably exists in solution of $Ta_2O_5.xH_2O$ in HFAq. There is no reaction between I and Ta_2O_5 mixed with C even at a very high temperature. $TaCl_5$ and $TaBr_5$ are readily decomposed by water, with formation of $Ta_2O_5.xH_2O$ and HXAq. Double compounds of TaF_5 with some metallic fluorides are known; they belong to the form $M^I_2TaF_7$ (*v.* FLUOTANTALATES). Oxyhaloid compounds probably exist, but none has been isolated with certainty.

Tantalum, nitrides of. $TaCl_5$ absorbs NH_3 at the ordinary temperature; by heating the product in NH_3, Joly (*Bl.* [2] 25, 206) obtained an amorphous, yellow solid, to which he gave the formula Ta_3N_5. By heating this yellow solid to redness in very dry NH_3, a black solid was obtained which, after washing with water and drying, had the composition TaN. This black solid conducts electricity; heated in air it burns to Ta_2O_5; NH_3 is given off by the action of molten KOH; it is insoluble in acids, except in a mixture of HFAq and HNO_3Aq (Joly, *l.c.*; *cf.* H. Rose, *P.* 100, 166).

Tantalum, nitrocarbide of; *v.* TANTALUM CARBONITRIDE, p. 639.

Tantalum, oxides and hydrated oxides of. The oxide Ta_2O_5 has been isolated, and also a hydrate of this oxide $Ta_2O_5.2H_2O$, and probably also another hydrate $2Ta_2O_5.3H_2O$. The existence of another oxide, TaO_2, is doubtful.

TANTALUM PENTOXIDE Ta_2O_5. (*Tantalic anhydride. Tantalic oxide.*) The preparation of this compound from *tantalite* is described at the the beginning of this article under *Preparation of tantalum* (p. 638). Ta_2O_5 is also obtained by decomposing $TaCl_5$ by water, or by adding H_2SO_4Aq to solution of a tantalate and boiling, and then heating the $Ta_2O_5.xH_2O$ thus ppd. Ta_2O_5 is a white powder; it has not been fused; by heating with boric acid or microcosmic salt in a porcelain oven it is obtained in rhombic prisms (Ebelmen, *A. Ch.* [3] 33, 34; Nordenskjöld a. Chydenius, *J.* 1860. 145). S.G. c. 7·6 (Marignac, *Ar. Sc.* 1868; Deville, *C. R.* 56, 894). Ta_2O_5 is insoluble in acids except HFAq; after being very strongly heated, it is insoluble in HFAq. Ta_2O_5 dissolves in molten alkalis, also in molten $KHSO_4$ (*v.* TANTALATES, p. 639).

HYDRATES OF TANTALUM PENTOXIDE. By decomposing $TaCl_5$ by water, $Ta_2O_5.xH_2O$ is obtained, which, after very thorough washing with water, then with NH_3Aq to remove adhering HCl, and finally with water, and drying at 100°, gives off from 6 to 7·8 p.c. water when heated to redness. The formula $2Ta_2O_5.3H_2O$ requires 5·7 p.c. H_2O, and the formula $Ta_2O_5.H_2O$ requires 7·5 p.c. H_2O. It is doubtful whether one or more than one definite hydrate exists in this pp. When SO_2 is passed into a solution of $Na_8Ta_6O_{19}$, a pp. of $Ta_2O_5.xH_2O$ is obtained, which, when thoroughly washed and dried at 100°, is said to be $Ta_2O_5.2H_2O = H_4Ta_2O_7$ (H. Rose, *P.* 100, 417). Strong acids, such as H_2SO_4, HNO_3, and HCl, ppt. $Ta_2O_3.xH_2O$ apparently in combination with the acid used as precipitant from solutions of alkali tantalates; weak acids ppt. insoluble alkali tantalates.

Tantalum dioxide TaO_2. (*Tantalum tetroxide* [Ta_2O_4].) The isolation of this oxide is doubtful. Berzelius obtained a brown powder by heating Ta_2O_5 to redness in a carbon crucible; it was not dissolved by any acids, not even by a mixture of HNO_3Aq and HFAq; when strongly heated in air it gave Ta_2O_5 (*P.* 4, 20).

Tantalum, oxyfluoride of. The white powder formed by decomposing K_2TaF_7 by boiling water may be an oxyfluoride, according to Marignac (*A. Ch.* [4] 9, 276).

Tantalum, salts of. No salt has been isolated by replacing the H of acids, except HCl and HF, by Ta. When alkali tantalates are decomposed by strong acids such as HCl, HNO_3, or H_2SO_4, the ppd. $Ta_2O_3.xH_2O$ retains some of the acid used as precipitant; compounds of Ta_2O_5 with these acids are perhaps formed.

Tantalum, sulphide of. By strongly heating Ta_2O_5 in CS_2 vapour, also by heating to redness a mixture of vapour of $TaCl_5$ and H_2S, a yellowish black solid is obtained, which has the composition TaS_2 according to Bérzelius (*P.* 4, 6; *v.* also H. Rose, *P.* 99, 575). Roasted in air, this solid gives Ta_2O_5; heated in Cl it produces $TaCl_5$ and S_2Cl_2; conc. HNO_3Aq oxidises it to $Ta_2O_5.xH_2O$ and H_2SO_4Aq. TaS_2 does not combine with alkali sulphides (R., *l.c.*); fused with KOH, it forms K_2S and potassium tantalates. M. M. P. M.

TARCHONYL ALCOHOL $C_{50}H_{102}O$ (?). Obtained from the leaves of *Tarchonanthus camphoratus* by extracting with alcohol (Canzoneri a. Spica, *G.* 12, 227). Silvery scales, insol. water and ether. Converted by PCl_5 into a chloride [70°] crystallising in small plates (from alcohol).

TARCONINE *v.* vol. iii. p. 496.

TARNINE *v.* vol. iii. p. 497.

TARTARIC ACID $C_4H_6O_6$ *i.e.* $CO_2H.CH(OH).CH(OH).CO_2H$. *Dextro-tartaric acid. Di-oxy-succinic acid.* [135°]. S.G. 1·764 (Schiff, *A.* 113, 189); 1·74 (Buignet, *J.* 1861, 15); $\frac{7}{4}$ 1·7594 (Perkin). S. 115 at 0°; 132 at 15°; 343 at 100° (Leidie, *Fr.* 22, 269; *C. R.* 95, 87; *cf.* Schiff, *J.* 1859, 41; Maisch, *J.* 1865, 392). S. (alcohol) 25·6 at 15°. S. (ether) ·4 at 15° (Bourgoin, *Bl.* [2] 29, 214; *A. Ch.* [5] 13, 400). $[\alpha]_D = 15{\cdot}06 - {\cdot}131p$ in a *p* per cent. solution (Landolt, *B.* 6, 1075; Lippmann, *B.* 24, 3300). H.F. 372,000 (Von Rechenberg). *Heat of solution*: −3454 at 9° (Pickering, *C. J.* 51, 376).

Occurs free or as K or Ca salt in grape-juice, tamarinds, unripe mountain-ash berries, madder-root, potatoes, Jerusalem artichokes, sorrel, gherkins, mulberries, pine-apples, black pepper, the leaves of *Chelidonium majus*, the bulbs of *Scilla maritima*, in beet-juice, and in many other plants.

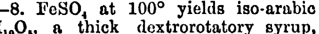
Formation.—1. Mostly together with racemic acid, by oxidation of saccharic acid, dextrose, cane-sugar, milk-sugar, starch, gum arabic, and sorbin by nitric acid (Dessaignes, *A. Suppl.* 2, 242; Hornemann, *J.* 1863, 381; Kiliani, *A.* 205, 175).—2. By the action of sodium-amalgam on an alcoholic solution of oxalic ether (Debus, *A.* 166, 124; *C. J.* 24, 376). The product is probably inactive tartaric acid.

Preparation.—Powdered chalk is added to a boiling solution of cream of tartar; the filtrate is ppd. by calcium chloride, and both pps. decomposed by the proper quantity of boiling dilute H_2SO_4. The filtrate from $CaSO_4$ is evaporated to crystallisation. It may be purified by saturating with $CaCO_3$, digesting with $ZnCl_2$, and decomposing the zinc salt by H_2S (Ficinus, *Ar. Ph.* [3] 14, 310).

Properties.—Monoclinic prisms, with hemihedral facets; $a:b:c = {\cdot}785:1:{\cdot}805$; $\beta = 79°\ 43'$. Dextrorotatory, the rotation being dependent on the concentration of the solution, and being also greatly affected by the presence of alcohols, acids, and other substances in the solution (Landolt, *B.* 13, 2329; Biot, *J.* 1850, 169; Pribram, *M.* 9, 485; *B.* 22, 6; Long, *Am. S.* 36, 351; Thomson, *J. pr.* [2] 35, 145). Sodium molybdate in the proportion of Na_2MoO_4 to $2C_4H_6O_6$ increases the rotation 37 times, while ammonium molybdate (1 mol.) increases the rotation of tartaric acid (3 mols.) 56 times (Gernez, *C. R.* 104, 783; 105, 803). Lithium and magnesium molybdate also increase the rotation. Sodium tungstate also increases the rotation, the maximum effect being 22 times (Gernez, *C. R.* 106, 1527; 108, 942). Crystals of tartaric acid are strongly pyro-electric. An aqueous solution of tartaric acid is ppd. by baryta, lime, and lead acetate. Potassium salts, when the solution is not too dilute, form a crystalline pp. of $KC_4H_5O_6$; the formation of the pp. being promoted by rubbing the sides of the vessel with a glass rod and by the addition of alcohol. $CaCl_2$ ppts. CaA'_2 from neutral solutions of tartrates; the ppn. is hindered by ammonium salts. Calcium tartrate dissolves in KOHAq and is re-ppd. in gelatinous form on boiling. Reduces ammoniacal $AgNO_3$, forming a mirror; the solution then contains oxalic acid (Claus, *B.* 8, 950). Tartaric acid prevents the ppn. by alkalis of the oxides of Al, Bi, Ni, Co, Cr, Cu, Fe, Pb, Pt, and Zn, even on boiling (Aubel a. Ramdohr, *A.* 103, 33; Grothe, *J. pr.* 92, 175). 1 mol. acid prevents the ppn. of 1 mol. $Cu(OH)_2$. A solution of tartaric acid, coloured by a drop of K_2CrO_4, gradually becomes colourless (difference from citric acid) (Salzer, *B.* 21, 1910). A saturated solution of potassium bichromate is slowly turned coffee-brown by tartaric (but not by citric) acid (Cailletet, *C. C.* 1879, 14). Boiling alkaline $KMnO_4$ is turned green, and finally brown, by tartaric acid, but only green by citric acid. Decolourises $KMnO_4$ in acid solution. When H_2SO_4 is present, twice as much $KMnO_4$ must be added to produce a permanent red colour as when it is absent, for in the latter case $MnC_4H_4O_6$ is formed (Fleischer, *B.* 5, 350). Tartaric acid gives an odour of burnt sugar when heated till carbonised. A crystal added to conc. H_2SO_4 containing 1 p.c. resorcin gives a red colour on warming (difference from citric and maleic acids) (Mohler, *Bl.* [3] 4, 728).

To detect small quantities of tartaric acid in presence of citric acid. Add about 1 g. citric acid to a 20 p.c. solution of molybdate of ammonia (1 c.c.), then two or three drops of a dilute solution of H_2O_2, and heat for three minutes on the water-bath. If the citric acid is pure the solution remains yellow. If 0·1 p.c. or more of tartaric acid is present, the liquid become blue (Crismer, *Bl.* [3] 6, 23).

Reactions.—1. Melts at 135°, changing to the isomeric metatartaric acid. The metatartaric acid may be reconverted into tartaric acid by boiling with water (Grosjean, *C. J.* 43, 334).—2. At 140°–150° water is eliminated and ditartrylic acid $C_8H_{10}O_{11}$ is formed. On further heating soluble tartaric anhydride (tartrelic acid), and then insoluble tartaric anhydride, are formed. On further heating the products of distillation (from 250 g.) are pyruvic acid (9 g.), pyrotartaric acid (2 g.), formic acid (·4 g.), resins, aldehydes and volatile acids (2 g.), and tarry bodies (3 g.) (P. Liebermann, *B.* 15, 428). 'Dipyrotartracetone' $C_8H_{12}O_2$ (230°), a colourless liquid, with aromatic odour, is among the products of the distillation of tartaric acid. It combines with bromine (Bourgoin, *C. R.* 86, 674).—3. By heating tartaric acid (10 pts.) with water (1 pt.) at 175° it is converted into racemic acid and inactive tartaric acid. At 165° there is a greater yield of the inactive acid (Jungfleisch, *J.* 1872, 515). Heated with more water at 150° it yields CO_2 and pyrotartaric acid (Wedard, *C. C.* 1888, 889).—4. *Potash-fusion* yields acetic and oxalic acids.—5. *Oxidation* by CrO_3, $KMnO_4$, PbO_2 or MnO_2, and H_2SO_4 yields CO_2 and formic acid. The rate of oxidation has been studied by Krutwig (*Z. P. C.* 2, 787). By slow oxidation by HNO_3 tartronic acid may be obtained.—6. Reduced by HI and P to malic and succinic acids.—7. PCl_5 forms chloro-fumaric chloride.—8. $FeSO_4$ at 100° yields iso-arabic acid $C_6H_{10}O_5$, a thick dextrorotatory syrup, $[\alpha]_D = 20°$, yielding the salts $CaA'_2 9aq$, $Ca_2OA'_2 8aq$, PbA'_2, and $Pb_3A'_2O_2$ (Ballo, *B.* 22, 750).—9. *Chloral* forms $C_8H_4Cl_6O_6$ [124°], crystallising from chloroform in small needles, insol. water, sol. warm alcohol and ether (Wallach, *A.* 193, 46).—10. On submitting tartaric acid to *electrolysis* and treating the syrupy mass with phenyl-hydrazine, glyoxal-osazone [160°] and glyoxal-carboxylic osazone [218°] are obtained (Friedel a. Combes, *Bl.* [3] 3, 770).—11. On adding powdered tartaric acid to fused glucose tartaric glucoside is obtained (Guyard, *Bl.* [2] 41, 291; *cf.* Berthelot, *A. Ch.* [3] 54, 78).—12. *m-Amido-benzoic acid* at 160° forms 'tartrylo-dibenzamic' acid $C_{18}H_{16}N_2O_8$ *i.e.* $(CO_2H.C_6H_4.NH.CO)_2C_2H_2(OH)_2$, a colourless powder, insol. water, sol. hot alcohol. Its alkaline salts form yellow solutions in which $Cu(OAc)_2$ ppts. $C_{18}H_{14}(CuOH)_2N_2O_8$. On heating to 190° it yields the anhydride $C_{18}H_{14}N_2O_7$, a greenish-yellow powder, converted by an alcoholic solution of aniline into tartranil dibenzamic acid



$$CO_2H.C_6H_4.N\!\left\langle\begin{array}{l}CO\\CH.CH(OH).CONHPh\end{array}\right.$$

[200°] (Schiff, *A.* 232, 156; *G.* 16, 28). Another product of the action of tartaric acid on *m*-amido-benzoic acid is 'tartryl-benzamic' acid

$$CO_2H.CH(OH).CH(OH).CO.NHC_6H_4.CO_2H,$$

which crystallises from water in pale-yellow aggregates, yields an acetyl derivative and an anhydride 'tartranbenzamic' acid $C_{11}H_9NO_6$, crystallising from water in green plates, forming $C_{11}H_7BaNO_6$ and $C_{11}H_7CuNO_6$, and converted at 210° in 'benzamtartridic' acid by dehydration. A warm alcoholic solution of aniline converts 'tartranbenzamic' acid into 'tartranilbenzamic' acid [245°], which yields an acetyl derivative [198°]. 'Tartryl-benzamic' acid heated with dry amido-benzamide at 140° forms the compound $C_2H_2(OH)_2(CO.NH.C_6H_4.CONH_2)_2$, a white powder, insol. water, sl. sol. alcohol, and yielding $C_{18}H_{15}CuN_3O_7$ aq.—13. *Glycerin* at 100° yields the compounds $C_3H_5(OH)_2.O.C_4H_5O_5$ and $C_3H_5(OH)(OC_4H_5O_5)_2$ (Desplats, *J.* 1859, 500). Glycerin at 140° gives $C_{11}H_{14}O_{12}$ and $C_{15}H_{22}O_{19}$.—14. *Erythrite* at 100° forms $C_{12}H_{18}O_{14}$, which gives $Ca_3(C_{12}H_{15}O_{14})_2 3aq$ (Berthelot, *A. Ch.* [3] 54, 84). 15. *Quercite* at 120° forms $C_{22}H_{32}O_7$, which gives $Ca_4C_{22}H_{26}O_7 2aq$.—16. *Pinite* at 120° forms $C_{30}H_{36}O_{35}$, which gives $Ca_3C_{30}H_{30}O_{35}$.—17. *Mannite* at 120° forms $C_{30}H_{36}O_{35}$, which yields $Mg_7O_4(C_{30}H_{30}O_{35}) 30aq$ and $Ca_3C_{30}H_{30}O_{35} 6aq$.—18. *Dulcite* forms $C_{14}H_{20}O_{15}$, which gives $Ca(C_{14}H_{19}O_{15})_2 4aq$.—19. *Phenyl hydrazine* (2 mols.) at 140° forms $C_{16}H_{18}N_4O_4$ *i.e.* $C_2H_4O_2(CO.N_2H_2Ph)_2$ [226°] (Bülow, *A.* 236, 196); [c. 240°] (Fischer a. Passmore, *B.* 22, 2734), crystallising from alcohol in plates.

Estimation.—Methods for estimating tartaric acid have been described by Scheurer-Kestner, *C. R.* 86, 1024; Berthelot, *Fr.* 3, 216; Vogel a. Braun, *Fr.* 7, 149; Kissel, *Fr.* 8, 409; Fleischer, *Fr.* 12, 328; Oliveri, *G.* 14, 453; Piccard, *Fr.* 21, 424; C. Schmitt a. Hiepe, *Fr.* 21, 539; Amthor, *Fr.* 21, 195; Nessler a. Barth, *Fr.* 21, 60; 22, 159; Kayser, *Fr.* 22, 123; 23, 29; Musset, *Fr.* 24, 279; Ferrari, *Fr.* 24, 279; Warington, *C. J.* 28, 25; Grosjean, *C. J.* 35, 341; Klein, *Fr.* 24, 379; Borntráger, *Fr.* 25, 327; 26, 699; Gantter, *Fr.* 26, 714; Von Lorenz, *Fr.* 27, 8; Philips, *Fr.* 29, 577; Goldenberg, *Fr.* 22, 270; Heidenhain, *Fr.* 27, 681; Weigert, *Fr.* 23, 357; Haas, *C. C.* 1888, 1045; Ward, *Ph.* [3] 19, 380.

Salts (Berzelius, *P.* 19, 305; 36, 4; *A. Ch.* [2] 67, 303; Werther, *J. pr.* 32, 383; Dumas a. Piria, *A. Ch.* [3] 5, 353; De la Provostaye, *A. Ch.* [3] 3, 129).—$(NH_4)_2A''$. $[\alpha]_D = 33\cdot7°$ in a 1·2 p.c. solution (Sonnenthal, *M.* 12, 603). Efflorescent monoclinic prisms, v. sol. water; $a:b:c = \cdot868:1:1\cdot244$ $\alpha = 88° 9'$. Give off NH_3 in air. Yield succinic acid on fermentation (Koenig, *G.* 11, 180).—$(NH_4)HA''$. $[\alpha]_D = 25\cdot7°$ (Landolt). Minute laminæ, sl. sol. cold water. Forms with ammonium malate $(NH_4)HA''(NH_4)C_4H_5O_5$, crystallising in prisms, S. 9 (Pasteur, *J.* 1853, 415).—$K_2A''\frac{1}{2}aq$. $[\alpha]_D = 25\cdot5°$ in a 2 p.c. solution. S. 133 at 2°; 158 at 23° (Osann). V. sl. sol. hot alcohol. Monoclinic crystals; $a:b:c = \cdot402:1:1\cdot109$; $\alpha = 75° 12'$.—KHA''. *Cream of tartar.* $[\alpha]_D = 22°$ in a ·4 p.c. solution. 100 g. solution contain $\cdot369 + \cdot000569t^2$ grammes at $t°$ (Blarez, *C. R.* 112, 434, 808). S. ·25 at 0°; ·4 at 10°; ·55 at 20°; 1·13 at 40° (Chancel, *C. R.* 60, 408; *cf.* Alluard, *C. R.* 59, 500). Obtained by crystallisation of argol, which is deposited during vinous fermentation. Trimetric crystals; $a:b:c = \cdot712:1:\cdot787$. Insol. alcohol.—$Na_2A'' 2aq$. $[\alpha]_D = 31°$ in a 1 p.c. solution (Sonnenthal; *cf.* Thomsen, *J. pr.* [2] 34, 80; 35, 145). S. 29 at 6°; 44 at 24°; 66 at 42·5° (Osann). Trimetric prisms; $a:b:c = \cdot770:1:\cdot387$. V. sol. hot water, insol. alcohol.—NaHA''. $[\alpha]_D = 24\cdot3°$ in a 1·3 p.c. solution (S.).—NaHA''aq (Dumas a. Piria, *A.* 44, 80). S. 11 in the cold; 55 at 100°. Minute crystals, with hemihedral facets. Insol. alcohol.—Li_2A''. $[\alpha]_D = 37\cdot5°$ in a ·7 p.c. solution (S.). Deliquescent.—LiHA'' 1½aq. Small crystals, v. sol. water (Dulk, *Schw. J.* 64, 180, 193; *A.* 2, 47).—LiHA''aq.—$Li_4H_2A''_4TeO$ 2aq. Needles (Klein, *A. Ch.* [6] 10, 118; *C. R.* 102, 47). — **Hydroxylamine salt** $(NH_4O)_2A''$. Very thin plates (Lossen, *A. Suppl.* 6, 233).—NH_4NaA'' 4aq. Trimetric crystals, with hemihedral facets, isomorphous with KNaA'' 4aq; *a:b:c* = ·823:1:·420. $[\alpha]_j = 26°$. $[\alpha]_D = 32·7°$ (Landolt). S. 26 at 0° (Pasteur, *J.* 1849, 309). — LiNaA'' 2aq. — $Na_2A''_2TeO$ 2aq. — $K_2A''TeO$ aq. — $(NH_4)KA''$. Monoclinic crystals, isomorphous with K_2A''. Give off NH_3 in air. V. sol. water. $[\alpha]_D = 31°$ (L.).—KLiA''aq.—KNaA'' 4aq. *Rochelle salt.* S. 30 at 3°, 66 at 26° (Osann). Heat of solution −6290 at 15°. The heat of solution of KNaA'' is −2989 (Pickering, *C. J.* 51, 351). Large trimetric prisms, with hemihedral facets. Melts at 70°–80° in its water of crystallisation, and becomes anhydrous at 215° (Fresenius, *A.* 53, 234). $[\alpha]_D = 29·7°$ (L.). *Molecular rotation*: Long, *Am. S.* 36, 351.—$K_2A''_2TeO$ (dried at 100°).—RbHA''. Trimetric prisms, isomorphous with the cæsium salt; *a:b:c* = ·726:1:·695 (J. P. Cooke, *Am. S.* [2] 37, 70). S. 1·18 at 25°; 11·7 at 100° (Allen, *Am. S.* [2] 34, 367).—NaRbA'' 4aq. Isomorphous with Rochelle salt (Piccard, *J.* 1862, 125).—Cs_2A''. Trimetric prisms. S. 10 at 25°; 100 at 100°.—Tl_2A'' ½aq. $[\alpha] = 4·8°$ in a 5 p.c. solution at 20°. Sl. sol. water and alcohol.—TlHA''. $[\alpha] = 12°$ in a 1 p.c. solution at 20°. Small flat prisms (De la Provostaye, *A. Ch.* [3] 3, 129; Kuhlmann, *J.* 1862, 188).—TlNaA'' 4aq. At 20° $[\alpha] = 0°$ in a 5 p.c. solution and 6·5° in a 20 p.c. solution.—TlLiA''aq. $[\alpha] = 9·5°$ in a 5 p.c. solution at 20°.—TlKA''. $[\alpha] = 10°$ in a 5 p.c. solution at 20°.—$Tl(NH_4)A''$. $[\alpha] = 10°$ in a 5 p.c. solution at 20°.—BaA''. White amorphous pp., becoming crystalline. S.G. $\frac{21·4}{4}$ 2·973 (Clarke, *Am.* 2, 174).—BaA''aq (Dulk). S. (amorphous) 1·2; (crystalline) ·077 (Vogel a. Reischauer, *J.* 1859, 288). $K_2BaA''_2$ 2aq. Powder, sl. sol. water.—$Na_2BaA''_2$ 2aq. Needles, sl. sol. water, more soluble in a solution of Rochelle salt. Ppd. on mixing a solution of Rochelle salt with $BaCl_2$.—BaA''TeO (dried at 100°).—SrA'' 4aq. Monoclinic prisms. S. ·7 at 16°. S.G. $\frac{19·8}{4}$ 1·966 (Clarke).—SrA'' 3aq (Marignac, *Ann. M.* [5] 15, 280).—$(NH_4)_2SrA''_2$ 12aq. Thin plates.—K_2SrA'' 2aq.—Na_2SrA'' *x*aq.—$CaH_2A''_2$. S. ·71 at 15·6°. Trimetric crystals.—CaA'' 4aq. Occurs in grapes. Ppd. as white crystalline powder on adding $CaCl_2$ to a solution of K_2A''. Small trimetric prisms. *a:b:c* = ·872:1:·908 (Anschütz, *A.* 226, 191). S. ·016 at 15°: ·3 at 100° (Mohr, *J.* 1865, 393). Forms, with calcium malate, the double salt $CaA''CaC_4H_4O_5$ 6aq, crystallising in needles, S. 1·25 at 17° (Ordonneau, *Bl.* [3] 6, 262).—MgA'' 4aq. S. ·8 at 16°. $[\alpha]_D = 36°$.—$Mg_2C_4H_2O_6$ 3aq. S. ·024. Ppd. by adding NH_3 to a solution of MgA'' (Mayer, *A.* 101, 166).—$MgNa_2A''_2$ 10aq.—MgK_2A'' 8aq.—$MgH_2A''_2$. S. 2 at 16°.—BeA'' 3aq (Atterberg, *Bl.* [2] 21, 162).—$BeK_2C_4H_2O_6$ 3aq. Prisms (Toczynski, *Z.* 1871, 277).—K(SbO)A'' ½aq. *Tartar emetic.* Prepared by boiling Sb_2O_3 (3 pts.) with cream of tartar (4 pts.) and water. Octahedra; *a:b:c* = ·956:1:1·054. $[\alpha] = 141°$ in a 4 p.c. solution at 20°. S.G. 2·6. Efflorescent. At 200° it becomes $K(SbO)C_4H_2O_6$. S. 5 at 8°; 8 at 21°; 52 at 100°. ·05 to ·1g. produce vomiting. Its solution reddens litmus, and gives a crystalline pp. of K(SbO)A'' with alcohol. Its solution is ppd. by mineral acids, by alkalis, and by H_2S. $HgCl_2$ is reduced by it to calomel. Heat of formation: Guntz, *C. R.* 104, 699. Volumetric estimation of Sb in tartar emetic (Dunstan a. Boole, *Ph.* [3] 19, 385). — $K(SbO)A''H_2A''$ 2½aq. Efflorescent prisms. Alcohol added to its aqueous solution ppts. tartar-emetic, leaving tartaric acid in solution (Knapp, *A.* 32, 76).—K(SbO)A''3KHA''. Mammellated groups of needles, v. sol. water.—$(K(SbO)A'')_2NaNO_3$ (Martenson, *J.* 1869, 539).—Na(SbO)A'' ½aq. Trimetric, hygroscopic prisms; *a:b:c* = ·922:1:1·08. — $(Na_2A'')_3 2Sb(OH)_3$ 3aq. Amorphous, v. sol. water (Clarke a. Evans, *B.* 16, 2385). — $NH_4(SbO)A''$ ½aq. — $NH_4(SbO)A''$ 2½aq (Berlin, *A.* 64, 359).—Rb(SbO)A'' ½aq. Isomorphous with tartar-emetic (Grandeau, *A. Ch.* [3] 67, 155).—$Tl(SbO)C_4H_4O_6$ aq. $[\alpha] = 100°$ in a 2 p.c. solution at 20° (Long, *Am. S.* [3] 38, 264).—Ag(SbO)A'' ½aq. Crystals (J. P. Cooke, *Am. S.* [3] 19, 393).—$Ba(SbOA'')_2$ 2½aq.—Cd(SbOA'') 2aq. Converted at 200° into $Cd(SbOC_4H_2O_5)_2$ (Schiff, *A.* 104, 328). — $(Ca(SbOA'')_2)_4Ca(NO_3)_2$ 24aq. Crystallises from a solution of tartar-emetic mixed with calcium nitrate in trimetric forms (Marignac, *Ann. M.* [5] 15, 280).—$Sr(SbOA'')_2$. Hexagonal crystals. — $Sr_2(SbOA'')_2(NO_3)_2$ 12aq. Very soluble crystals (Kessler, *P.* 75, 410).—$Pb(SbOA'')_2$ 4aq. — $Ba_3Sb_2(C_4H_2O_6)_3$. — $Sb(HA'')_3$ 4aq. Needles, v. sol. water (C. a. E.).—$Sb_2A''_3$ 6aq.—(SbO)HA''aq (Clarke a. Stallo, *B.* 13, 1788).—(SbO)HA'' (Guntz, *C. R.* 104, 850).—$C_4H_4O_5Sb_2O_3$aq. White granular pp., formed by adding alcohol to a solution of Sb_2O_3 in aqueous tartaric acid (Berzelius). Converted by heat into $SbOC_4H_2O_5$.—$(C_4H_3O_{11})_4Sb_2O_3$ 6aq (Péligot, *A. Ch.* [3] 20, 289).—$(C_4H_3O_{4½})_2Sb_2O_3$ (dried) (P.). — $(C_4H_4O_5)_2Sb_2O_3H_2O$. Crystals (Guntz, *A. Ch.* [6] 13, 396).—**Berberine salt** $C_{20}H_{18}NO_4(SbO)A''$ (Stenhouse, *J.* 1863, 452).—**Brucine salt** $C_{23}H_{27}N_2O(SbO)A''$.—**Quinine salt** $C_{20}H_{25}N_2O_2(SbO)A''$ (Clarke, *B.* 15, 1540).—**Atropine salt** $C_{17}H_{24}NO_3(SbO)A''$ 2aq.—**Aniline salt** $C_6H_7N(SbO)A''$. Long white prisms. S.G. 1·89 at 11°.—$NH_4(AsO)A''$ ½aq. Large efflorescent trimetric crystals; *a:b:c* = ·876:1:·694. Got by dissolving As_2O_3 in NH_4HA'' (Mitscherlich; Werther, *J. pr.* 32, 409).—$K(AsO_2)A''$ 2½aq. Got by dissolving arsenic acid in a solution of cream of tartar (Pelouze, *A. Ch.* [3] 6, 68).—$(Sr(AsOA'')_2)_2NH_4NO_3$ 12aq. Large trimetric crystals (Marignac).—$Bi_2A''_3$ 6aq. Small crystals, decomposed by water (Schneider, *P.* 88, 55).—$K(BiO)C_4H_2O_6$ (Schwarzenberg, *A.* 61, 244).—$Bi_2K(BiO)(C_4H_2C_6)_2$ (Frisch, *J.* 1866, 401).—K(BO)A'' (dried at 100°). *Potassium borotartrate.* Amorphous mass, v. sol. water, insol. alcohol. At 100° it becomes $K(BO)C_4H_2O_5$. Purgative. $[\alpha] = 58°$ in a 20 p.c. solution at 20°.—$K_2(BO)C_4H_3O_6$.—$K_2(BO)_2C_4H_2O_6$.—Na(BO)A''.—$Na_2(BO)C_4H_3O_6$.—$Na_2(BO)_2C_4H_2O_6$ (Duve, *J.* 1869, 540). — $K_2(BO)_2C_4H_2O_6Na(BO)A''$. — $Ba(BO)C_4H_3O_6$.—$Ba(BO)_2C_4H_2O_6$.—PbA''. S.G. $\frac{17·2}{4}$ 4·012 (Clarke, *Am.* 2, 174). White crystalline pp., v. sol. HNO_3.—$Pb_2C_4H_2O_6$ aq (Erdmann, *A.* 21, 14). Insol. water, v. sol. KOHAq. — $Pb_3(C_4H_3O_6)_2$. — $Ce_2A''_3$ 9aq (?). — $Th_2K_2A''_3$. — CuA'' 3aq. S. ·06 in the cold; ·3 at 100°. Light-green powder.—$CuA''4NH_3$ (Schiff, *A.* 123, 46).—$(H(NH_4)A'')_2(HgO)_3 3H_2O$ (Harff, *Brandes' Arch.* 5, 259; Burckhardt, *ibid.* [2] 11, 257).—$(KHA'')_4HgCl_2 6aq$.—$K_2NiA''_2$ (dried at 110°). Efflorescent, apple-green crystalline powder (Fabian, *A.* 103, 248).—$CoCl(HA'')_2 5NH_3 2\frac{1}{2}aq$ (Jörgensen, *J. pr.* [2] 18, 239).—$ZnA''2aq$ (Schiff, *A.* 125, 146).—$Zn_2C_4H_2O_6 \frac{1}{2}aq$. Powder, insol. water.—$Cr(OH)A''$. Violet flakes, turning dark-blue over H_2SO_4 (Schiff, *A.* 125, 145). At 220° it yields $CrC_4H_3O_6$.—$K(CrO)A'' 3\frac{1}{2}aq$ (Malaguti, *C. R.* 16, 457).—$(UrO_2)A'' 3aq$ (Péligot, *A.* 56, 231).—$K_2(UrO_2)A''_2$ (dried at 200°).—$(SbO)_2(UrO_2)A''_2 8aq$.—SnA''. Minute crystals.—$K(FeO)A''4$ or 5aq. Prepared by digesting cream of tartar with water and $Fe(OH)_3$. Brown scales, red by transmitted light. Acids ppt. from its solutions a basic salt, sol. excess.—$NH_4(FeO)A''4$ (or 5) aq.—$Fe_2A''_3$.—FeA''. Formed by boiling tartaric acid with water and iron wire (Méhu, *N. J. P.* 40, 257). Minute crystalline powder. S. ·877 at 15·6° (Dulk, *A.* 2, 62).—$K(MnO)A''4aq$ (Descamps, *Z.* 1870, 317).—Ag_2A''. Amorphous curdy pp. got by adding $AgNO_3$ to a cold solution of Rochelle salt. Crystallises from a warm solution in white scales. Nearly insol. water. Its ammoniacal solution deposits Ag on warming (Liebig a. Redtenbacher, *A.* 38, 132; Erdmann, *J. pr.* 25, 504).—$AgHA''$ (Perkin, *C. J.* 51, 369). Monoclinic tables.

Ethylene-diamine salt $C_4H_4O_6(N_2H_6C_2H_4)$. Dextrorotatory. Leaflets, v. sol. water. The acid salt is sl. sol. water, S. 8 at 15°, and the solution is dextrorotatory (Colson, *Bl.* [3] 7, 808).

Mono-methyl ether $MeHA''$. Formed by boiling tartaric acid with MeOH (Guérin, *A.* 22, 248). Prisms.—$KMeA''$.—$BaMe_2A''_2 aq$ (Dumas a. Péligot, *A. Ch.* [2] 61, 200; [3] 5, 373).

Di-methyl ether Me_2A''. [48°]. (280° i.V.). S.G. (liquid) $\frac{15}{}$ 1·340. $[\alpha]_D = 2{\cdot}454$ at 18° (Anschütz a. Pictet, *B.* 13, 1176; 18, 1399); $= 2{\cdot}14$ (Phillips a. Guye, *C. R.* 110, 714). Yields an acetyl derivative [103°] $[\alpha]_D = -14°$ and a dibenzoyl derivative $[\alpha]_D = -88{\cdot}8°$.

Mono-ethyl ether $EtHA''$. [90°]. Formed by dissolving tartaric acid in boiling alcohol (G.; Marian, *N. J. T.* 13, 2, 43; Trommsdorff, *N. J. T.* 24, 1, 11; Guérin, *A. Ch.* [2] 62, 57). Very deliquescent prisms.—$NaEtA''$. Powder, sl. sol. alcohol (Mulder, *B.* 8, 370).—$KEtA''$. S. 106° at 23·5°. Colourless trimetric prisms; $a:b:c = {\cdot}288:1:{\cdot}417$.—$Ca(EtA'')_2 5aq$.—$Ba(EtA'')_2 2aq$. S. 38 at 23°; 128 at 100°.—$Pb(EtA'')_2$.—$Cu(EtA'')_2 6aq$. Blue silky efflorescent needles.—$AgHA''$. Prisms.

Di-ethyl ether Et_2A''. (280° i.V.); (233° cor. at 197 mm.). S.G. $\frac{15}{15}$ 1·2097; $\frac{25}{25}$ 1·2019. $[\alpha]_D = 9$ at 18° (Anschütz a. Pictet, *B.* 13, 1176); 7·22 at 12°; 8·02 at 20° (Perkin, *C. J.* 51, 863). M.M. 8·766 at 14·8°. Liquid miscible with water (Demondesir, *A.* 80, 301). Sodium forms $CO_2Et.CH(ONa).CH(OH).CO_2Et$ and $CO_2Et.CH(ONa).CH(ONa).CO_2Et$, the latter being converted by EtCl into a deposit and a liquid, part of which is soluble in alcohol and ether and part insoluble in alcohol and ether (Mulder, *R. T. C.* 8, 375; 9, 238; 10, 171; *cf.* Cohn, *B.* 20, 2003). The soluble product mixed with alcoholic $CuCl_2$ and poured into water forms a pp. crystallising in light-green needles, sol. alcohol and ether, insol. water and $CuC_{16}H_{24}O_{11}$. Tartaric ether is converted by treatment with gaseous HCyO into allophanyl-tartaric ether $NH_2.CO.NH.CO.O(C_4H_3Et_2O_5)$ [188°], which is m. sol. hot water and alcohol.

Acetyl derivative of the ether $CO_2Et.CH(OAc).CH(OH).CO_2Et$. Formed from the ether and AcCl, the mixture becoming hot (Perkin, *C. J.* 20, 145). Heavy oil, sl. sol. water, insol. saline solutions. Neutral to litmus.

Di-acetyl derivative of the ether $CO_2Et.CH(OAc).CH(OAc).CO_2Et$. [67°]. (292°) (Pictet, *B.* 14, 2790); (230° at 100 mm.). Formed by heating tartaric ether with AcCl at 100° (Perkin; Wislicenus, *A.* 129, 187). Prisms (from water), v. sl. sol. water. Slowly saponified by KOHAq.

Acetyl-benzoyl derivative of the ether $CO_2Et.CH(OAc).CH(OBz).CO_2Et$. Formed by heating the mono-benzoyl derivative of the ether with AcCl at 150° (Perkin). Heavy oil.

Mono-benzoyl derivative of the ether $CO_2Et.CH(OH).CH(OBz).CO_2Et$. [64°]. Formed by heating the ether with BzCl at 100°. Prisms, sl. sol. hot Aq. Saponified by alcoholic potash yielding $C_2H_2(OH)(OBz)(CO_2Et).CO_2K$, $C_2H_2(OH)(OBz)(CO_2K)_2$, and finally, potassium tartrate. $C_2H_2(OH)(OBz)(CO_2Et).CO_2H$ forms tufts of needles, sl. sol. water.

Di-benzoyl derivative of the ether $[\alpha]_D = -60°$ (Phillips a. Guye, *C. R.* 110, 716).

Di-n-propyl ether Pr_2A''. (303° i.V.). S.G. $\frac{17}{}$ 1·1392. $[\alpha]_D = 13{\cdot}77$ at 18° (A. a. P.); $= 12{\cdot}44$ (P. a. G.).

Di-isopropyl ether Pr_2A''. (275°). S.G. $\frac{20}{}$ 1·130. $[\alpha]_D = 14{\cdot}89$ at 20° (Pictet, *J.* 1882, 856). Liquid.

Di-isobutyl ether $(Pr.CH_2)_2A''$. [68°]. (324°). S.G. $\frac{100}{}$ 1·015. $[\alpha]_D = 19{\cdot}9°$ (P.). Yields a dibenzoyl derivative $[\alpha]_D = -42°$.

Isoamyl ether $(C_5H_{11})HA''$. Formed by digesting tartaric acid (150 pts.) with isoamyl alcohol (88 pts.) at 130° (Balard, *A. Ch.* [3] 12, 309; Breunlin, *A.* 91, 314). Nodular mass, with very bitter taste.—$KC_5H_{11}A'' aq$. Crystalline.—$NaC_5H_{11}A''$. Nodules.—$Ba(C_5H_{11}A'')_2 2aq$: pearly plates (from water).—$Pb(C_5H_{11}A'')_2$.—$Ca(C_5H_{11}A'')_2$.—$AgC_5H_{11}A''$. Tufts of needles.

Di-acetyl derivative $C_8H_{10}O_8$ *i.e.* $CO_2H.CH(OAc).CH(OAc).CO_2H$. $[\alpha]_D = -23{\cdot}14$ (Phillips a. Guye, *C. R.* 110, 716). Formed slowly from the anhydride by the action of water. Hard deliquescent crystals (containing 3aq), melting at 58°. V. sol. water, alcohol, and ether, sl. sol. benzene. Lævorotatory. Its salts form lævorotatory solutions (Colson, *Bl.* [3] 7, 806; *C. R.* 114, 417). Converted into tartaric acid by hot KOHAq.—KHA'': crystalline powder.—BaA'': slender deliquescent needles.—CaA''.—CuA''.—Ag_2A'': white crystalline mass.—Ethylene-diamine salt $C_8H_8O_8(N_2H_6C_2H_4)$. Lævorotatory. V. sol. water.

Anhydride of the di-acetyl derivative $C_8H_8O_7$. [127°]. Formed by heating tartaric acid with AcCl (Ballik, *Sitz. W.* 29, 26; Pilz, *Sitz. W.* 44 [2] 7; Perkin, *C. J.* 20, 149). Slender needles (from benzene). Dextrorotatory.

Benzoyl derivative $C_{11}H_{10}O_7$ *i.e.* $CO_2H.CH(OH).CH(OBz).CO_2H$. Formed by heating tartaric acid with benzoic acid at 150°

(Dessaignes, *J. Ph.* [3] 32, 47). Minute crystals, v. sol. water, sl. sol. alcohol.—Ag_2A'': white pp.

Di-benzoyl derivative $C_{18}H_{14}O_8$ *i.e.* $CO_2H.CH(OBz).CH(OBz).CO_2H$. [90°]. $[\alpha]_D = -116°$ in alcohol. Formed by dissolving its anhydride in hot water. Needles (containing aq). Converted by heat into a crystalline substance melting at 132°.

Anhydride $C_{18}H_{12}O_7$. [174°]. $[\alpha]_D = 143°$ in acetone at 18°. Formed by heating tartaric acid with BzCl. Small needles, insol. cold water, sol. alcohol, benzene, and alkalis. Dextrorotatory.

Di-nitroxyl- derivative $CO_2H.CH(NO_3).CH(NO_3).CO_2H$. *Nitrotartaric acid.* Formed by dissolving tartaric acid (1 pt.) in HNO_3 (4½ pts.), and stirring with an equal volume of H_2SO_4 (Dessaignes, *A.* 82, 362; 89, 339). The crystals are dried and crystallised from ether (Kekulé, *A.* 221, 245). Silky prisms, decomposed by hot water, forming oxalic and tartronic acids, CO_2, and NO. Alcohol containing HNO_2 forms di-oxy-tartaric acid. Ammonium sulphide reduces it to tartaric acid.—$(NH_4)HA''$.—Ag_2A'' aq. V. sol. water.—Et_2A''. [46°]. S.G. $\frac{15}{}$ 1·278. Formed by dissolving tartaric ether in a mixture of HNO_3 and H_2SO_4 and ppg. with water.

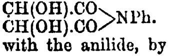
Amide $C_2H_4O_2(CO.NH_2)_2$. Formed by passing NH_3 into an alcoholic solution of the ether, or of its di-acetyl derivative (Demondesir, *A.* 80, 303; Pasteur, *C. R.* 35, 176; Grote, *A.* 130, 202; Ruhemann, *B.* 20, 3366). Trimetric crystals (from water), v. e. sol. water. Dextrorotatory.

Amic acid $C_4H_7NO_5$ *i.e.* $CO_2H.CH(OH).CH(OH).CO.NH_2$. Formed by passing NH_3 over tartaric anhydride moistened with alcohol (Laurent, *Compt. Chim.* 1845, 153). Formed also, together with tartaric acid, by heating tartaric ether with NH_3Aq at 100° (Grote). Syrup.—CaA'_2 6aq: tetrahedra, v. sol. water.—$Pb_3(C_4H_4NO_5)_2$.—BaA'_2 8aq.—EtA′.

Anilide $C_2H_4O_2(CO.NHPh)_2$. [250°]. Formed by boiling aniline with tartaric acid (Polikier, *B.* 24, 2959). Pearly scales, insol. water, sl. sol. other solvents. Yields mono-, di-, and tri-acetyl derivatives, melting at 227°, 216°, and 137° respectively.

Phenyl-amic acid $C_{10}H_{11}NO_5$ *i.e.* $CO_2H.CH(OH).CH(OH).CO.NHPh$. [180°]. Formed by boiling the phenylimide with NH_3Aq (Arppe, *A.* 93, 352). Plates, v. sol. water and alcohol.—BaA'_2: spangles, m. sol. hot water.—AgA′: white powder, v. sl. sol. water.

Phenylimide $C_{10}H_9NO_4$ *i.e.*



$\begin{array}{l}CH(OH).CO\\CH(OH).CO\end{array}\!\!>\!NPh$. [230°]. Formed, together with the anilide, by heating tartaric acid with aniline at 150°. Pearly plates, v. sol. water.

Di-o-toluide $C_2H_4O_2(CO.NH.C_6H_4Me)_2$. [183°]. White plates, insol. water (Bischoff, *B.* 23, 2049). Ac_2O at 140° yields a di-acetyl compound [222°].

Di-p-toluide $C_2H_4O_2(CO.NH.C_6H_4Me)_2$. [264°]. Got by heating *p*-toluidine with tartaric acid at 185°. Silky needles (from alcohol). Converted by Ac_2O into a di-acetyl derivative [202°].

Hydrazide $C_2H_2(OH)_2(CO.NH.NH_2)_2$. [183°]. Formed from tartaric ether and hydrazine hydrate (Von Rothenburg, *B.* 26, 2057). Needles, sl. sol. alcohol. Converted by benzoic aldehyde into $C_2H_2(OH)_2(CO.N_2H:CHPh)_2$ [225°], crystallising in yellowish plates (from alcohol).

Lævo- tartaric acid

$CO_2H.CH(OH).CH(OH).CO_2H$. *Anti-tartaric acid.* [170°]. When a solution of racemic acid is divided into two equal parts and one is neutralised by ammonia and the other by soda, and the solutions mixed and allowed to evaporate, hemihedral crystals of $Na(NH_4)C_4H_4O_6$ are obtained. Half of these crystals have the hemihedral faces oppositely situated to those of the other half; and on carefully selecting the two kinds of crystals (the solutions of which exhibit equal and opposite action on polarised light), ppg. their solutions by lead nitrate, and decomposing the lead salts by H_2S or H_2SO_4, solutions are obtained which on evaporation yield crystals, the one of dextro- and the other of lævo- tartaric acid (Pasteur, *A. Ch.* [3] 28, 56). If in a solution of sodium ammonium racemate of S.G. 1·26 a crystal of the dextro- salt be put on one side and one of the lævo- salt be put on the other side of the vessel, the two salts will crystallise separately (Jungfleisch, *J. Ph.* [5] 5, 346). The separation of sodium ammonium racemate into the dextro- and lævo- tartrates does not take place if the solution is heated to 118° in a sealed tube and allowed to crystallise without access of air (Bichat, *Bl.* [2] 46, 54). According to Wyrouboff (*C. R.* 102, 627), the splitting up of the sodium ammonium racemate depends upon strength of solution and temperature only.

Lævo-tartaric acid is exactly like dextro tartaric acid in solubility and S.G. Its crystals are like the reflection of those of the dextro-acid. The two acids are oppositely pyro-electric. Solutions of the lævo- acid exhibit an effect on light equal and opposite to that produced by solutions of the dextro- acid of like strength. When conc. solutions of equal quantities of the dextro- and lævo- acids are mixed, heat is given out and racemic acid separates. The salts of the lævo-tartaric acid have the same amount of water of crystallisation, and the same crystalline form as the salts of dextro-tartaric acid. They exhibit opposite hemihedry, opposite rotation, and are oppositely pyro-electric. Differences are observed between the compounds of the two acids with optically active substances. Acid ammonium (active) malate combines with acid ammonium dextro- (but not lævo-) tartrate. Cinchonine lævo- tartrate $C_{19}H_{22}N_2OC_4H_6O_6$ contains aq, while the dextro-tartrate contains 4aq.

Di-methyl-ether Me_2A''. [48°]. (160° at 16 mm.). Lævorotatory (Anschütz, *B.* 18, 1398; *A.* 247, 112).

Di-acetyl derivative of the di-methyl ether $CO_2Me.CH(OAc).CH(OAc).CO_2Me$. [103°]. $[\alpha]_D = -1·3$ (in a 3·6 p.c. solution in alcohol of S.G. ·826). Formed by heating Me_2A'' with AcCl. Monoclinic plates (from benzene); $a:b:c = 1·052:1:1·007$; $\beta = 87° 54'$. On mixing with the corresponding dextro- compound it forms the isomeric racemic compound [86°].

Amide $C_4H_4O_4(NH_2)_2$. Combines with the amide of active malic acid, forming needles, S. more than 33.

Racemic acid $C_4H_6O_6$. *Paratartaric acid.* [206°] (Bischoff, *B.* 22, 1812). S.G. (of H_2A'') = 1·778; (of H_2A'' aq) 1·687 (Perkin, *C. J.* 51, 366). S. (of H_2A'') 8·16 at 0°; 18 at 20°; 137·8 at 100°. S. (of H_2A'' aq) 9·23 at 0°; 20·6 at 20°; 184·9 at 100° (Liedie, *C. R.* 95, 87). Heat of solution at 9°: −5675 (for H_2A''); −7065 (for H_2A'' aq) (Pickering, *C. J.* 51, 367). H.C. (for H_2A'') 1,851,190 (Ossipoff, *C. R.* 108, 1105). H.F. (for H_2A'' aq) 278,400. Acid potassium racemate either occurs sometimes in crude argol, or is produced therefrom in the purification processes (Kestner; Jungfleisch, *C. R.* 85, 805). On crystallisation of cream of tartar, acid potassium racemate remains in the mother-liquor.

Constitution.—Assuming racemic acid to be a compound of the dextro- and lævo-tartaric acids, its formula must be at least $(C_4H_6O_6)_2$.

Formation.—1. By mixing solutions of dextro- and lævo- tartaric acids.—2. By heating tartaric acid (30 g.) with water (4 c.c.) for 30 hours at 175° (Jungfleisch, *Bl.* [2] 18, 203).—3. By heating the dextro- or lævo- tartrate of quinine or cinchonine at 170° (Pasteur, *A.* 72, 164; 84, 157; 88, 211).—4. By heating tartaric ether.—5. By heating inactive tartaric acid at 200° or by boiling it with HClAq (Dessaignes, *Bl.* 1865, i. 34).—6. By oxidation of fumaric acid by aqueous $KMnO_4$ (Kekulé a. Anschütz, *B.* 13, 2150; *A.* 226, 191; *cf.* Tanatar, *B.* 12, 2293). 7. By the action of HNO_3 on lævulose, mucic acid, and inulin; and, together with tartaric acid, by the action of HNO_3 on milk sugar, cane sugar, saccharic acid, dulcite, and mannite (Carlet, *Rép. Chim. pure*, 2, 345; 4, 17; Hornemann, *J. pr.* 89, 283).—8. Together with inactive tartaric acid by boiling silver di-bromo-succinate with water (Perkin a. Duppa, *C. J.* 13, 102; Pasteur, *A. Suppl.* 2, 242; Jungfleisch, *Bl.* [2] 19, 198).—9. By boiling silver iso-di-bromo-succinate with water (Demuth a. Meyer, *B.* 21, 268). 10. By boiling glyoxal with dilute HCy and HCl (Schöyen, *A.* 132, 168; Strecker, *Z.* [2] 4, 216).—11. By the action of zinc-dust (2 mols.) and dilute HOAc (3 mols.) on glyoxylic acid (1 mol.) at 100° (Genviesse, *Bl.* [3] 7, 225; *C. R.* 114, 555).—12. From piperic acid, sorbic acid, and $CHO.CH{:}CH.CH{:}CH.CO_2H$ by careful oxidation with dilute $KMnO_4$ below 4° (Doebner, *B.* 23, 2374).—13. By heating a solution of desoxalic acid (Löwig, *J.* 1861, 605; Klein, *J. pr.* [2] 20, 157).

Preparation.—Sodium ammonium racemate, got from the mother-liquor from which cream of tartar has separated, is treated exactly in the same way as cream of tartar in the preparation of tartaric acid. The small opaque needles of racemic acid can be separated by handpicking from the large transparent crystals of tartaric acid.

Properties.—Triclinic crystals (containing aq); $a{:}b{:}c = {·}484{:}1{:}{·}806$; $\alpha = 120°$; $\beta = 96°\ 19'$; $\gamma = 76°\ 5'$ (De la Provostaye, *A. Ch.* [3] 3, 131). Slightly efflorescent. Gives off aq at 100°. Less soluble than tartaric acid. In dilute solutions of racemic acid the lowering of the freezing-point is the same as with an equal weight of tartaric acid (Raoult, *Z. Ph.* 2, 186). Absorption of a solution of racemic acid by filter paper does not separate the dextro- and lævo- acids (Marchlewski, *B.* 26, 983). A solution of racemic acid is ppd. by $CaSO_4$ (unlike tartaric acid). Calcium racemate is insol. acetic acid (unlike calcium tartrate). NH_4Cl does not hinder the ppn. of calcium racemate. When heated above 200° racemic acid yields the same products as tartaric acid. By various ferments (*e.g. Penicillium glaucum*) racemic acid, when free or as acid ammonium salt, is converted into tartaric acid (Pasteur; *cf.* E. Mulder, *R. T. C.* 1, 231). A solution in HNO_3 (S.G. 1·52) poured into half its volume of H_2SO_4 deposits the crystalline $C_2H_2(O.NO_2)_2(CO_2H)_2$ (Dessaignes, *J. Ph.* [3] 32, 46). AcCl converts racemic acid into di-acetyl-racemic anhydride $C_2H_2(OAc)_2C_2O_3$ [123°]. Racemic acid and its salts are inactive to light.

Salts (Fresenius, *A.* 41, 1; 53, 230).—$(NH_4)_2A''$. Trimetric prisms; $a{:}b{:}c = {·}509{:}1{:}{·}847$. V. sol. water, nearly insol. alcohol. Give off NH_3 in air.—$(NH_4)HA''$. S. 1 at 20°; less sol. boiling water. Monoclinic prisms. Reddens litmus.—K_2A'' 2aq. Six-sided tables. S. 103 at 25°. Nearly insol. alcohol.—KHA''. S. ·55 at 19°; ·7 at 100°. Insol. alcohol.—$K(NH_4)A''$. Striated prisms.—Na_2A''. S. 38 at 25°. Trimetric prisms. Insol. alcohol.—$NaHA''$aq. S. 9 at 19°. Monoclinic prisms (from water). Ppd. from aqueous solution by addition of alcohol.—$Na(NH_4)A''$aq. S.G. 1·746 (Wyruboff, *A. Ch.* [6] 9, 229).—$NaKA''$4aq. S. 47 at 6° (Fresenius, *A.* 53, 230).—$NaKA''$3aq. Monoclinic crystals (Wyruboff, *A. Ch.* [6] 9, 232).—RbA''.—CaA''4aq. Acicular prisms (Anschütz, *A.* 226, 191).—BaA'' 2½aq. S. ·05. Crystalline pp.—SrA''4aq. —TlA'' (De la Provostaye, *A.* 126, 79).—$LiTlA''$2aq (Wyruboff).—$NaTlA''$2aq. S. 25 at 25°.—MgA''5aq. S. ·85 at 19°.—CdA'' (Schiff, *A.* 104, 326).—PbA'' (dried at 100°).—$Pb_2C_4H_2O_6$ (Krug, *J.* 1861, 367).—CuA''2aq. Pale-blue needles, sol. alkalis and solution of Na_2CO_3.—$Na_2CuC_4H_2O_6$ 4aq.—MnA''aq.—NiA''5aq.—$NH_4(AsO)A''$½aq. S. 9·4 at 15°. Efflorescent crystals.—$K(AsO)A''$ 1½aq. S. 13 at 16°. Decomposed by hot water with liberation of As_2O_3.—$Na(AsO)A''$2½aq. S. 7 at 19°. Non-efflorescent white crystals (Werther, *J. pr.* 32, 385).—$K(SbO)A''$ ½aq. Monoclinic prisms.—Ag_2A''. Shining scales, less sol. Aq than silver tartrate.

Mono-methyl ether $MeHA''$. Formed by evaporating racemic acid with MeOH (Guérin-Varry, *A. Ch.* [2] 62, 77; *A.* 22, 252). Rectangular prisms, v. e. sol. cold water. Decomposed by hot water into the parent substances.—$KMeA''$½aq. Prisms.—$Ba(MeA'')_2$ 4aq. Monoclinic prisms.—$AgMeA''$. Pp.

Di-methyl ether Me_2A''. [85°]. (282° i.V.). Formed by methylation of racemic acid, and also by mixing equal weights of the di-methyl ethers of the lævo- and dextro-tartaric acids (Anschütz a. Pictet, *B.* 13, 1178; 18, 1397; *A.* 247, 116). Monoclinic crystals; optically inactive. Yields a di-acetyl derivative $C_2H_2(OAc)_2(CO_2Me)_2$ [86°] in trimetric crystals; $a{:}b{:}c = {·}8095{:}1{:}{·}6728$. This compound, examined by Raoult's method, has the same molecular weight as the di-acetyl derivative of di-methyl tartrate.

Mono-ethyl ether $EtHA''$. Deliquescent prisms, v. sol. alcohol. Inactive to light.—$KEtA''$ aq.—$Ba(EtA'')_2$ 2aq.—$AgEtA''$. Prisms.

Di-ethyl ether Et_2A''. (238° cor. at 197 mm.) S.G. $\frac{15}{15}$ 1·2098; $\frac{25}{25}$ 1·2021. M.M. 8·759 at 15·5° (Perkin, *C. J.* 51, 364). Yields an oily acetyl derivative and a di-acetyl derivative $C_2H_2(OAc)_2(CO_2Et)_2$, [51°] (230° at 100 mm.). BzCl forms $C_2H_2(OH)(OBz)(CO_2Et)_2$ [57°]. The compound $C_2H_2(OEt)_2(CO_2Et)_2$ (147° at 15 mm.) is formed from di-bromo-succinic ether [58°] and NaOEt (Michael, *J. pr.* [2] 46, 234).—Ag_2A''.—$AgHA''$. Monoclinic, $a{:}b{:}c = {\cdot}721{:}1{:}{\cdot}869$; $\beta = 70° 10'$.

Inactive tartaric acid $CO_2H.CH(OH).CH(OH).CO_2H$. *Mesotartaric acid.* [140°–143°]. S. 125 at 15°.

Formation.—1. By heating cinchonine tartrate or racemate for several hours at 170° (Pasteur, *A.* 88, 212). The product is mixed with $CaCl_2$, which ppts. calcium racemate, and the filtrate slowly deposits calcium inactive tartrate.—2. By boiling tartaric or racemic acid for 400 hours with HClAq (Dessaignes; Pasteur, *Bl.* 1862, 107).—3. By heating tartaric acid (30 g.) or racemic acid with water (4 c.c.) for 2 days at 165°. Separated by means of its very soluble acid K salt (Jungfleisch, *Bl.* [2] 19, 101).—4. A product of the action of HNO_3 on sorbin (Dessaignes, *C. R.* 55, 769), erythrite (Przybytek, *B.* 17, 1412; *Bl.* [2] 43, 126) and glycerin.—5. By oxidation of lævulose (Kiliani, *B.* 14, 2530).—6. By oxidation of phenol by alkaline $KMnO_4$ at 0° (Doebner, *B.* 24, 1755).—7. A product of the action of moist Ag_2O on di-bromo-succinic acid. 8. By the action of nitrous acid on di-amido-succinic acid (Lehrfeld, *B.* 14, 1819).—9. By oxidation of maleïc acid by alkaline $KMnO_4$ (Kekulé a. Anschütz, *B.* 14, 713).

Properties.—Prisms (containing aq). Loses its aq at 100°; at 200° it yields pyrotartaric and racemic acids. Prolonged boiling with HCl aq converts it into racemic acid (Dessaignes). The conversion is also effected by heating the acid with a little water at 175°. The ether is converted by AcCl into $C_2H_2(OAc)_2(CO_2Et)_2$ [48°], crystallising in silky needles.

Salts KHA''. Needles. S. 12·5 at 19°.—$RbHA''\frac{1}{2}aq$. — $Rb_2A''aq$. — $RbNaA''2\frac{1}{2}aq$. — $CaA''3aq$. S. ·17 at 100°. S. (HOAc) ·028 at 18°; ·085 at 100°.—$PbA''aq$: amorphous pp. — $ZnA''2aq$ (dried at 110°). — $TlHA''$. — Tl_2A''.—$NaTlA''2\frac{1}{2}aq$.—$Ag_2A''aq$: white pp.

Metatartaric acid $(C_4H_6O_6)_x$. A deliquescent, glassy mass, v. sol. water, obtained by melting tartaric acid (Braconnot, *A. Ch.* [2] 68, 299; Erdmann, *A.* 21, 9; Laurent a. Gerhardt, *A.* 70, 848). It is sometimes formed when a solution of tartaric acid is evaporated over a water-bath (Grosjean, *C. J.* 43, 334). Converted by boiling water into tartaric acid.

Salts.—$(NH_4)HA''$. Minute needles. More soluble than the acid ammonium tartrate. Its solution is ppd. by $CaCl_2$ and NH_3Aq only when highly concentrated. $CaA''4aq$. Minute lenticular grains, sol. dil. HClAq, converted by boiling water into calcium tartrate.

Ditartaric acid $C_8H_{10}O_{11}$. An anhydride of tartaric acid, got by heating tartaric acid at 170° till it is no longer ppd. by lime-water (Fremy, *A.* 19, 197; 29, 142; 78, 297). Amorphous and very deliquescent. Sol. alcohol, insol. ether. Its salts are amorphous, v. sol. water, and ppd. by alcohol. They are converted into metatartrates, and finally into tartrates, by boiling water.—CaA''.—BaA''.—PbA''.—CuA''.—Ag_2A''. V. sol. water (Schiff, *A.* 125, 129).

Ethyl ether Et_2A''. Fat-like solid.

Tartrelic acid $C_4H_4O_5$. *Soluble tartaric anhydride.* Formed by quickly heating small quantities of tartaric acid till the fused mass swells up. Yellowish deliquescent mass, sol. water, forming an acid solution, from which $CaCl_2$ ppts. CaA'_2 as an amorphous mass, which becomes crystalline on adding alcohol. Tartrelic acid is converted into tartaric acid by boiling water.

Insoluble tartaric anhydride $C_4H_4O_5$. Formed by heating tartaric acid for some time at 150° and exhausting the product with cold water. Powder, insol. water, alcohol, and ether. Converted by hot water into tartaric acid.

TARTRONIC ACID $C_3H_4O_5$ *i.e.* $CH(OH)(CO_2H)_2$. *Oxy-malonic acid.* Mol. w. 120. [187°]. *Heat of solution* −4331 (Gal a. Werner, *Bl.* [2] 46, 803).

Formation.—1. By spontaneous decomposition of nitro-tartaric acid in aqueous solution (Dessaignes, *C. R.* 34, 731; 38, 44).—2. By the reduction of mesoxalic acid by sodium-amalgam (Baeyer, *J.* 1864, 641).—3. By the action of Ag_2O on bromo-malonic acid (Petrieff, *B.* 11, 414).—4. By boiling chloro-malonic ether with KOHAq, the yield being 25 p.c. of the theoretical amount (Conrad a. Bischoff, *A.* 209, 222).—5. From di-bromo-pyruvic acid and baryta-water at 40° (Grimaux, *B.* 10, 903).—6. From glyoxylic acid by treatment with KCy, the resulting nitrile being saponified (Böttinger, *B.* 14, 729).—7. A product of the action of alkaline cupric solution on glucose (Claus, *Z.* [2] 5, 152; *A.* 147, 114).—8. By slow oxidation of glycerin (Sadtler, *B.* 8, 1456; Campani a. Bizzari, *G.* 12, 1).—9. By heating sodium carboxy-tartronate (Gruber, *B.* 12, 514).

Preparation.—1. By boiling the di-nitrate of tartaric acid (20 g.) with alcohol (60 g. of S.G. ·925) (Demole, *B.* 10, 1778).—2. By warming tri-chloro-lactic ether $CCl_3.CH(OH).CO_2Et$ with a 10 p.c. solution of NaOHAq (5 mols.), neutralising with HOAc and ppg. with $BaCl_2$ (Pinner *B.* 18, 752, 2852).

Properties.—Prisms (containing ½aq), v. sol. water and alcohol, sl. sol. ether. After drying at 100° it loses its water of crystallisation and becomes v. sol. ether. Massol (*C. R.* 114, 422) obtained anhydrous crystals [155°]. Decomposed by fusion, yielding CO_2 and glycolide $C_2H_2O_2$. Reduced by HIAq to malonic acid.

Salts.—Na_2A'' (dried at 100°). V. sol. water. — $K_2A''aq$. — $(NH_4)_2A''$. Needles. — $(NH_4)HA''$. Yields glycollic amide on heating. —$BaA''2aq$. Micro-crystalline powder, v. sl. sol. water (Pinner).—$BaA''aq$ (G.).—$CaA''2\frac{1}{2}aq$ (P.). —$CaA''aq$ (C. a. B.).—CdA''.—PbA'' (dried at 120°).—MnA''.—Ag_2A''. Needles (from hot Aq).

Ethyl ether Et_2A''. (c. 224°). Heavy oil (Freund, *B.* 17, 786; Pinner).

The acetyl derivative $CH(OAc)(CO_2Et)_2$ (c. 161° at 60 mm.), S.G. $\frac{12.5}{16}$ 1·131, is formed from bromo-malonic ether and KOAc in EtOH at 50° (Conrad a. Brückner, *B.* 24, 2997). Br converts it into mesoxalic ether $C(OH)_2(CO_2Et)_2$ [57°].

Amide $CH(OH)(CO.NH_2)_2$. [196°]. Six-sided plates, m. sol. hot water.

Amic acid $CO_2H.CH(OH).CO.NH_2$. [160°]. Formed by boiling sodium dialurate with water (Menschutkin, *A.* 182, 82). Needles, sl. sol. cold water. Converted by nitrous acid into glycollic acid.—KA′ aq.—BaA′$_2$ aq.—PbA′$_2$ ½aq. Needles, v. sol. hot water.—AgA′. Needles.

Phenyl derivative $CH(OPh)(CO_2H)_2$. Formed by saponification of its ether $CH(OPh)(CO_2Et)_2$ (230°–240° at 60 mm.), which is got from bromo-malonic ether, phenol, and NaOEt (C. a. B.). At 196° it forms $CH_2(OPh).CO_2H$.

TARTRONYL-UREA *v.* Dialuric acid.

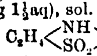
TAURINE $C_2H_7NSO_3$ *i.e.* $CH_2(NH_2).CH_2.SO_3H$. *Amido-ethane sulphonic acid.* Mol. w. 125. S. 6·5 at 12°. H.F. 185,700 (Berthelot a. Matignon, *A. Ch.* [6] 22, 182). Obtained by the action of acids and alkalis on taurocholic acid (Gmelin, *Tiedemann a. Gmelin's Die Verdauung*, 1, 43; Domarçay, *A.* 27, 286; Dumas a. Pelouze, *A.* 27, 292; Redtenbacher, *A.* 57, 170; Strecker, *A.* 65, 132; 67, 34; 91, 101). Occurs in the free state in putrid bile and in the muscles of the oyster, in shark's blood, in the liver, spleen, and kidneys of the ray, and in the lungs of oxen (Valenciennes a. Fremy, *C. R.* 41, 735; Städeler a. Frerichs; Clöetta, *A.* 99, 289). Formed also by heating β-chloro-ethane sulphonic acid with NH_3Aq at 100° (Kolbe, *A.* 122, 33), and by the action of SO_2 on vinylamine (Gabriel, *B.* 21, 2667). Prepared by evaporating ox-bile with dilute HCl at 100°, decanting from a resin, allowing to crystallise, and re-crystallising from water. It may be purified by means of the lead salt.

Properties.—Transparent crystals, m. sol. water, insol. alcohol. Neutral to litmus. Not melted below 240°. Converted by nitrous acid into isethionic acid (Gibbs, *Am. S.* [2] 25, 30). Decomposed by potash-fusion.

Salts.—NaA′. Very deliquescent (Lang, *Bl.* [2] 25, 180).—CaA′$_2$. Slender needles, v. e. sol. water.—PbA′$_2$. Needles, v. e. sol. water.—$Pb_3A'_4(OH)_2$.—CdA′$_2$.—HgA′$_2$.—$Hg_2A'_2O$ (Engel, *Bl.* [2] 23, 532).—AgA′.

Benzoyl derivative $NHBz.C_2H_4.SO_3H$. Formed by heating μ-phenyl-thiazole tetrahydride with HCl and bromine-water (Gabriel a. Heymann, *B.* 23, 159). Syrup.—AgA′. Spherical groups of plates.

Phthalyl derivative $(C_8H_4O_2):N.CH_2.CH_2.SO_3H$. Got by oxidising di-phthalimido-di-ethyl-disulphide with HNO_3 (S.G. 1·25) (Gabriel, *B.* 24, 1116). Crystals (containing 1½aq), sol. EtOAc. Tastes bitter.

Imide 
$C_2H_4<\begin{smallmatrix}NH\\SO_2\end{smallmatrix}>$. [45°–50°]. Prepared from β-chloro-ethane-sulphonic chloride $CH_2Cl.CH_2.SO_2Cl$ by treatment with ammonia (James, *C. J.* 49, 491). Solid, resembling gum arabic; bitter in taste. V. sl. sol. cold, v. sol. hot, water, insol. alcohol and ether. Ppd. HgO appears to form the compound $(C_2H_4SO_2N)_2Hg$.

Ethyl-taurine *v.* Ethyl-amido-ethane sulphonic acid.

Methyl-taurine *v.* Methyl-amido-ethane sulphonic acid.

TAUROCHENOCHOLIC ACID $C_{29}H_{49}NSO_6$. Occurs as K and Na salts in goose-bile (Heintz a. Wislicenus, *P.* 108, 547; Otto, *A.* 149, 192). Amorphous, sol. water and alcohol. Decomposed by boiling with baryta or potash into taurine and chenocholic acid.—NaA′aq (dried at 110°). Small tables. Its aqueous solution gives pps. with $CaCl_2$, $AgNO_3$, and lead subacetate, but not with lead acetate.

TAUROCHOLIC ACID $C_{26}H_{45}NSO_7$. Occurs as Na salt in the bile of most animals (Strecker, *A.* 67, 30; 70, 169; Hüfner, *J. pr.* [2] 19, 302; Copeman a. Winston, *J. Physiol.* 10, 213). Obtained by ppg. with lead acetate, filtering from lead glycocholate, and ppg. lead taurocholate by lead subacetate. Deliquescent silky needles, v. sol. water and alcohol, m. sol. ether. Dextrorotatory, $[\alpha]_D = 25°$ (Hoppe-Seyler, *Arch. Path. Anat.* 15, 126). Boiling water splits it up into taurine and cholic acid. Antiseptic, and ppts. albumen completely from its solutions (Maly, *M.* 4, 89).

Salts.—NaA′ (dried at 120°). Ppd. by alcohol in an amorphous state, rendered crystalline by ether.—KA′. Needles, resembling wavellite.

TAUROCYAMINE $C_3H_9N_3SO_3$ *i.e.* $NH:C(NH_2).NH.CH_2.CH_2.SO_3H$. [226°]. S. 4 at 21°. Formed by heating taurine with cyanamide (1 mol.) and water at 110° (Engel, *B.* 8, 1597; Dittrich, *J. pr.* [2] 18, 63). Small white prisms, v. sol. water, insol. alcohol and ether. From cold water it crystallises with aq.

TAXINE $C_{37}H_{52}NO_{10}$. [82°]. Obtained from the leaves, twigs, and fruit of the yew (*Taxus baccata*) by extracting with ether (Lucas, *Ar. Ph.* [2] 85, 145; Van der Harst, *R. T. C.* 3, 279; Marmé, *Bl.* [2] 26, 417; Hilger a. Brande, *B.* 23, 464). The ethereal solution is quickly shaken with acidulated water, and the solution ppd. by NH_3Aq. Crystalline. Gives off aromatic fumes on melting. V. sl. sol. water, v. sol. alcohol and ether, insol. benzene. Conc. H_2SO_4 gives a deep purple; Fröhde's reagent a reddish-violet colour. Gives yellow pps. with sodium phosphomolybdate, I in KI, and potassium bismuth iodide. Insol. alkalis. The salts crystallise with difficulty.—**Salts:** B′HCl.—$B'_2H_2SO_4$.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$.—B′EtI.

TECTOQUINONE. [171°]. Obtained from teak resin or by the distillation of teak wood (Romanis, *C. J. Proc.* 4, 116). Amber-yellow crystals, sol. alcohol. Reduced by zinc-dust and HOAc to $C_{18}H_{22}$. Yields a nitro-derivative and a bromo-derivative [165°].

TELLURATES. Salts of telluric acid, H_2TeO_4 (*q.v.*, p. 649). The *normal tellurates* of monovalent metals have the composition $M_2TeO_4.xH_2O$; there are also *acid tellurates* $MHTeO_4.xH_2O$; and two classes of *tetratellurates*, (1) $M_2Te_4O_{13}.xH_2O$, which are soluble in water when M is an alkali metal, and (2) $M_2Te_4O_{13}$, which are insoluble in water. The hydrated tetratellurates may be represented as *acid ditellurates* derived from the hypothetical acid $H_2Te_2O_7$; thus $K_2Te_4O_{13}.4H_2O = 2KHTe_2O_7.3H_2O$. Some acid salts may be represented as derived from hypothetical ditelluric acid, *e.g.*

$$PbTe_2O_7\ (= PbTeO_4.TeO_3).$$

The normal alkali tellurates are obtained by saturating H_2TeO_4 with MOHAq or M_2CO_3Aq and crystallising. Alkali acid tellurates, and hydrated tetratellurates, are obtained by interactions of acids with the normal tellurates; anhydrous (insoluble) tetratellurates of the alkali

metals are formed by heating the acid tellurates; thus $6KHTeO_4 = K_2Te_4O_{13} + 2K_2TeO_4 + 3H_2O$. Most of the other tellurates are obtained from the alkali salts by double decomposition.

The alkali tellurates, other than those of the form $M_2Te_4O_{13}$, are soluble in water; most of the other tellurates are insoluble or sparingly soluble in water. Tellurates generally dissolve easily in HClAq; the solutions are not ppd. by water, but on boiling the solutions become yellow, give off Cl, and then yield a pp. of H_2TeO_3 on addition of water. Acidulated solutions of tellurates are slowly decomposed by H_2S, probably with ppn. of TeS_3 (*v.* TELLURIUM SULPHIDES, p. 655). Solutions of tellurates are slowly reduced by SO_2, more quickly on heating, with separation of Te. When tellurates are heated to redness they give off O and form tellurites; heated with K_2CO_3 and charcoal, they give K_2Te.

The tellurates have been examined chiefly by Berzelius (*P.* 32, 577); and some of them also by Oppenheim (*J. pr.* 71, 267).

Potassium tellurates. The *normal salt* $K_2TeO_4.5$aq is obtained by dissolving H_2TeO_4 and K_2CO_3, in the ratio $H_2TeO_4:K_2CO_3$, in hot water and crystallising; also by dissolving H_2TeO_4 in excess of KOHAq, heating, and allowing to cool slowly. Crystallises in rhombic prisms, isomorphous with K_2SO_4 (Handl, *J.* 1861. 266). The crystals become moist in air and form $KHTeO_4.x$aq and K_2CO_3. The *acid salt* $2KHTeO_4.3$aq separates on adding to K_2TeO_4Aq sufficient H_2SO_4Aq, or other strong acid, to remove half the potassium; the salt is crystallised from hot water. This salt is slightly soluble in cold water, but much more soluble in hot water; when heated it is converted into K_2TeO_4 and $K_2Te_4O_{13}$. The *tetratellurate* $K_2Te_4O_{13}$ is obtained, as a yellow powder, by heating $2KHTeO_4.3$aq below redness and washing out K_2TeO_4 in water. $K_2Te_4O_{13}$ is insoluble in water, also in HClAq or HNO_3Aq except after prolonged boiling. The *hydrated tetratellurate* $K_2Te_4O_{13}.4H_2O$—which may also be regarded as an *acid ditellurate* $2KHTe_2O_7.3H_2O$—is formed by adding H_2SO_4Aq, or another strong acid, to K_2TeO_4Aq in quantity to remove 6K from $4K_2TeO_4$ ($4K_2TeO_4Aq + 3H_2SO_4Aq = K_2Te_4O_{13}Aq + 3H_2O + 3K_2SO_4Aq$), and crystallising. The salt is fairly soluble in cold water; it is partly decomposed to $KHTeO_4$ and H_2TeO_4Aq by repeatedly crystallising in aqueous solution.

The following tellurates have been described (Berzelius, *l.c.*; Oppenheim, *l.c.*): *Ammonium salts* $(NH_4)_2TeO_4$, $(NH_4)_2Te_2O_7$, $(NH_4)_2Te_4O_{13}$, obtained by ppg. solutions of the corresponding salts of K or Na with NH_4Cl. *Barium salts* $BaTeO_4.3$aq, $BaH_2(TeO_4)_2.2$aq, $BaTe_4O_{13}$, obtained by ppn. *Cadmium salt* $CdTeO_4$, obtained by ppn. *Calcium salt* $CaTeO_4$, obtained by ppn. *Lead salts* $PbTeO_4$, $PbTe_2O_7$, $PbTe_4O_{13}$, by ppn; a basic salt is also said to exist. *Silver salts* Ag_2TeO_4, and several basic salts $xAg_2O.yTeO_3$. *Sodium salts* $Na_2TeO_4.x$aq, $NaHTeO_4.x$aq, $NaHTe_2O_7.x$aq, and $Na_2Te_4O_{13}$, obtained similarly to the potassium salts. Tellurates of Al, Cr, Co, Cu, Fe, Li, Mg, Mn, Hg, Ni, and Sr have also been described, but only very superficially.

M. M. P. M.

TELLURHYDRIC ACID H_2Te; *v.* HYDROGEN TELLURIDE, vol. ii. p. 727.

TELLURIC ACID H_2TeO_4; crystallises from solutions as $H_2TeO_4.2H_2O$.

Formation.—1. By oxidising Te by *aqua regia.*—2. K_2TeO_4 is formed by the interaction of Cl with K_2TeO_3Aq, also by fusing TeO_2 with KNO_3 or $KClO_3$.

Preparation.—1. A mixture of TeO_2, $KClO_3$, and KOH, in the ratio $TeO_2:2KClO_3:2KOH$ is thoroughly fused; the fused mass is dissolved in water and $BaCl_2$Aq is added; the pp. of $BaTeO_4$ is purified by recrystallisation from hot water, and is then dried at 100°; the dry $BaTeO_4$ is mixed with its own weight of water and one-fourth its weight of conc. H_2SO_4, and heated till decomposition is complete, when $BaSO_4$ is removed by filtration, and the filtrate is evaporated at 100° to the crystallising point; the crystals that separate are dried, powdered, washed repeatedly with alcohol to remove H_2SO_4, and recrystallised from water (Oppenheim, *J. pr.* 71, 267). Berzelius (*P.* 28, 392; 32, 1) fused TeO_2 with an equal weight of K_2CO_3 or Na_2CO_3, dissolved in water, added KOH equal to the weight of TeO_2 used, passed in Cl until the liquid smelt strongly thereof, ppd. by $BaCl_2$Aq, and proceeded as described above.—2. TeO_2 is dissolved in HNO_3Aq, the solution is boiled with PbO_2 and filtered, Pb is ppd. from the filtrate by H_2SO_4Aq, the filtrate from $PbSO_4$ is evaporated to dryness at 100°, the residue is digested with alcohol and ether to remove H_2SO_4, and is then crystallised from hot water *in vacuo* (Becker, *A.* 180, 257).

Properties and Reactions.—$H_2TeO_4.2H_2O$ is obtained by slow crystallisation in white, monoclinic crystals, resembling gypsum, S.G. 2·9999 at 25·5° (Clarke, *Am. S.* [3] 16, 401). When obtained by rapid evaporation $H_2TeO_4.2H_2O$ appears as a glassy solid. Heated to c. 130° H_2TeO_4 is obtained; decomposition begins at a little above 160° to TeO_3 and H_2O, and at c. 180° TeO_3 begins to decompose to TeO_2 and O, this decomposition being complete at c. 350° (Wills, *C. J.* 35, 704). H_2TeO_4 has S.G. 3·425 at 18·8° (Clarke, *l.c.*). $H_2TeO_4.2H_2O$ is slightly soluble cold water; it is dissolved fairly easily by boiling water; soluble in acid and alkali solutions; almost, if not quite, insoluble in alcohol. H_2TeO_4 dissolves very slowly in boiling water. Aqueous solutions of H_2TeO_4 have a metallic, not a sour, taste; they very slightly redden litmus. Thomsen (*Th.* 2, 277) gives the following H.F.: $[Te,O^3,Aq] = 98,380$; $[TeO^3Aq,O] = 21,200$. H_2TeO_4 dissolves gradually in hot, fairly conc. HClAq, with evolution of Cl and formation of H_2TeO_3Aq. H_2TeO_4Aq is not reduced by passing H_2S into it, but if the solution is saturated with H_2S and kept in a warm place, in a closed flask, for some time, the liquid becomes brown, and flakes, probably of TeS_3 (*v.* TELLURIUM SULPHIDES, p. 655), are deposited.

H_2TeO_4Aq reacts with alkalis to form salts M_2TeO_4 and $MHTeO_4$; salts of the forms $MHTe_2O_7$ and $M_2Te_4O_{13}$ are also known (*v.* TELLURATES, p. 648).

M. M. P. M.

TELLURIDES. Any compound of Te with a single element more positive than itself is called a telluride. Tellurides of the heavier metals are generally formed by melting the metals with Te, also by passing H_2Te into solutions of salts of the metals; tellurides of K and Na are formed by heating TeO_2 with K_2CO_3 or Na_2CO_3 and charcoal; many tellurites and tellurates give tellurides when heated in a current of H. Te ppts. tellurides of Cu, Ag, and some other metals, by boiling solutions of salts of these metals with Te (Parkmann, *C. C.* 1862. 814). Tellurides of K and Na dissolve in water with a red colour; this colour is due either to polytellurides or to the presence of traces of oxides according to Demarçay (*Bl.* [2] 40, 99). Berthelot a. Fabre (*C. R.* 105, 92) obtained colourless solutions of alkali tellurides by passing pure H_2Te into solutions of alkalis; a trace of O produced a red colour and separated Te. Tellurides react with HClAq giving off H_2Te; they are oxidised to tellurites by HNO_3Aq, and to tellurites and tellurates by *aqua regia*. Warmed in Cl tellurides give metallic chlorides and $TeCl_4$.

Tellurides of Sb, As, Bi, Au, Fe, K, Ag, and Na are mentioned under these metals (*cf.* Brauner, *C. J.* 55, 388). M. M. P. M.

TELLURITES. Salts of tellurous acid H_2TeO_3 (*q. v.*, p. 656). The *normal* and *acid tellurites* of monovalent metals belong to the forms M_2TeO_3 and $MHTeO_3$. Some salts are also known containing relatively more of the acidic radicle; these may be formulated as $M_2O.xTeO_2$ where x is 2 and 4; or they may be regarded as $M_2TeO_3.xTeO_2$, where x is 1 and 3; or finally these *hyperacid salts* may be looked on as $M_2Te_2O_5$ and $M_2Te_4O_9$—that is, as derivatives of the hypothetical acids $H_2Te_2O_5$ and $H_2Te_4O_9$.

Tellurites are generally formed by heating together basic oxides and TeO_2 in the proper proportions; some tellurites of the heavier metals are obtained by ppn. from solutions of alkali tellurites. Tellurites of the alkali metals dissolve readily in water; those of the alkaline earth metals are less soluble; the others are insoluble in water. Most tellurites dissolve in HClAq, forming yellow solutions which do not give off Cl on heating; this reaction distinguishes them from tellurates (*v.* p. 649). Solutions of tellurites in a little HClAq deposit H_2TeO_3 on dilution. Most tellurites are fusible, and crystallise on cooling; the hyperacid alkali tellurites form colourless glass-like solids after fusion. By strongly heating with charcoal and K_2CO_3 most tellurites give K_2Te.

Tellurites of potassium. The *normal salt* K_2TeO_3, and the *acid salt* $K_2TeO_3.TeO_2$ ($=K_2Te_2O_5$ or $K_2O.2TeO_2$) are prepared by fusing TeO_2 with K_2CO_3 in the proper proportions. K_2TeO_3 melts at a red heat; dissolves slowly in cold water, more quickly in boiling water; the aqueous solution has an alkaline taste and reaction, and is decomposed by the CO_2 in the air. $K_2O.2TeO_2$ melts below redness, and solidifies again to a transparent, colourless, crystalline mass; dissolved by boiling water, and the solution on cooling deposits $K_2O.4TeO_2$. The *tetra-tellurite* or *hyperacid tellurite* $K_2O.4TeO_2.4H_2O$ ($=K_2TeO_3.3TeO_2.4H_2O$ or $K_2Te_4O_9.4H_2O$) is prepared by boiling H_2TeO_3Aq with K_2CO_3 and filtering at 100°; the salt is deposited on cooling in microscopic six-sided prisms and tablets. This salt reacts with cold water to give a solution of K_2TeO_3 and $K_2Te_2O_5$ and a gelatinous pp. of H_2TeO_3; when heated $4H_2O$ is given off, and $K_2O.4TeO_2$ remains as a salt which melts at a moderate red heat and solidifies on cooling to a colourless glass.

The tellurites have been examined chiefly by Berzelius (*P.* 32, 577; *v.* also Oppenheim, *J. pr.* 71, 267). Salts of the following metals have been isolated, but many have been studied in a very superficial way: Al, NH_4, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, Ag, Na, Sr, and Zn. M. M. P. M.

TELLURIUM. Te. At. w. c. 125 (*v. infra*). Mol. w. c. 250 (*v. infra*). Melts at c. 455° (Carnelley a. Williams, *C. J.* 37, 125). Boils at c. 1390° (Deville a. Troost, *C. R.* 91, 83). S.G. 6·2549 at 0° (after compression); 6·2322 at 0° (uncompressed) (Spring, *B. B.* 5, 854); 6·2549 at 18·2° (after melting in H) (Přiwoznik, *C. C.* 1892. ii. 962; for further data *v.* Clarke's *Table of Specific Gravities* [2nd ed.] 10). V.D. at c. 1390° to c. 1440° = 130 (Deville a. Troost, *C. R.* 56, 891). S.H. (21° to 51°, crystalline) ·0475 (Kopp, *T.* 1865. 71); (at 98°, crystalline) ·0483; (at 98°, after distillation in SO_2) ·0518 (Fabre, *A. Ch.* [6] 14, 101). C.E. (linear, at 0°) ·00001675 (Fizeau, *C. R.* 68, 1125). E.C. ·000777 at 19·6 (Ag at 0° = 100) (Matthiesen, *P.* 103, 428); conductivity increases slightly when light falls on Te; the increase is very much less than in the case of Se (*v.* Adams a. Day, *Pr.* 24, 163; 25, 113). E.C. decreases slightly to c. 100°-140°, and then increases to 200°; on cooling after fusion E.C. decreases regularly and markedly; the following values are given by Exner (*P.* 158, 625) ·0035 at 200°, ·00286 at 20° (after fusion), ·000435 at 20° (after very slow cooling from fusion). Te crystallises in rhombohedra; $a{:}c = 1{:}1{\cdot}3298$; it is isomorphous with S and Se (*v.* Muthmann, *Z. P. C.* 8, 396). For emission-spectrum *v.* Plücker a. Hittorf (*Pr.* 13, 153); Thalen; Salet (*A. Ch.* [4] 28, 51); Ditte (*C. R.* 73, 622); Hartley a. Adeney (*T.* 1884 [1] 117). For absorption-spectrum of vapour of Te *v.* Gernez (*C. R.* 74, 1190). H.C. $[Te,O^3,Aq] = 98,380$ (*Th.* 2, 278).

Historical.—Examining a mineral containing gold from the Seven Mountains in 1782 Müller von Reichenstein suspected the presence of a new metal (*Abhand. einer Privatgesellschaft in Böhmen*). He sent a specimen of the mineral to Bergmann, who said that it contained a metal which was not the same as that in blende. In 1798 Klaproth received some of the mineral from M. von R., and isolated the characteristic element, to which he gave the name tellurium (from *tellus* = the earth) (K., *Beiträge zur chem. Kenntniss der Mineralkörper*, 3, 1; *cf. Crell's Ann.* 1798. 91; and *G. A.* 12, 246). The compounds of Te were more fully examined by Berzelius (*S.* 6, 311; 34, 78; *P.* 8, 411; 28, 392; 32, 1, 577).

Occurrence.—Te is found native, in small quantities, and in a few localities—chiefly in Hungary and Transylvania, and in Virginia, U.S.; it generally accompanies Au and Ag; specimens have been obtained with 97–98 p.c. Te. Tellurides are also found in small quantities in Hungary, Mexico, California, Bolivia, and some other places; in considerable quantities in Colorado; these are generally compounds of Te with Bi, Ag, Pb, Bi and S, Ag and Au, Au, Pb and Sb; *tellurite* (or *tellurium-ochre*) containing TeO_2 is found in small quantities in the Seven Mountains (*v.* G. Rose, *P.*

18, 64; Rammelsberg, *J. M.* 1874. 30; Burkart, *J. M.* 1873. 476; Silliman a. Marvine, *Am. S.* [3] 8, 25; Mathewson, *J. M.* 1866. 93; Genth, *J. M.* 1875. 188, 314).

Formation.—1. By passing SO_2 into H_2TeO_3Aq; $H_2TeO_3Aq + 2SO_2 + H_2O = 2H_2SO_4Aq + Te$. Also by ppg. solution of $TeCl_4$ in dilute HClAq, or of a Te compound in H_2SO_4Aq, by an alkali sulphite. 2. By reducing a boiling solution of $(NH_4)_2TeO_4Aq$ by grape sugar (Stolba, *J.* 1873. 214).—3. By decomposing K_2TeAq by air or oxygen (*v.* Oppenheim, *J. pr.* 71, 267; 81, 308; Himly, *J.* 1877. 213).—4. By ppn., by means of zinc, from solutions of Te compounds in H_2SO_4Aq (*v.* Löwe, *J. pr.* 60, 163).

Preparation.—There are several methods of preparing crude Te from the minerals that contain it. Native bismuth telluride is made into a paste with oil and K_2CO_3, and gradually heated to whiteness in a covered crucible; K_2Te is extracted from the fused mass by boiling water, and the solution deposits Te on standing in air. Or the mineral containing Te is powdered and treated with dilute HClAq; the insoluble matter is gradually added to three times its weight of conc. H_2SO_4, and heating is continued until SO_2 ceases to be given off; the solid that forms on cooling is dissolved in water containing a little HCl; the solution is filtered from AgCl, Te is ppd. from the filtrate by zinc, and undissolved zinc is removed by digestion with dilute HClAq. For details and other methods *v.* Berzelius (*P.* 8, 411; 28, 392); Löwe (*J. pr.* 60, 163); Wöhler (*A.* 84, 69); Oppenheim (*J. pr.* 81, 308); Schnitzer (*D. P. J.* 211, 484, 492); Schwarz (*D. P. J.* 186, 29).

To prepare pure Te, Brauner (*C. J.* 55, 382; *cf. M.* 10, 411) recommends to digest the crude material with HClAq in a large flask, and to oxidise by HNO_3Aq added little by little till the solid matter becomes white, to evaporate several times with conc. HClAq (to remove HNO_3), and then to dilute cautiously with water, taking care not to add enough water to ppt. H_2TeO_3 along with any $PbCl_2$ which may come down. He then adds some saturated SO_2Aq, warms to 60°-70°, and ppts. Te by passing SO_2 into the warm solution. The Te thus obtained generally contains a little copper and lead selenides. The pp. is dried and fused in small portions with KCy; the fused mass, which contains K_2Te, is dissolved in water, from which air has been removed, in a stoppered flask; the liquid is allowed to clear (there is generally a small pp. of tellurides of heavy metals mixed with a trace of Te) and is then poured off, and a current of air is passed through it, whereby Te is ppd. The Te is dried, placed in a porcelain boat, which is introduced into a wide tube of hard glass surrounded by wire gauze, and distilled in a current of pure dry H. (For a method of purification based on the ppn. of Te from $(NH_4)_2TeO_4Aq$ by grape sugar, *v.* Stolba, *J.* 1873. 214.)

Properties.—As prepared by sublimation in H, tellurium is a white, shining, crystalline, very brittle solid, unchanged by exposure to air. During distillation in H, Brauner (*l.c.*) noticed that some H_2Te was formed, and was decomposed with deposition of needle-shaped crystals of Te, some of which were 1 centim. in length. The crystals of Te are hexagonal rhombohedra, isomorphous with S and Se (*v.* Muthmann, *Z. P. C.* 8, 396). By allowing K_2TeAq to decompose in air, H. Rose obtained six-sided prisms with rhombohedral summits (*P.* 21, 443; *cf.* Fabre a. Berthelot, *C. R.* 104, 1405). Amorphous Te is obtained as a brown powder by ppg. H_2TeO_3Aq by SO_2; on warming, the amorphous variety changes to the crystalline, giving off a large quantity of heat (F. a. B., *l.c.*). Te that has been melted and cooled quickly seems to contain both the crystalline and the amorphous varieties. According to Fabre (*A. Ch.* [6] 14, 100), both varieties have practically the same S.H. at c. 100°. Te melts at c. 455° and boils at c. 1390°; the vapour is golden yellow. Heated in air it burns with a brilliant blue-green flame to white clouds of TeO_2, which are poisonous; the smell, like that of decaying radishes, that is noticed on burning impure Te is due to the oxidation products of Se, which is commonly present in specimens of crude Te. Te dissolves in very conc. boiling KOHAq, forming a red liquid that contains K_2TeO_3 and K_2Te; on allowing to cool, or on adding water, the whole of the Te separates. HClAq is without action on Te; conc. hot H_2SO_4 dissolves it slightly, but the Te separates on dilution; when heated strongly with conc. H_2SO_4 Te dissolves to H_2TeO_3 with evolution of SO_2. Te dissolves in SO_3, forming $TeSO_3$. Conc. HNO_3Aq forms a solution of H_2TeO_3; *aqua regia* forms H_2TeO_3 and some H_2TeO_4. Molten KNO_3 produces K_2TeO_4.

In its physical properties Te approaches the metals, and especially resembles Sb. In its chemical properties Te is, on the whole, non-metallic; but the oxide TeO_2 combines with certain anhydrides of strong acids to form salt-like compounds, and the oxide TeO is said to dissolve in H_2SO_4Aq, forming $Te(SO_4)_2$. Te is closely related to Se, and less closely to S; it shows distinct analogies with Cr, Mo, W, and U (*v.* Oxygen group of elements, vol. iii. p. 705, and Chromium group of elements, vol. ii. p. 168). The atom of Te is divalent in the gaseous molecules TeH_2 and $TeCl_2$, and tetravalent in the gaseous molecule $TeCl_4$.

Atomic weight of tellurium. The at. w. of Te was determined by Berzelius in 1812, 1818, and 1832 by oxidising Te by HNO_3Aq and weighing the TeO_2 produced; he obtained values varying from 127·9 to 128·5 (*P.* 8, 24; 28, 395; 32, 16). In 1857 von Hauer analysed K_2TeBr_6, and obtained values from 126·5 to 128·1 (*W. A. B.* 25, 135). In 1879 Wills determined the weight of TeO_2 obtained by oxidising Te by HNO_3Aq and by *aqua regia*, and he also made analyses of K_2TeBr_6; his results varied from 126·1 to 129·3 (*C. J.* 35, 704). In 1883 Brauner obtained numbers varying from 124·94 to 125·4, by oxidising Te to TeO_2, by converting Te and TeO_2 into $(TeO_2)_2SO_3$, and by synthesising Cu_2Te (*J. R.* 1883. [1] 433; abstract in *B.* 16, 3055). In 1889 Brauner made a very careful revision of the at. w. of Te (*C. J.* 55, 382):—(i.) by oxidising Te to TeO_2 he obtained values varying from 124·48 to 127·28; (ii.) by converting TeO_2 into $(TeO_2)_2SO_3$, the numbers varied from 124·7 to 129 (one result gave 135·9); (iii.) by conversion of Te into $(TeO_2)_2SO_3$, the numbers varied from 124·3 to 129·7; (iv.) by syntheses of tellurides of Ag, Cu, and Au, the numbers varied from 125·7 to 129·9; (v.) by analysis of TeO_2 the value 127·2 was obtained, but only one satisfactory analysis was made; (vi.) by analyses of $TeBr_4$ the numbers varied from 127·27 to 127·31. The results obtained by analysing $TeBr_4$ were more concordant than any obtained by the other methods; but the value 127·3 is almost ·75 units greater than the at. w. of iodine; hence it seems as if the at. w. of Te is greater than that of I. But if this is so, Te must be separated from S, Se, and the chromium metals, which are placed in Group VI. in the periodic arrangement of the elements; and Te must be placed either with the halogens in Group VII. (I being put into Group VI.), or this element must find a place in Group VIII. (I remaining in Group VII., and an empty place being left in Group VI., Series 7). The chemical properties of Te show that it belongs to the same group as S and Se; and the chemical properties of I make it impossible to place that element elsewhere than with F, Cl, and Br.

Is tellurium a homogeneous body? Rather than doubt the applicability of the periodic law, Brauner made the hypothesis that tellurium is not a homogeneous body, but that it contains an admixture of foreign substances. He dissolved Te, and ppd. in fractions by SO_2, fused the fractions with KCy, dissolved in water, and ppd. fractionally by a current of air; he then distilled each fraction in H, and converted it into $TeBr_4$, and analysed each fraction. The values thus obtained for the at. w. of Te were almost identical, the mean being 127·33. Pure TeO_2 was then dissolved in HClAq, and the solution was ppd. in eight fractions by ammonia; the filtrate from the eighth fraction was ppd. by SO_2 in presence of HClAq; after boiling off SO_2 from the filtrate from the ninth fraction, the liquid was saturated with H_2S, and the TeO_2 in solution was obtained, converted into Te, and this converted into $TeBr_4$; the at. w. thus obtained (in three experiments) was 127·32, the three experiments agreeing extremely well. Te was then fused, but not distilled, in a current of H; it was then converted into $TeBr_4$, which was freed from $TeBr_2$ by fractional sublimation *in vacuo*, without converting the $TeBr_4$ into vapour, and analysed; the values obtained for the at. w. of Te differed very much, ranging from 128·5 to 137·4. From these results Brauner concluded that 'if tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. . . . If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained. . . . It is therefore very probable that on distilling tellurium in a current of hydrogen, and the tetrabromide in a vacuum, one constituent of tellurium escapes partly, the presence of which in the last cases renders the atomic weight higher.' Brauner prepared $TeBr_2$ by fusing $TeBr_4$ with excess of Te, and subliming either *in vacuo* or in a current of CO_2; the analyses of different specimens of $TeBr_2$ showed percentages of Br varying from 54·658 to 55·14; the percentage of Br calculated for Te = 127·32 is 55·6. Brauner concluded that '*tellurium is not a simple substance.*' This conclusion is still held by B. to be correct. In a private communication (January 1894) he says: 'I consider Te to be a mixture of two elements that cannot be separated by ordinary chemical means, not even by fractionation. It cannot, however, be shown that the at. w. of Te is about 125, for all attempts I have made in this direction have failed completely. All atomic weight determinations made by me, and others, giving values higher or lower than 127·3 are due, partly to impurities, but in most cases to some undetected source of error.'

Molecular weight of tellurium. Deville a. Troost (*C. R.* 56, 891) found the V.D. of Te between c. 1390° and c. 1440° to be 130; this gives the mol. w. of c. 260. As the at. w. of Te is not known with certainty, it is not possible at present to correct the value deduced for the mol. w. from the determinations of V.D. The gaseous molecule of Te is diatomic.

Reactions and Combinations.—1. Heated in *air*, or *oxygen*, Te is burnt to TeO_2.—2. Heated in excess of *chlorine* $TeCl_4$ is produced; with *bromine* $TeBr_4$ is produced; with *iodine* the product is TeI_2.—3. Te and *sulphur* can be melted together in all proportions; it is doubtful whether definite compounds are formed or not (*v.* Tellurium sulphides, p. 655). Te and *selenion* can also be melted together in all proportions; no definite compound has been isolated.—4. *Nitric acid* forms H_2TeO_3; according to Klein a. Morel (*Bl.* [2] 43, 198), cold HNO_3Aq first forms $4TeO_2.N_2O_5.xaq$ (*v.* Tellurium dioxide, p. 655). *Aqua regia* produces a mixture of H_2TeO_3 and H_2TeO_4.—5. Te dissolves in hot conc. *potash solution*, forming a red solution that contains K_2Te and K_2TeO_3; on addition of water Te separates ($2K_2TeAq + K_2TeO_3Aq = 3K_2OAq + 3Te$).—6. Fusion with *potassium nitrate* produces K_2TeO_4.—7. Fusion with *potassium carbonate* produces a mixture of K_2Te and K_2TeO_3.—8. Te dissolves in *sulphur trioxide*, forming $TeSO_3$ (*v. thio-oxide* under Tellurium oxides, p. 655).

Detection and Estimation.—Free Te is readily detected by fusing with charred cream of tartar and dissolving in water, whereby a red solution is obtained that deposits Te in dark-brown flakes on standing in air. Tellurous acid and tellurites dissolve in dilute HClAq, and addition of water ppts. white H_2TeO_3; SO_2 ppts. Te from solutions of tellurites in dilute HClAq or HNO_3Aq. Solutions of tellurates in acids give no pps. with water; solutions in HClAq give off Cl on boiling, being reduced to tellurites, and are then ppd. by water. For a test for Te based on the formation of red $TeSO_3$ by passing TeH_2 into H_2SO_4Aq *v.* Divers a. Shimosé, *C. J.* 43, 329. Te is generally estimated by ppg. the element, from solution of H_2TeO_3 or a tellurite, by alkali sulphite, SO_2, or grape sugar (Kastner, abstract in *C. J.* 29, 440; *cf.* Donath, abstract in *C. J.* 60, 242). In *C. J.* 59, 238, Brauner describes a method for the volumetric estimation of Te by $KMnO_4Aq$.

Tellurium, acids of; *tellurhydric acid* H_2Te (vol. ii. p. 727); *tellurous acid* H_2TeO_3 (this vol., p. 656); *telluric acid* H_2TeO_4 (this vol., p. 649). The existence of the potassium salt of HCNTe is probable (*v.* Tellurocyanides, vol. ii. p. 353).

Tellurium, alloys of. The compounds of Te with metals are sometimes classed with the more definite alloys (*v.* TELLURIDES, p. 649).

Tellurium, antimonides of, *v.* ANTIMONY; *Combinations*, No. 7, vol. i. p. 283.

Tellurium, arsenides of, *v.* ARSENIC; *Combinations*, No. 6, vol. i. p. 303.

Tellurium, bromides of. Two bromides have been isolated, $TeBr_2$ and $TeBr_4$; both are formed by the direct combination of Te and Br. The bromides can be sublimed, under reduced pressure, without change. The V.D. of neither has been determined; but, from the analogy of $TeCl_2$ and $TeCl_4$, the formulæ are probably molecular.

TELLURIUM DIBROMIDE $TeBr_2$. Formula probably molecular, from analogy of $TeCl_2$. Prepared by fusing $TeBr_4$ with excess of powdered Te, and subliming either *in vacuo* or in a current of dry CO_2. A blackish-green crystalline mass; obtained in steel-grey needles by slow sublimation (Brauner, *C. J.* 55, 410). Melts c. 305°, and boils c. 343° (Carnelley, *Melting- and Boiling-point Tables*, 1, 21). $TeBr_2$ is very hygroscopic; it is decomposed by water to H_2TeO_3Aq and HBrAq. Dissolves in tartaric acid solution, forming $TeBr_4$ and Te (Brauner, *l.c.*).

TELLURIUM TETRABROMIDE $TeBr_4$. (*Telluric bromide.*) Formula probably molecular, from analogy of $TeCl_4$. Prepared by shaking together powdered Te and Br, in the proportion Te:4Br, warming in a current of dry CO_2, and then subliming *in vacuo* (for details and description of apparatus, *v.* Brauner, *C. J.* 55, 396). Forms a crystalline crust, which is fiery red when hot and orange coloured when cold. S.G. $\frac{15^\circ}{4^\circ} = 4{\cdot}31$ (Brauner, *l.c.*, p. 407). Melts at c. 380°, and boils at 414°–427°, according to Carnelley a. Williams (*C. J.* 35, 563; 37, 125). Dissolves in a little water without change; on dilution a colourless liquid is obtained, containing HBr and H_2TeO_3; crystals are obtained by evaporating over H_2SO_4, and are said by Berzelius to be $TeBr_4.xH_2O$. By adding $AgNO_3Aq$ to a solution of $TeBr_4$ in tartaric acid, Brauner (*C. J.* 55, 398) obtained AgBr and also crystalline scales probably $(C_4H_4O_5)_2.Ag_2O.TeO_2.2aq$; this compound is called by B. *tellurium-silver tartar emetic* (*cf.* Klein a. Morel, *C. R.* 100, 1140). $TeBr_4$ forms *double salts* with alkali bromides. The salt $TeBr_4.2KBr$ ($=K_2TeBr_6$) is prepared by dissolving the proper quantity of KBr in water, adding Te, running in Br, shaking till the Te is dissolved, filtering, and evaporating at 100° (Wills, *C. J.* 35, 711; *cf.* von Hauer, *W. A. B.* 25, 135). Dark-red, opaque, lustrous crystals; orthorhombic, $a:b:c = 1:1{\cdot}4901:1{\cdot}3658$ (W., *l.c.*); *cf.* Wheeler (*Am. S.* [3] 45, 267), where some other salts of the form M_2TeBr_6 are described.

Tellurium, chlorides of. Two compounds are known, $TeCl_2$ and $TeCl_4$; both have been gasified, and the formulæ of both are molecular. The chlorides are formed by the direct combination of their elements.

TELLURIUM DICHLORIDE $TeCl_2$. Mol. w. c. 196. Powdered Te is heated in a distillation-flask in a stream of Cl until the Te is completely converted into $TeCl_4$; Te is added equal in weight to the original quantity used, the whole is heated for a little time, an inverted condenser being attached to the flask, and the $TeCl_2$ is then distilled off at 320°–330° (Michaelis, *B.* 20, 2488). $TeCl_2$ is a black, amorphous solid, melting at 175° (M., *l.c.*) to a black liquid; Carnelley a. Williams give m.p. as 209° (*C. J.* 37, 125). Boils at 327° (C. a. W., *l.c.*). The vapour of $TeCl_2$ is reddish, and gives a characteristic absorption-spectrum (M., *l.c.*). V.D. at 440°, in vapour of N, = 98·2 (M., *l.c.*). The vapour becomes yellowish in presence of air or O; TeO_2 and $TeCl_4$ are formed, and after continued heating these react to produce $TeOCl_2$ (M., *l.c.*). $TeCl_2$ absorbs moisture when exposed to the air, but does not fume; on addition of much water H_2TeO_3 is formed; HClAq forms Te, and TeO_2 which remains dissolved in the acid (M., *l.c.*).

TELLURIUM TETRACHLORIDE $TeCl_4$. (*Telluric chloride.*) Mol. w. c. 269. Powdered Te is heated, in a distillation flask, in a stream of dry Cl until the solid becomes pale yellow, when it is distilled in a stream of dry CO_2 (Michaelis, *B.* 20, 1780). $TeCl_4$ is a colourless, crystalline solid, melting at 214°, and boiling without decomposition at 380° (M., *l.c.*; Carnelley a. Williams give the m.p. as 224° [*C. J.* 37, 125], and the b.p. as 414° [*C. J.* 35, 563]). V.D. 131 at 440°, 125 at 530° (M., *l.c.*). The vapour of $TeCl_4$ shows no absorption-spectrum (M., *B.* 20, 2488). $TeCl_4$ dissolves without change in dilute HClAq. It deliquesces in the air, cold water ppts. an oxychloride, and H_2TeO_3 is also formed; boiling water dissolves $TeCl_4$, and H_2TeO_3 separates on cooling.

$TeCl_4$ combines with alkali chlorides to form salts $TeCl_4.2MCl = M_2TeCl_6$; these salts are best obtained by adding MClAq to a slight excess of $TeCl_4$ dissolved in dilute HClAq and crystallising (*v.* Wheeler, *Am. S.* [3] 45, 267). The salts crystallise in regular yellow octahedra, without water. Weber (*P.* 104, 422) described a compound $TeCl_4.3AlCl_3$, obtained by melting together $TeCl_4$ and $AlCl_3$. $TeCl_4$ absorbs NH_3, forming a greenish-yellow solid that is unchanged in air and has the composition $TeCl_4.2NH_3$ (Espenschied, *A.* 113, 101).

Tellurium, fluorides of. Only one fluoride of Te has been isolated. The formula TeF_4 is probably molecular, from the analogy of $TeCl_4$.

TELLURIUM TETRAFLUORIDE TeF_4. (*Telluric fluoride.*) Prepared by dissolving H_2TeO_3 in HFAq, evaporating at 100° to a syrup, allowing to cool, separating the white nodules that are formed, and heating in a Pt basin (Högborn, *Bl.* [2] 35, 60). If carbonate or hydroxide of an alkali metal, or of Ba, is added to the solution of H_2TeO_3 in HFAq before evaporation, *double salts* of the forms $TeF_4.M^IF$ and $2TeF_4.M^{II}F_2$ are obtained; these salts are decomposed by water (H., *l.c.*).

Tellurium, haloid compounds of. These compounds belong to the forms TeX_2 and TeX_4, where X = Cl, Br or I; the only fluoride that has been isolated is TeF_4. The chlorides $TeCl_2$ and $TeCl_4$ have been gasified, and the formulæ are molecular; the formulæ of the other haloid compounds are also probably molecular. An iodide containing more I than TeI_4—perhaps TeI_6, corresponding with SI_6—may exist in the

solution of H_2TeO_3 in HIAq. No compound corresponding with S_2Cl_2, Se_2Cl_2, Se_2Br_2, and Se_2I_2 has been isolated. The haloid compounds of Te are more stable towards heat than the corresponding compounds of Se or S. The haloid compounds of Te are decomposed by water, giving H_2TeO_3 and HXAq; cold water is said to ppt. an oxychloride from $TeCl_4$. The compounds TeX_4 combine with the haloid compounds of the alkali metals to form salts M_2TeX_6; when X = F the salts are said to be of the form $MTeF_5$.

Tellurium, hydride of, TeH_2 *v.* HYDROGEN TELLURIDE, vol. ii. p. 727.

Tellurium, iodides of. Two iodides have been isolated, TeI_2 and TeI_4; a third—perhaps TeI_6—may exist in the solution of H_2TeO_3 in HIAq. TeI_2 is formed by directly combining Te and I; TeI_4 is obtained by digesting H_2TeO_3 with HIAq.

TELLURIUM DI-IODIDE TeI_2. Prepared by gently warming a mixture of powdered Te and excess of I; may be sublimed as a black, crystalline crust; when strongly heated I is given off. Not changed by water, hot or cold (Berzelius, *Lehrbuch*, 5th edit., 3, 1139).

TELLURIUM TETRA-IODIDE TeI_4. (*Telluric iodide.*) Obtained by digesting powdered H_2TeO_3 with HIAq in a closed flask, whereby hard black granules are formed. Melts when heated, and gives off I. Boiling water causes decomposition, probably forming an oxyiodide. If a solution of H_2TeO_3 in HIAq is evaporated over H_2SO_4 and CaO_2H_2 *in vacuo*, lustrous prisms are obtained that are perhaps a compound of TeI_4 and HI (B., *l.c.*). By dissolving alkali iodides in TeI_4 dissolved in dilute HIAq, and crystallising, black salts of the form M_2TeI_6 are formed in regular octahedra; the potassium salt contains $2H_2O$ and crystallises in monoclinic forms (Wheeler, *Am. S.* [3] 45, 267).

Tellurium, oxides of. Three oxides have been isolated, TeO, TeO_2, and TeO_3. TeO is probably slightly basic; TeO_2 is the anhydride of the weak acid H_2TeO_3, but it also shows feebly basic properties; TeO_3 is a very weak acidic oxide. None of the oxides has been gasified; all are known in the solid state only. An oxide of Te and S, $TeSO_3$, is also known.

TELLURIUM MONOXIDE TeO. This oxide was prepared in 1883 by Divers a. Shimosé (*C. J.* 43, 319). It is obtained by long-continued heating $TeSO_3$ to 180°-230° *in vacuo* until SO_2 ceases to be given off, powdering the residual solid, digesting it with water containing a little Na_2CO_3, washing with hot water, then with alcohol, and drying in a steam oven. TeO is a black, amorphous solid, with a slight brown shade, showing a graphitic lustre when pressed with a hard body. It is unchanged in air, but when heated it burns to TeO_2; when strongly heated *in vacuo* TeO_2 and Te are formed. TeO is scarcely affected by cold KOHAq; boiling KOHAq decomposes it, giving Te. SO_2, even if boiling, scarcely acts on TeO. The oxide dissolves in hot H_2SO_4Aq; D. a. S. say that the solution deposits $Te(SO_4)_2$ on cooling, but no analyses of the crystals that separate are given; Magnus (*P.* 10, 491) gave this formula to the product of the interaction of Te with hot conc. H_2SO_4. Heated in HCl gas $TeCl_2$ is formed. TeO is slowly reduced to Te by SO_2.

TELLURIUM DIOXIDE TeO_2. (*Tellurous oxide. Tellurous anhydride.*)

Occurrence.—As *tellurite* or *tellurium ochre*, in the Seven Mountains.

Formation.—1. Te is heated in the air.—2. By decomposing a boiling solution of $TeCl_4$ in HClAq by boiling water.—3. By heating H_2TeO_3. 4. By oxidising Te by HNO_3Aq, and heating the solution.—5. According to Hilger (*A.* 171, 211) by heating Te with H_2SO_4, SO_2 is evolved and TeO_2 separates on cooling.

Preparation.—Powdered Te is dissolved in warm HNO_3Aq, S.G. 1·25, and the solution is heated somewhat above 20°; below 8° H_2TeO_3 separates, between 8° and 20° both TeO_2 and H_2TeO_3 are formed, and the solid that forms from the solution above 20° is TeO_2 only (Klein a. Morel, *Bl.* [2] 43, 198). By allowing the solution of Te in HNO_3Aq to stand for some hours, and then adding some alcohol, TeO_2 is obtained in crystals (Oppenheim, *J. pr.* 71, 267; *cf.* Berzelius, *P.* 28, 392).

Properties. — A white, crystalline solid; melts at a red heat to a transparent, yellow liquid, which on cooling forms a white crystalline mass, giving off so much heat that the solid glows feebly. TeO_2 may be sublimed in a slow stream of air. Clarke (*Am. S.* [3] 14, 285) gives S.G. as 5·7559 at 12·5°. As obtained from a solution of Te in HNO_3Aq, TeO_2 forms quadratic octahedra; S.G. 5·65 to 5·68 at 0° (K. a. M., *l.c.*). As obtained by heating H_2TeO_3 till all water is removed and the residue melts, TeO_2 forms orthorhombic needles; S.G. 5·88 to 5·91 at 0° (K. a. M., *l.c.*). Freshly-prepared TeO_2 has no taste, but after a time it acquires a disagreeable metallic taste (Berzelius, *P.* 28, 392). It does not redden litmus paper. It is almost insoluble in water; 1 pt. dissolves in 150,000 pts. of water (K. a. M., *l.c.*). TeO_2 is very slightly soluble in most acids; it is more soluble in HClAq (*v. infra*, *Reactions*, No. 3). Dissolves readily in solutions of caustic alkalis, but in alkali carbonate solutions and in ammonia only after long-continued boiling. TeO_2 does not form H_2TeO_3 by reacting with water, but as it is obtained by heating this acid it may be called tellurous anhydride.

Reactions and Combinations.—1. Reduced to Te by heating in *hydrogen* to the temperature whereat Te vaporises.—2. Easily reduced to Te by heating with *carbon*.—3. TeO_2 absorbs *hydrogen chloride*, giving off much heat and forming compounds $TeO_2.xHCl$. At −10°, after saturation with HCl, the compound $TeO_2.3HCl$ is formed; on slightly warming HCl is given off, and $TeO_2.2HCl$ remains, and does not change when heated to 90°; on heating more strongly, $TeOCl_2$ is formed (Ditte, *A. Ch.* [5] 10, 82). *Hydrogen bromide* is also absorbed by TeO_2; by saturating TeO_2 with HBr at −15°, a black solid, resembling I, and having the composition $TeO_2.3HBr$, is formed; this compound begins to decompose at −40°, above this temperature $TeO_2.2HBr$ is produced, which remains unchanged to c. 300°, at which temperature it decomposes to $TeOBr_2$ and H_2O (D., *l.c.*). *Hydrogen iodide* and *hydrogen fluoride* are also absorbed by TeO_2, but the products have not been examined.—4. Tellurites (*q. v.*, p. 650) are formed by dissolving TeO_2 in *caustic alkali solutions*, or by fusing TeO_2 with *alkali carbonates*.—5. A compound of TeO_2 with *sulphuric anhydride* $2TeO_2.SO_3$—sometimes called basic tellurium sulphate—is formed by dissolving TeO_2 in hot H_2SO_4 diluted with 3 to 4 times its weight of water, and evaporating; it crystallises in rhombic tablets, somewhat soluble in cold dilute H_2SO_4Aq (Klein, *C. R.* 99, 326).—6. A compound with *nitric anhydride* $2(4TeO_2.N_2O_5).3H_2O$ is described by Klein a. Morel (*Bl.* [2] 43, 198), as obtained, in rhombic needles, by dissolving TeO_2 in moderately conc. HNO_3Aq, and also by dissolving Te in excess of HNO_3Aq, S.G. 1·15 to 1·35, and evaporating at a gentle heat. This compound—which is sometimes described as basic tellurium nitrate—is decomposed at c. 330°, giving off N oxides and leaving TeO_2; with much hot water it gives a pp. of TeO_2.—7. A compound, probably $TeO_2.Ag_2O.(C_4H_4O_5)_2.2aq$, is formed by dissolving TeO_2 in HBrAq, adding *tartaric acid*, and ppg. by $AgNO_3Aq$ (*v.* Brauner, *C. J.* 55, 398; *cf.* Klein a. Morel, *C. R.* 100, 1140).

TELLURIUM TRIOXIDE TeO_3. (*Telluric oxide. Telluric anhydride.*) Obtained, as an orange-yellow, crystalline mass, by heating H_2TeO_4 (*v.* TELLURIC ACID, p. 649) to somewhat above 160°. If the temperature becomes too high some of the TeO_3 is decomposed to TeO_2 and O; it is advisable, therefore, to digest the residue with cold HClAq (to remove any TeO_2), to wash out HCl by water, and to dry at 100°. TeO_3 is not changed by cold, nor by boiling, water; nor is it acted on by cold HClAq, by hot or cold HNO_3Aq, nor by dilute KOHAq. Very conc. boiling KOHAq slowly dissolves TeO_3, forming K_2TeO_4. TeO_3 dissolves in boiling HClAq, Cl is slowly given off, and H_2TeO_3 is formed in the solution (*v.* Berzelius, *P.* 28, 392). Clarke (*Am. S.* [3] 14, 286) gives S.G. of TeO_3 as 5·0704 at 14·5°.

TELLURIUM THIO-OXIDE $TeSO_3$. (*Tellurium sulphoxide. Tellurium-sulphur trioxide.*) This compound is obtained by dissolving pure Te in pure SO_3, and warming after a time to c. 30°, pouring off SO_3, and drying *in vacuo* (Weber, *J. pr.* [2] 25, 218; for description of apparatus, and details, *v.* Divers a. Shimosé, *C. J.* 43, 323). $TeSO_3$ is a red amorphous solid, melting at 30°. When pure it remains unchanged, in a sealed tube, for months (D. a. S., *l.c.*). The colour gradually changes to brown by heating to 35°; the change is instantaneous at 90°. The product, which is a brown solid, has the composition $TeSO_3$ (D. a. S., *l.c.*). At c. 180° SO_2 is given off and black TeO remains (D. a. S., *l.c.*). $TeSO_3$ is not acted on by SO_3; it dissolves in H_2SO_4Aq, giving an amethyst-red solution; water decomposes it to H_2TeO_3, TeO, Te, H_2SO_3Aq, and H_2SO_4Aq (D. a. S., *l.c.*).

$TeSO_3$ may perhaps be regarded as *tellurium sulphite*.

Tellurium, oxyacids of, H_2TeO_3, *v.* TELLUROUS ACID (p. 656); H_2TeO_4, *v.* TELLURIC ACID (p. 649).

Tellurium, oxybromide of, $TeOBr_2$. A pale-yellow solid; obtained by heating $TeO_2.2HBr$ (*v.* TELLURIUM DIOXIDE; *Reactions*, No. 8, p. 654) above 300°. Melts at red heat, forming a very dark-coloured liquid, which gives off almost black vapour with partial decomposition to TeO_2 and $TeBr_4$ (Ditte, *A. Ch.* [5] 10, 82).

Tellurium, oxychloride of, $TeOCl_2$. Prepared by heating $TeO_2.2HCl$ (*v.* TELLURIUM DIOXIDE; *Reactions*, No. 8) to above 90°. Very similar to $TeOCl_2$ (Ditte, *A. Ch.* [5] 10, 82). Decomposed at fairly high temperature to TeO_2 and $TeCl_4$.

Tellurium, oxyiodide of. According to Berzelius (*Lehrbuch* [5th edit.] 3, 1141), a greyish-brown, heavy powder is formed by digesting TeI_4 with boiling water, and this powder is probably an oxyiodide of Te; no analyses are given.

Tellurium, salts of. No compounds have been prepared by directly replacing the H of oxyacids by Te. According to Divers a. Shimosé (*C. J.* 43, 319), $Te(SO_4)_2$ is formed by dissolving TeO in hot H_2SO_4Aq and cooling, but no analyses are given; Magnus (*P.* 10, 491) gave the formula $Te(SO_4)_2$ to the product of the interaction of Te and hot conc. H_2SO_4. The compounds $2TeO_2.SO_3$ and $2(4TeO_2.N_2O_5).3aq$ are sometimes called *basic tellurium sulphate* and *basic tellurium nitrate* respectively; the compound $TeSO_3$ (*v. supra*, TELLURIUM THIO-OXIDE) may perhaps be looked on as *tellurium sulphite*; and a compound, probably $TeO_2.Ag_2O.(C_4H_4O_5)_2.2aq$, is called *tellurium-silver tartar emetic* (*v.* TELLURIUM DIOXIDE; *Reactions*, Nos. 5, 6, and 7, *supra*).

Tellurium silver tartar emetic *v.* TELLURIUM DIOXIDE; *Reactions*, No. 7, *supra*.

Tellurium, sulphides of. Berzelius (*P.* 8, 411) described two sulphides, TeS_2 and TeS_3, corresponding with the oxides TeO_2 and TeO_3. According to Becker (*A.* 180, 257), CS_2 removes almost all the S from these supposed compounds. B. concludes that the substances described by Berzelius are not definite compounds; he thinks that compounds of Te and S are probably formed by passing H_2S into TeO_2Aq and TeO_3Aq. As the substances obtained by Berzelius seem to have very definite properties, they are shortly described here.

TELLURIUM DISULPHIDE TeS_2. A dark-brown pp. formed by passing H_2S into H_2TeO_3Aq, or into an acidified solution of an alkali tellurite; softens when heated and cools to a grey, somewhat lustrous mass; gives off S when strongly heated. TeS_2 reacts as an acidic sulphide, forming compounds $xMS.TeS_2$, where M $=(NH_4)_2$, Cd, Li_2, Fe, Mg, Pb, K_2, Na_2, Zn, &c. The *thiotellurites* of the alkali metals are best obtained by saturating aqueous solutions of the tellurites with H_2S, and crystallising *in vacuo*; the thiotellurites of alkaline earth metals are formed by boiling the sulphides of these metals with TeS_2 and water; the thiotellurites of the heavy metals are obtained by ppn. from solutions of the alkali salts (Berzelius, *P.* 8, 411).

TELLURIUM TRISULPHIDE TeS_3. A blackish grey, lustrous solid; formed by saturating H_2TeO_4Aq with H_2S, and allowing to stand for some time in a closed vessel in a warm place. *Thiotellurates* of the alkali metals, $xM_2S.TeS_3$, are formed by saturating M_2TeO_4Aq with H_2S (*v.* Oppenheim, *J. pr.* 71, 267).

Tellurium, sulphoxide of, *v.* TELLURIUM THIO-OXIDE, *supra*.

Tellurium, thio-oxide of, *v. supra*.

Tellurium, thio-salts of, *v.* Tellurium disulphide, p. 655; and Tellurium trisulphide, p. 655. M. M. P. M.

TELLUROCYANIDES *v.* vol. ii. p. 853.

TELLUROUS ACID H_2TeO_3.

Formation.—1. By dissolving Te in HNO_3Aq, S.G. 1·25, and at once ppg. by water; if the solution is left for some time before adding water the pp. is TeO_2.—2. By decomposing $TeCl_4$ by cold water.

Preparation.—TeO_2 is fused with an equal weight of K_2CO_3 or Na_2CO_3 as long as CO_2 is given off; the tellurite thus formed is dissolved in water, and HNO_3Aq is added until the liquid has a very distinctly acid reaction; the flocculent pp. thus produced is allowed to remain in contact with the liquid for some hours, and is then thoroughly shaken up with the liquid, a little HNO_3Aq being added if the acid reaction disappears during this process; the pp. is then washed with ice-cold water, and dried at the ordinary temperature (Berzelius, *P.* 28, 392; *cf.* Oppenheim, *J. pr.* 71, 267). The solution of the alkali tellurite in HNO_3Aq may be decomposed by adding water, but this must be done at once, as after standing water ppts. TeO_2.

Properties and Reactions.—A white, light, amorphous solid, with a bitter, metallic taste. Reddens litmus paper. Dissolves slightly in cold water; when the aqueous solution is heated to c. 40° TeO_2 separates. When slightly heated gives TeO_2 and H_2O. H_2TeO_3 dissolves in many acids; from the solution in HClAq, water or alkalis ppts. H_2TeO_3; the solution in HNO_3Aq gives a pp. of TeO_2 on addition of water after standing for some time. From the solution in H_2SO_4Aq and HNO_3Aq the compounds $2TeO_2.SO_3$ and $2(4TeO_2.N_2O_5).3aq$ have been obtained (*v.* Tellurium dioxide; *Reactions*, No. 5 and 6, p. 655). H_2TeO_3 forms *tellurites* (*q. v.*, p. 650). Thomsen (*Th.* 2, 278) gives $[Te,O^2,H^2O] = 77,180$. M. M. P. M.

TELLURIUM, *Organic Compounds of.*

Methyl telluride Me_2Te. (82°). Formed by distilling K_2Te with $Ba(SO_4Me)_2$ (Wöhler a. Dean, *A.* 93, 233; Heeren, *Dissertation*, Göttingen, 1861). Pale-yellow, mobile, heavy oil, with persistent alliaceous smell. Oxidised by HNO_3 to $Me_2TeOHNO_3$, crystallising in prisms.—$Me_2TeHOAc$. Transparent cubes, v. sol. water. Its solution gives with HCl a pp. of Me_2TeCl_2 which crystallises in long prisms [97·5°].—Me_2TeBr_2 [89°]. Prisms.—$(Me_2Te)_2H_2CO_3$. Difficult to crystallise.—Formate $Me_2TeCH_2O_2$. Deliquescent needles.—Me_2TeI_2. Formed by heating Te with MeI at 80° (Demarçay, *Bl.* [2] 40, 100).—$(Me_2Te)_2H_2C_2O_4$.—Me_2TeO. Got from Me_2TeCl_2 and Ag_2O. Deliquescent crystalline mass, alkaline to litmus.—Me_2TeOCl_2. Got from the chloride and NH_3Aq. Short prisms (from alcohol). — $(Me_2Te)_2OBr_2$. — $(Me_2Te)_2H_2SO_4$. Cubes, v. sol. water, insol. alcohol.

Methyl-iodide Me_3TeI. Crystalline, sl. sol. water. Converted by moist Ag_2O into an alkaline base which yields $(Me_3TeCl)_2PtCl_4$.

Ethyl telluride *v.* vol. ii. p. 519.

TEMPLIN OIL. An essential oil obtained from fir cones (Flückiger, *J.* 1855, 642; Berthelot, *J. Ph.* [3] 29, 38). Colourless, becoming greenish-yellow in air. Boils at 155°–177°. S.G. ^{12} ·862. Yields on rectification a lævorotatory terpene (172°) S.G. ^{0} ·856. HNO_3 ($\frac{1}{4}$ vol.) and alcohol ($\frac{1}{8}$ vol.) yield terpin hydrate $C_{10}H_{20}O_2$ aq [118°] (250°) S. 9 at 100°. Alcohol and HCl yield crystalline $C_{10}H_{16}HCl$ and $C_{10}H_{16}2HCl$ [55°].

TERACONIC ACID $C_7H_{10}O_4$ *i.e.* $CMe_2{:}C(CO_2H).CH_2.CO_2H$. *Propylidene-succinic acid.* [163°]. Formed in small quantity by distilling the isomeric terebic acid (Geisler, *A.* 208, 50). Na and NaOEt convert terebic ether into sodium ethyl teraconate (W. Roser, *B.* 15, 293). Formed also by treatment of the ether $CO_2Et.CBrPr.CH_2.CO_2Et$ with alcoholic potash (Schleicher, *A.* 267, 130). Crystals, sol. alcohol and ether, v. sol. cold water. Above 163° it yields H_2O and an anhydride. Conc. HBrAq at 0° forms terebic acid.

Salts.—BaA''.—CaA''. Pp., v. sl. sol. water. —Ag_2A''. Needles, m. sol. water.

Mono-ethyl ether EtHA''. Oil. Decomposes Na_2CO_3, forming crystalline NaEtA'', a solution of which gives with $AgNO_3$ a pp. of the unstable AgEtA''.

Di-ethyl ether Et_2A''. (255 i.V.). Oil.

TERACRYLIC ACID $C_7H_{12}O_2$. (218° i.V.). A product of the distillation of terpenylic acid (Fittig a. Krafft, *B.* 10, 521, 1659, 1740; *A.* 208, 79; Amthor, *J. pr.* [2] 42, 389). Liquid, smelling like valeric acid, sl. sol. and lighter than water. Yields acetic acid on fusion with potash. Fuming HBr forms $C_7H_{13}BrO_2$, which gradually splits up into HBr and heptolactone $C_7H_{12}O_2$.—CaA'_2 5aq. Prisms or needles.—AgA': needles.

Ethyl ether EtA'. (191°). Fruity oil.

TERBIUM. Tr. At. w. not determined with certainty; probably c. 162 (*v. infra*).

The examination of *gadolinite*, a rare Swedish mineral, by Mosander, Cleve, and others made probable the existence therein of at least seven earths, to one of which the name terbia was given (*v.* Erbium, vol. ii. p. 456, where the history of these earths is stated more fully, with references to original memoirs). It is still very doubtful whether the substance called terbia is a homogeneous body or a mixture of more than one compound (*cf.* Metals, rare, vol. iii. p. 242). Delafontaine (*A. Ch.* [5] 14, 238) prepared an orange-yellow, earthy compound, which he regarded as pure terbia, from *samarskite*, by a long process of fractional ppn., first by K_2SO_4Aq, then by oxalic acid, and finally by formic acid (*cf.* Marignac, *A. Ch.* [5] 14, 247; Cleve, *Bl.* [2] 31, 197).

Terbia Tr_2O_3 is described as an orange-yellow amorphous solid; when heated in H for some time it becomes white. Tr_2O_3 dissolves in acids, forming salts of the type Tr_2X_3, where X = SO_4, CO_3, $2NO_3$, &c. The emission spectrum of terbia has been mapped by Roscoe a. Schuster (*C. J.* 41, 283). The at. w. of Tr—the supposed element has not been isolated—was determined by Delafontaine to be 113·5; Marignac found the value 148·5; Lecoq de Boisbaudran found 163·1, 161·4, and by later work 159·5 (*C. R.* 102, 395; 111, 474). M. M. P. M.

TEREBENE *v.* Terpenes.

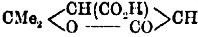
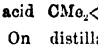
TEREBENTHENE *v.* Terpenes.

DITEREBENTHYL $C_{20}H_{30}$. V.D. 4·6. (345°). S.G. ^{12} ·9688. $[\alpha]_D = 59°$. A product of distillation of colophony (Renard, *C. R.* 105, 865; 106, 856). Oil, resinified by air. $KMnO_4$ oxidises it to propionic, acetic, and formic acids and CO_2. Cold fuming HNO_3 forms $C_{20}H_{27}(NO_2)_3$, a yellow powder, sol. alcohol and ether. Br in CS_2 at −10° forms $C_{20}H_{30}Br_2$, which on heating yields diterebenthylene $C_{20}H_{28}$ (347°) S.G. ^{12} ·9821, whence Br forms $C_{20}H_{24}Br_4$. HNO_3 produces $C_{20}H_{25}(NO_2)_3$, and H_2SO_4 forms $C_{20}H_{27}SO_3H$, all amorphous solids. Bromine-water gives rise to $C_{20}H_{21}Br_8$, a brown, amorphous solid. Gaseous HCl passed into the ethereal solution forms $C_{20}H_{30}\frac{1}{2}HCl$. H_2SO_4 yields $C_{20}H_{29}SO_3H$, which is sol. water, alcohol, and ether, forming fluorescent solutions. Diterebenthyl passed through a red-hot tube forms H, C_2H_4, C_3H_6, pentane, hexane, hexylene, hexinene, heptinene, cymene, and other hydrocarbons.

TEREBENTILIC ACID $C_8H_{10}O_2$. [90°]. (250°). Got by passing the vapour of the hydrate of oil of turpentine $C_{10}H_{16}2H_2O$ over soda-lime at 400° (Personne, *A.* 100, 253; *cf.* Hempel, *A.* 180, 86). Crystalline powder, sol. hot water, v. sol. alcohol and ether. May be sublimed.—AgA′. Crystalline.

TEREBENTIC ACID $C_9H_{14}O_5$. Got by digesting oil of turpentine with oxide of lead (Weppen, *A.* 41, 294). Crystals (from alcohol).

TEREBIC ACID $C_7H_{10}O_4$ *i.e.*


$CMe_2<\begin{matrix}CH(CO_2H)\\O\text{———}CO\end{matrix}>CH_2$. Mol. w. 158. [176°]. H.C.v. 766, 642 (Ossipoff, *C. R.* 108, 812). S. (ether) 2·856 at 35° (Amthor, *J. pr.* [2] 42, 385). Formed by the action of nitric acid on oil of turpentine (Bromeis, *A.* 37, 297; Rabourdin, *J. Ph.* [3] 6, 185; Cailliot, *A. Ch.* [3] 21, 27; Svanberg a. Eckmann, *J. pr.* 66, 220; Mielck, *A.* 180, 47; Bredt, *A.* 208, 37; Erdmann, *A.* 228, 179). Formed also by oxidising pinol (Wallach, *A.* 253, 256; 259, 317). Terebic acid is perhaps identical with oxyhexic acid (Gorboff, *J. R.* 1887, 605). Monoclinic crystals (from alcohol), sl. sol. cold, v. sol. hot water. V. sol. alcohol and ether. Not attacked by fuming HNO_3. Split up by water at 150° into CO_2 and pyroterebic acid. On boiling with H_2SO_4 (2 pts.) and water (1 pt.) it is converted into the lactone of oxy-isohexoic acid  $CMe_2<\begin{matrix}CH_2\\O.CO\end{matrix}>CH_2$, CO_2 being evolved. On distillation it yields pyroterebic (hexenoic) acid, oxy-isohexoic lactone, and a little teraconic acid. On heating for 15 hours at 160° with excess of a saturated solution of baryta it is converted into acetone and succinic acid (Frost, *A.* 226, 363). Fuming HIAq yields $CH_2Pr.CH_2.CO_2H$. Alkalis form salts of diaterebic acid, of which terebic acid is the lactone.

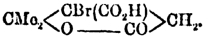
Salts.—NH_4A': very soluble prisms.—$KA'\frac{1}{2}aq$. —$NaA'\frac{1}{2}aq$.—$BaA'_2 2aq$: amorphous. —AgA′. Prisms, v. sol. water.

Ethyl ether EtA′. (274° i.V.). S.G. ^{19} 1·111. Formed from terebic acid, alcohol, and HCl. Dilute NaOH dissolves it, forming mono-ethyl diaterebate; on cautious acidification the ether separates again, but only after warming (Ekmann). Sodium dissolves in its ethereal solution, giving off hydrogen and forming the sodium salt of acid ether of teraconic acid (*q.v.*). Alcoholic NaOEt acts in the same way, excess forming a white pp. of disodic teraconate.

Diaterebic acid
$CMe_2(OH).CH(CO_2H).CH_2.CO_2H$. The salt BaA″ 3aq is formed by boiling terebic acid with excess of baryta-water. It crystallises from alcohol, but on acidification at once yields the lactone, terebic acid. $AgNO_3$ added to a solution of the Ba salt ppts. Ag_2A''.—CaA″ 3aq.—CaA″.—PbA″ 3aq.—$Pb_3A''_2(OH)_2$ aq.

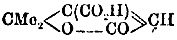
Ethyl ether Et_2A''. Formed from Ag_2A'' and EtI. Oil. Converted by acetyl chloride into $CMe_2(OAc).CH(CO_2Et).CH_2.CO_2Et$, an unstable oil.

β-Bromo-terebic acid $C_7H_9BrO_4$ *i.e.*


$CMe_2<\begin{matrix}CBr(CO_2H)\\O\text{———}CO\end{matrix}>CH_2$. [151°]. Formed by adding Br (1 mol.) to powdered teraconic acid (1 mol.) covered with water (Frost, *A.* 226, 363). Large crystals, m. sol. CS_2, v. sl. sol. chloroform and benzene. Decomposed by boiling with water into HBr and terebilic acid $C_7H_8O_4$. Reduced by sodium-amalgam to terebic acid.

References.—CHLORO- and OXY-TEREBIC ACID.

TEREBILENIC ACID $C_7H_8O_4$ *i.e.*


$CMe_2<\begin{matrix}C(CO_2H)\\O\text{---}CO\end{matrix}>CH$ (?) [169°]. Formed by heating α-chloro-terebic acid at 200° (Roser, *B.* 15, 296; *A.* 220, 261) and by evaporating β-chloro-terebic acid with water (Frost, *A.* 226, 370). Small prisms or needles (from water), v. sol. alcohol and ether. Crystallises from alcohol or conc. HBrAq in trimetric forms; $a:b:c =$ ·809:1:·858. May be sublimed. Excess of KOH forms the diaterebilenate $K_2C_7H_8O_5$, but this splits up on warming with water into KOH and potassium terebilenate. Does not combine with Br or HBr. Sodium-amalgam reduces it to terebic acid.—CaA'_2.—AgA′. Prisms.

Reference.—CHLORO-TEREBILENIC ACID.

TERECHRYSIC ACID $C_6H_8O_5$. A product of the action of HNO_3 (S.G. 1·2) on turpentine (Cailliot, *A.* 64, 376). Orange-red crystals, v. e. sol. water, alcohol, and ether.—PbA″: crystals.

TERELACTONE $C_8H_8O_2$ *i.e.* $C_5H_8<\begin{matrix}O\\CO\end{matrix}$. [12°]. (210° i.V.). Formed by the action of boiling water on di-bromo-isohexoic acid derived from pyroterebic acid and Br (Geisler, *A.* 208, 47). Mobile liquid, sol. water. Boiling baryta-water converts it into amorphous $Ba(C_6H_{11}O_3)_2$, which is sol. water and deposits $BaCO_3$ on boiling.

TEREPHTHALIC ACID $C_8H_6O_4$ *i.e.* $C_6H_4(CO_2H)_2$. *p-Phthalic acid.* Mol. w. 166. H.C.p. 770,900. H.C.v. 771,200. H.F. 188,100 (Stohmann, *J. pr.* [2] 40, 139).

Formation.—1. By the action of HNO_3 on oil of turpentine (Cailliot, *A. Ch.* [3] 21, 28; De la Rue a. Hugo Müller, *A.* 121, 86; Schreder, *B.* 7, 704; *cf.* W. C. Williams, *B.* 6, 1094).—2. By the oxidising action of chromic acid mixture on *p*-xylene (Beilstein, *A.* 133, 32; 137, 301), cuminic acid, cuminic aldehyde, cymene (Hofmann, *A.* 97, 197), *p*-toluic acid (Beilstein a. Yssel, *A.* 137, 308), di-ethyl-benzene, and amyl-toluene (Fittig, *A.* 141, 167). — 3. By the action of boiling dilute HNO_3 on cymene and on terpenes (Schwanert, *A.* 132, 257; Homeyer, *Ar. Ph.* [3] 5, 326).—4. By oxidation of *o*-ethyl-toluene by aqueous $KMnO_4$ (Claus a. Pieszcek, *B.* 19, 3083).—5. By fusing potassium *p*-sulpho-benzoate with sodium formate (Remsen, *B.* 5, 379).—6. From its nitrile, which is obtained by distilling K_4FeCy_6 with potassium benzene *p*-disulphonate (Garrick, *Z.* 1869, 551), *p*-chloro-benzene sulphonate (Nölting, *B.* 8, 1113), or *p*-

bromo-benzene sulphonate (Irelan, *Z.* 1869, 164; Barth a. Senhofer, *A.* 174, 242; Limpricht, *A.* 180, 88).—7. The semi-nitrile is also formed by the action of a hot solution of cuprous potassium cyanide upon *p*-diazobenzoic acid (Sandmeyer, *B.* 18, 1497).—8. By heating *p*-di-bromo-benzene with chloroformic ether and 1 p.c. sodium-amalgam at 110° and saponifying the product (Bonz, *B.* 18, 2305).—9. By the action of 5 p.c. $KMnO_4$ on an oil (258°–263°) which remains as a residue in the manufacture of aniline and toluidine (Hell a. Rockenbach, *B.* 22, 505).

Preparation.—1. Br (2 mols.) is added to boiling *p*-xylene (100 g.), and the resulting $C_6H_4(CH_2Br)_2$ decomposed by alcoholic KOAc on the water-bath. After evaporating the alcohol the $C_6H_4(OAc)_2$ is extracted with ether, and oxidised by adding 4·5 litres of 10 p.c. $KMnO_4$ to its solution in water (1 litre) and NaOH (500 g. of S.G. 1·22). Finally more $KMnO_4$ is added till the solution remains violet, the solution kept at 100° for 3 hours, filtered, and ppd. by HCl (Baeyer, *A.* 245, 139).—2. By oxidising *p*-xylene with chromic acid mixture (Beilstein, *A.* 133, 41). 3. From *p*-toluidine by Sandmeyer's reaction, the resulting *p*-toluic acid being oxidised by $KMnO_4$ (Baeyer a. Herb, *A.* 258, 1).

Properties.—White crystalline powder, nearly insol. water, alcohol, ether, chloroform, and HOAc. Sublimes without previous fusion. Does not yield an anilide on boiling with aniline (Michael a. Palmer, *B.* 19, 1376). It is ppd. from its salts by phthalic acid. Yields benzene when distilled with slaked lime. Reduced by sodium-amalgam in a current of CO_2 to the $\Delta^{2,5}$ or (1,4)- dihydride. If CO_2 be not used the product is the $\Delta^{1,4}$ or (3, 6)- dihydride, which is also got by boiling the (1,4)-dihydride with NaOHAq (Baeyer, *A.* 269, 153; *cf.* Mohs, *Z.* [2] 3, 68). The (1,4)-dihydride gives benzoic acid on oxidation by MnO_2 and dilute H_2SO_4, while the (3,6)-dihydride forms terephthalic acid (Baeyer, *A.* 269, 182). By heating its alkaline solution with sodium-amalgam terephthalic acid is reduced to a tetrahydride, and this is further reduced by HIAq at 240° to a hexahydride (Baeyer, *B.* 19, 1805).

Salts. — $(NH_4)_2A''$. Small crystals. — CaA'' 3aq. S. ·08 at 6°.—BaA'' 4aq. S. ·28 at 5°.—SrA''. S. ·19 at 17°.—Ag_2A''. Curdy pp.

Mono-methyl ether $MeHA''$. [c. 230°]. Formed by the action of conc. H_2SO_4 or alcoholic potash on the di-methyl ether (Baeyer, *A.* 245, 141). Needles, sol. Na_2CO_3Aq and hot water.

Di-methyl ether Me_2A''. [140°]. S. ·3 at 100°. H.F. 172,300 (Stohmann, *J. pr.* [2] 43, 2). Formed by heating the acid with PCl_5 on the water-bath and pouring the product into methyl alcohol. Trimetric plates; $a:b:c$ = ·843:1:3·083. Insol. cold water, sl. sol. hot MeOH, m. sol. EtOH.

Di-ethyl ether Et_2A''. [44°]. Prisms.

Propyl ether Pr_2A''. [31°]. Needles.

Isopropyl ether Pr_2A''. [56°]. Plates.

n-Butyl ether $(C_4H_9)_2A''$. Liquid.

Isobutyl ether $(CH_2Pr)_2A''$. [52·5°]. Needles, v. sol. ether (Berger, *B.* 10, 1742).

Isoamyl ether $(C_5H_{11})_2A''$. Pearly scales.

Phenyl ether Ph_2A''. [194°] (Baeyer, *A.* 258, 44). Formed from the chloride and phenol. Leaflets.

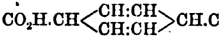
Chloride $C_6H_4(COCl)_2$. [78°]. (259°).

Amic acid $C_6H_4(CONH_2).CO_2H$. [214°]. Formed from *p*-diazo-benzoic acid by Sandmeyer's reaction (Sandmeyer, *B.* 18, 1498). Minute plates (from water), m. sol. cold water.

Amide $C_6H_4(CONH_2)_2$. Formed from the chloride and NH_3Aq. Amorphous.

Nitrile $C_6H_4(CN)_2$. [220°] (Luckenbach, *B.* 17, 1428). Formed from the amide and P_2O_5. Got also by distilling calcium bromo-benzene *p*-sulphonate with K_4FeCy_6. Conc. HIAq forms $C_6H_4(CI_2.NH_2)_2$ (Biltz, *B.* 25, 2543).

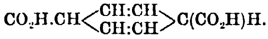
Γ *cistrans* $\Delta^{2,5}$ or (1,4)- **Dihydride**


$CO_2H.CH\left<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}\right>CH.CO_2H$. S. ·3 in the cold. H.F. 182,600 (Stohmann, *J. pr.* [2] 43, 538). Formed by reducing terephthalic acid in a current of CO_2 by sodium-amalgam (Baeyer, *A.* 251, 257; 269, 153). Monoclinic prisms (from EtOAc); $a:b:c$ = ·982:1:1·019; β = 78° 2′. M. sol. ether. Not attacked by sodium-amalgam in the cold. Unites with bromine (4 atoms). Transformed into the $\Delta^{1,5}$ isomeride by boiling with water, and into the $\Delta^{1,4}$ acid by boiling with NaOHAq. Alkaline $KMnO_4$ re-oxidises the acid to terephthalic acid. A warm solution of the acid readily reduces $AgNO_3$. On warming with aqueous cupric acetate it gives off CO_2 and forms a white pp. which, on adding HOAc and warming, yields Cu_2O, the liquid then containing benzoic acid. The (3,6), (3,4), and (2,3) isomerides do not reduce $AgNO_3$ and cupric acetate. The Ba salt crystallises in plates, and is v. sol. water.

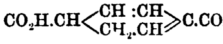
Methyl ether Me_2A''. [77°]. Yields a di- and a tetra-bromide. Br in $CHCl_3$ forms a dibromide [170°] and a tetrabromide [98°].

Di-phenyl ether Ph_2A''. [146°]. Formed from the chloride and phenol at 100°. Small crystals, sl. sol. alcohol, ether, and ligroïn.

Γ *cis* $\Delta^{2,5}$ or (1,4)- *Dihydride*

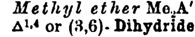

$CO_2H.CH\left<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}\right>C(CO_2H)H$. Extracted by ether from the mother-liquor from which the preceding isomeride has separated. Closely resembles its *cistrans* isomeride, but the *cis* acid and its salts are the more soluble.

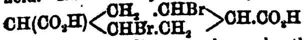
$\Delta^{1,5}$ or (3,4)- **Dihydride**


$CO_2H.CH\left<\begin{matrix}CH{:}CH\\CH_2.CH\end{matrix}\right>C.CO_2H$. S. ·042 in the cold. H.F. 185,300. Formed by boiling the (1,4)- dihydride with water, and obtained, therefore, by reducing terephthalic acid with sodium-amalgam (Baeyer, *A.* 245, 142; 251, 257; 269, 148). Converted into the (3,6)- acid by NaOHAq. Sodium-amalgam in the cold reduces it to the Δ^2 tetrahydride.—BaA'' 4aq. Trimetric crystals; $a:b:c$ = ·319:1: ·352 (Baeyer a. Herb, *A.* 258, 22).

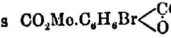
Methyl ether Me_2A''. [40°].

$\Delta^{1,4}$ or (3,6)- **Dihydride**


$CO_2H.C\left<\begin{matrix}CH_2.CH\\CH\ .CH_2\end{matrix}\right>C.CO_2H$. S. ·0059 in the cold. H.F. 191,900. Formed by reduction of terephthalic acid in alkaline solution by sodium-amalgam (Baeyer, *A.* 245, 142). Got also by boiling the (1,4)- dihydride with NaOHAq. Slender needles (from water), almost insol. ether. Much resembles terephthalic acid. On sublimation it is partially converted into terephthalic

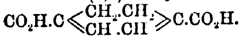
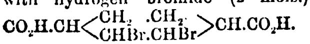
acid. Immediately oxidised by $KMnO_4$. Forms  $CH(CO_2H)<\substack{CH_2.CHBr\\CHBr.CH_2}>CH.CO_2H$ by uniting with HBr. Sodium-amalgam in the cold reduces it to a slight extent, forming the two isomeric Δ^2 tetrahydrides.—BaA″4aq. Crystals, resembling its $\Delta^{1,5}$ and $\Delta^{1,3}$ isomerides.

Mono-methyl ether MeHA″. [225°]. Got from Me_2A'' and alcoholic potash. Needles (from hot water).

Di-methyl ether Me_2A''. [130°]. H.F. 172,700. Formed from the dihydride by successive treatment with PCl_5 (2 mols.) and MeOH. Monoclinic plates (from EtOAc); $a:b:c = 1{\cdot}52:1:2{\cdot}79$; $\beta = c.\ 74°$. Sl. sol. water, m. sol. hot alcohol, v. e. sol. ether. Br in $CHCl_3$ yields a dibromide $C_6H_6Br_2(CO_2Me)_2$ [90°] and a tetrabromide [150°]. Excess of Br yields  $CO_2Me.C_6H_6Br<\substack{CO\\O}$ [188°]. HBr forms $C_6H_8Br_2(CO_2H)_2$ which yields $C_6H_8Br_2(CO_2Me)_2$ [166°].

Di-phenyl ether Ph_2A''. [191°]. Formed by treating the chloride with phenol (Baeyer a. Herb, *A.* 258, 31). Small scales (from hot MeOH), sl. sol. ether.

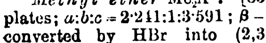
$\Delta^{1,3}$ or (5,6)- **Dihydride**

 $CO_2H.C<\substack{CH_2.CH_2\\CH:CH}>C.CO_2H$. S. ·0053 in the cold. Formed by the action of alcoholic potash on the dibromide of the Δ^2 tetrahydride and on the tetrahydride of di-bromo-terephthalic acid got by bromination of the hexahydride. Unites with hydrogen bromide (2 mols.) forming  $CO_2H.CH<\substack{CH_2.CH_2\\CHBr.CHBr}>CH.CO_2H$. Easily reduced by Zn and HOAc and by sodium-amalgam to the two Δ^2 tetrahydrides. Boiling water converts it into the (3,4)- isomeride. Boiling NaOHAq forms the (3,6)- isomeride.—BaA″ 4aq. Needles (from hot water).

Methyl ether Me_2A''. [85°]. Monoclinic plates; $a:b:c = 2{\cdot}241:1:3{\cdot}591$; $\beta - 87°\ 13'$. Slowly converted by HBr into (2,3)-di-bromo-terephthalic acid hexahydride, which is reduced by zinc-dust and acetic acid to the Δ^2 tetrahydride of terephthalic acid. Yields a dibromide [64°].

Di-phenyl ether Ph_2A''. [175°]. Large needles (from MeOH), sl. sol. cold alcohol.

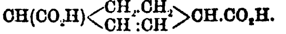
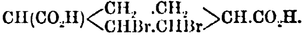
Δ^1 or (3,4,5,6)- **Tetrahydride.**

 $CH(CO_2H)<\substack{CH_2.CH\\CH_2.CH_2}>C.CO_2H$. [above 300°]. S. ·102 at 16°; ·83 at 100°. H.F. 214,200 (Stohmann, *J. pr.* [2] 43, 5). Formed by boiling a solution of terephthalic acid (1 pt.) in NaOHAq for twenty hours with gradual addition of 4 p.c. sodium-amalgam (100 pts.) (Baeyer, *B.* 19, 1805; *A.* 245, 160; 258, 32). Prisms, more sol. water than terephthalic acid or its dihydrides. Combines with HBr and with Br (1 mol.). Immediately reduces alkaline $KMnO_4$, yielding oxalic acid.—BaA″ 3½aq. M. sol. cold water. Reduced by HIAq at 240° to the hexahydride.—Ag_2A''. Amorphous.

Methyl ether Me_2A''. [39°]. H.F. 196,200. Plates. Its ethereal solution shows blue fluorescence and gives a fugitive rose-red pp. with NaOEt. HBr gives $C_6H_8Br(CO_2H)_2$, whence Me_2A'' [95°]. Bromine forms $C_6H_8Br_2(CO_2Me)_2$ [81°].

Di-phenyl-ether Ph_2A''. [145°]. Formed from the acid by successive treatment with PCl_5 and phenol. Monoclinic crystals; $a:b:c = 2{\cdot}824:1:2{\cdot}470$, m. sol. cold alcohol and ether.

Γ *cistrans* Δ^2 or (1,4,5,6)- **Tetrahydride**

 $CH(CO_2H)<\substack{CH_2.CH_2\\CH:CH}>CH.CO_2H$. [c. 220°]. S. ·17. Formed by reducing $\Delta^{1,5}$ dihydride and also the dibromide of the $\Delta^{1,3}$ dihydride. Oxidised by $KMnO_4$ in the cold to succinic acid and a soluble acid [150°]. Alkaline K_3FeCy_6 gives terephthalic acid. Yields three dibromides  $CH(CO_2H)<\substack{CH_2.CH_2\\CHBr.CHBr}>CH.CO_2H$. [171°], [51°], and [94°]. The Ba and Cd salts are more sol. water than those of the Δ^1 isomeride.

Methyl ether Me_2A''. [c. 3°].

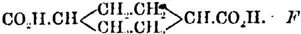
Amide. Dimetric needles; $a:c = 1:2{\cdot}151$.

Diphenyl ether Ph_2A''. Formed, in two modifications [107°] and [c. 190°] by the successive action of PCl_5 and phenol (Baeyer a. Herb, *A.* 258, 39). The modification [c. 190°] probably is a mixture containing the Δ^1 isomeride.

Dibenzyl ether $(C_7H_7)_2A''$. [48°]. From Ag_2A'' and benzyl chloride.

Γ *cis* Δ^2 or (1,4,5,6)- **Tetrahydride.** [150°–155°]. S. 2·7 in the cold. Formed, together with the *cistrans* isomeride, by reducing the $\Delta^{1,4}$ dihydride by sodium-amalgam in the cold. The Ba, Cd, and Ag salts are amorphous. This acid and the *cistrans* isomeride are converted into the Δ^1 isomeride by boiling with NaOHAq.

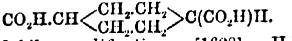
Γ *cistrans* **Hexahydride**

 $CO_2H.CH<\substack{CH_2.CH_2\\CH_2.CH_2}>CH.CO_2H$. *Fumaroid or stable modification.* [300°]. S. ·086 at 16°; 1·3 at 100°. H.F. 236,500 (Stohmann, *J. pr.* [2] 43, 7). Formed by heating the tetrahydride with HIAq for 6 hours at about 240° (Baeyer, *B.* 19, 1806; 245, 170; 251, 257). Formed also by heating ethyl butane tetracarboxylate with NaOEt and ethylene bromide at 100°; the product being hydrolysed and heated at 220° till evolution of CO_2 ceases (Mackenzie a. Perkin, jun., *C. J.* 61, 174). Prepared by reducing the hexahydride of bromo-terephthalic acid with zinc-dust and HOAc. Small prisms, sol. hot water. May be sublimed. Not oxidised by cold alkaline $KMnO_4$. Br (2 mols. at 100°) forms $C_6H_9Br(CO_2H)_2$ [71°], and a maleic isomeride [205°]. Treatment with PCl_5 followed by Br at 150° forms $C_6H_8Br_2(CO_2H)_2$ in a fumaroid modification which yields Me_2A'' [150°] and a maleic modification which yields Me_2A'' [68°] and an anilide [200°]. The K and Ba salts are v. sol. water; the Ca salt is sl. sol. water.

Methyl ether Me_2A''. [71°]. S. ·5 at 100°. H.F. 218,100. Exhibits no fluorescence. Volatile with steam.

Diphenyl ether Ph_2A''. [151°]. Needles.

Γ *cis* **Hexahydride**

 $CO_2H.CH<\substack{CH_2.CH_2\\CH_2.CH_2}>C(CO_2H)H$. *Maleic or labile modification.* [162°]. H.F. 237,400. Formed by reducing the very soluble hexahydride of bromo-terephthalic acid with zinc-dust and HOAc. Plates (from water), v. sol. alcohol and ether. Changes on heating with HClAq at 180° into its isomeride. Its Ba salt and methyl ether do not crystallise.

References.—Bromo-, Chloro-, Nitro-, and Oxy- terephthalic acid.

TEREPHTHALIC ALDEHYDE $C_6H_4(CHO)_2$[1:4]. [116°]. (247°). S. 1·7 at 100°. Formed by boiling $C_6H_4(CH_2Cl)_2$ or $C_6H_4(CH_2Br)_2$ (1 pt.) with lead nitrate (1 pt.) and water (20 pts.) (Grimaux, *C. R.* 83, 825; Löw, *A.* 231, 363). Formed also by the action of fuming HNO_3 on di-ω-bromo-*p*-xylene (Löw, *B.* 18, 2072), and by boiling $C_6H_4(CHCl_2)_2$ with water (Colson a. Gautier, *Bl.* [2] 45, 6, 508). Obtained from $CH_2(OH).C_6H_4.CH_2OEt$ by successive treatment with PCl_5 and water (Colson, *Bl.* [2] 42, 152).

Preparation.—*p*-Xylene (1 pt.) is heated with Br (6 pts.) at 140° to 200° with inverted condenser. The crystalline tetra-ω-bromo-xylene [169°] thus obtained is heated with three times its weight of H_2SO_4 (S.G. 1·825 at 120°–130°), the product poured into water, and the needles that separate recrystallised from water (Hönig, *M.* 9, 1153).

Properties.—Long needles, v. sl. sol. hot water and cold ether, v. sol. alcohol. Slightly volatile with steam. Dissolves in 25 pts. of saturated aqueous $NaHSO_3$ at 45°.

Reactions.—1. Oxidised by *chromic acid mixture* to *p*-aldehydo-benzoic acid and then to terephthalic acid.—2. Conc. NaOHAq forms terephthalic acid, ω-oxy-toluic acid, and di-ω-oxy-xylene.—3. KNO_3 and excess of H_2SO_4 at 110° form nitro-terephthalic aldehyde.—4. Cold conc. NH_3Aq forms tri-*p*-aldehydo-hydrobenzamide $(C_6H_4(CHO).CH)_3N_2$, a crystalline powder, insol. water, alcohol, and ether, yielding on oxidation by $KMnO_4$ crystalline $N_2(CH.C_6H_4.CO_2H)_3$ (Oppenheimer, *B.* 19, 574).—5. Dry or alcoholic NH_3 forms crystalline $C_6H_4(CH:NH)_2$.—6. NaOAc and Ac_2O give *p*-aldehydo-cinnamic acid.—7. *Acetone* and dilute NaOH give a white pp. of $C_6H_4(CH:CH.CO.CH_3)_2$, which crystallises from ether-acetone in matted needles [156°], insol. water and alcohol, and gives a deep-red solution in conc. H_2SO_4. An intermediate body is $C_6H_4(CH(OH).CH_2.CO.CH_3)_2$.—8. $NPhMe_2$ and $ZnCl_2$ form $C_6H_4(CHO).CH(C_6H_4NMe_2)_2$, the leuco derivative of the aldehyde of malachite green.—9. Cold conc. aqueous KCy added to a cold saturated alcoholic solution of the aldehyde ppts. amorphous $C_{16}H_{12}O_4$, which probably has the formula $C_6H_4(CHO).CH(OH).CO.C_6H_4(CHO)$ [170°–174°]. This body reduces cold ammoniacal $AgNO_3$, forming a mirror. It also reduces warm Fehling's solution and combines with phenyl-hydrazine. $KMnO_4$ oxidises it to benzoin di-*p*-carboxylic acid. NaOHAq dissolves it, forming benzoïn di-*p*-carboxylic acid, di-ω-oxy-*p*-xylene, and other bodies (Oppenheimer, *B.* 19, 1814).

Phenyl-hydrazide [230°].

Oxim $C_6H_4(CH:NOH)_2$. [200°]. Formed from the aldehyde and an alkaline solution of hydroxylamine (Westenberger, *B.* 16, 2994). Crystalline, v. sol. alcohol and ether, sl. sol. water. Yields $C_6H_4(CH:NOEt)_2$ [55°] and $C_6H_4(CH:NOAc)_2$ [155°].

Reference.—NITRO-TEREPHTHALIC ALDEHYDE.

TEREPHTHALIC AMIDINE $C_8H_{10}N_4$ *i.e.* $C_6H_4(C(NH).NH_2)_2$. The salt B″2HCl, formed by digesting terephthalic imido-ethyl ether with alcoholic NH_3, is crystalline, and yields $B''H_2PtCl_6$ (Luckenbach, *B.* 17, 1436).

TEREPHTHALOPHENONE *v.* **PHTHALOPHENONE.**

TERPENES $C_{10}H_{16}$; also **Sesquiterpenes** $C_{15}H_{24}$ and **Polyterpenes** $(C_{10}H_{16})_n$. The greater number of these hydrocarbons exist ready formed as constituents of essential oils secreted by plants. Others are produced from the natural terpenes by the action of heat or of chemical agents. A dihydrocymene isomeric with the natural terpenes has been obtained synthetically from methyl-isopropyl succino-succinic ester and the homologous dihydroparaxylene and dihydrobenzene by corresponding processes (Baeyer, *B.* 25, 1840, 2122; 26, 232). The natural terpenes are generally optically active liquids, with right- or left-handed rotatory power. The only exception is the racemic compound dipentene (*q. v.*). The following isomerides are known:—

1. **Pinene.** This includes two varieties, australene or dextropinene and terebenthene or lævopinene. American spirit of turpentine consists chiefly of dextropinene. (156°). $[\alpha]_j = +21{\cdot}5$ (Berthelot, *A.* 83, 105; 88, 345, 110, 367, *Suppl.* ii. 226). S.G. $\frac{0}{4} = {\cdot}8765$; $\frac{25}{25} = {\cdot}8586$; $\frac{100}{100} = {\cdot}8278$ (Tilden, *unpubl. expts.*). French turpentine oil consists almost wholly of lævopinene. (156·5°). $[\alpha]_j = -40{\cdot}32$. S.G. $\frac{0}{0} = {\cdot}8767$; $\frac{17{\cdot}88}{17{\cdot}88} = {\cdot}8619$ (Riban, *C. R.* 78, 788; 79, 314). It is also present in oil of rosemary (Bruylants, *J.* 1879, 944), oil of lemon (Tilden, *Ph.* [3] 9, 654), sage and juniper (*C. J.* 31, 554), thyme and anise (Brühl, *B.* 21, 156), and other essential oils.

For production and properties of turpentine oils *v.* OILS, ESSENTIAL, Thorpe's DICTIONARY OF APPLIED CHEMISTRY.

Different specimens of the pinenes, both dextro- and lævo-, obtained by fractional distillation from turpentine exhibit considerable variations in their rotatory power. An optically inactive liquid has been obtained by Wallach (*A.* 258, 343) from pinene nitrosochloride by treatment with aniline, whereby a diazo-compound is formed, which with the neighbouring chlorine atom gives rise to diazobenzenechloride and regenerates the hydrocarbon

$$-CCl-C.NO- + H_2NC_6H_5 = -CCl-C(N:NC_6H_5)- + H_2O \text{ and}$$

$$-CCl-C(N:NC_6H_5)- = -C{=}C- + ClN_2C_6H_5.$$

The hydrocarbon thus obtained boils at 155°–156°, has a density ·858 at 20°, a refractive index for D 1·46553 at 21°, and is supposed to be identical in constitution with the pinenes. It is apparently not resolvable into a mixture of dextro- and lævo- pinenes, but with nitrosyl chloride and other reagents it behaves in the same manner as pinene.

Dry pinene unites with one molecule of dry hydrogen chloride, forming a crystalline compound formerly called artificial camphor [125°], which appears quite saturated, as it is unacted upon either by excess of hydrogen chloride or bromine. The hydrochloride prepared from dextropinene is dextrorotatory, while that from lævopinene is lævorotatory. The compound is very stable; it may be distilled almost without change, mere traces of hydrogen chloride being evolved; and it is unacted upon by aqueous solutions of the alkalis, except at high temperatures under pressure. Heated with sodium stearate, benzoate, or acetate, or with alcoholic potash, it loses the elements of hydrogen chloride and yields solid camphene (*v.* CAMPHENE, *infra*). In the presence of water, alcohol, ether, or acetic acid, pinene takes up two mols. of hydrogen chloride, producing a compound of different character [50°], which on the application of heat is readily split up into hydrogen chloride and a mixture of liquid hydrocarbons (*v.* DIPENTENE, *infra*). Nitrosyl chloride passed into a solution of pinene in chloroform at −10° yields a compound $C_{10}H_{16}NOCl$ [103°], which is ppd. as a white crystalline powder on the addition of alcohol (Tilden, *C. J.*, June 1875). The same compound is formed by adding hydrochloric acid to a cooled mixture of the terpene with amyl nitrite and glacial acetic acid (Wallach, *A.* 245, 245). The nitrosochloride gently heated with alcoholic potash yields a nitroso- compound, $C_{10}H_{15}NO$ [129°] (Tilden). For crystallography *v.* Story-Maskelyne (*C. J.*, June 1875, and *Phil. Mag.*). Nitrosopinene unites with two atoms of bromine, forming a crystalline dibromide, which decomposes on melting [132°]. Mixed with alcohol and nitric acid both pinenes form crystallised terpin hydrate $C_{10}H_{18}(OH)_2.OH_2$ (Wiggers, *A.* 33, 358; 57, 247; Tilden, *C. J.* 33, 217; Hempel, *A.* 180, 71). Pinene dissolved in carbon tetrachloride and mixed with bromine yields a mixture of products, from which a well-defined crystalline dibromide $C_{10}H_{16}Br_2$ [169°–170°] may be isolated. On heating this with aniline it gives up hydrogen bromide, and ordinary cymene is produced. The yield, however, amounts only to about 10 p.c. of the bromide employed (Wallach, *A.* 264, 1). Exposed to the action of air or oxygen, in sunlight, the pinenes produce a crystalline compound $C_{10}H_{18}O_2$ (Sobrero, *C. R.* 33, 66) which when distilled with dilute acid yields a compound called by Armstrong 'Sobrerone' (Armstrong a. Pope, *C. J.* 59, 311), which is identical with one of the products of the action of nitrous acid on pinene, isolated by Wallach a. Otto, and called by them 'Pinol' (*A.* 253, 249). Pinene distilled with bleaching powder and water yields a large quantity of chloroform. Picric acid has no action upon pinenes in the cold, but at the b.p. of the latter a brisk reaction sets in, and if the liquid is afterwards allowed to cool a compound is deposited in colourless scales, which on boiling with alkali yield borneol (Lextreit, *C. R.* 102, 555; Tilden a. Forster, *C. J.* 63, 1388).

2. Limonene. This compound, like pinene, occurs in two optically active varieties. Dextro-limonene (175°–176°), S.G. $\frac{20}{20}$ ·846, $[\alpha]_D = +106{\cdot}8$ (Wallach, *A.* 252, 145) occurs in oils of the fruit of oranges and lemons, also in caraway and dill, &c. The most convenient source is the essential oil of sweet orange, *Citrus aurantium*. Lævo-limonene is obtained from the oil distilled from the leaves of *Pinus sylvestris* and *P. picea.* This oil occurs in the drug houses as 'Fir-Wool oil,' but is now much adulterated with common turpentine, and the commercial oil seldom yields more than a small percentage of limonene. (175°–176°), S.G. $\frac{20}{20}$ = ·846, $[\alpha]_D = -105°$ (Wallach, *A.* 227, 287, 246, 221). The limonenes, treated with perfectly dry hydrogen chloride, yield a liquid monochloride. In the presence of alcohol they give, with excess of hydrogen chloride, a quantitative yield of a dihydrochloride [50°], identical with the compound obtained from the pinenes. By the action of nitrosyl chloride (Tilden a. Shenstone, *C. J.* May, 1877), or by the use of amyl or ethyl nitrite and hydrogen chloride (Wallach), they yield a crystalline nitrosochloride, which, whether formed from dextro- or lævo-limonene, is always a mixture of two isomerides separable from each other by cold chloroform or ether. There are therefore four isomeric limonene nitroso-chlorides, as follows:

FROM *d.* LIMONENE:
α compound [103°–104°] $\alpha_D = +313°$
β ,, [105°–106°] $\alpha_D = +240°$
FROM *l.* LIMONENE:
α compound [103°–104°] $\alpha_D = -314°$
β ,, [100°] $\alpha_D = -242°$

From the nitroso-chlorides by the action of heat (Tilden a. Shenstone), or by boiling with alcohol (Goldschmidt a. Zürrer, *B.* 18, 2220), is produced an isonitroso-limonene, which when made from lævo-limonene is identical in every respect with carvoxim $C_{10}H_{14}N.OH$, from carvol, extracted from oil of caraway (Goldschmidt a. Zürrer, *B.* 18, 1732). For a comparison of the rotatory powers of the two limonenes and their derivatives, see Wallach (*A.* 252, 141). The limonenes are further characterised by the formation of a crystalline tetrabromide [104°–105°] by direct addition of bromine (Wallach, *A.* 227, 277).

By mixing together equal quantities of dextro- and lævo- limonenes an optically inactive mixture is obtained, which behaves in many respects as a distinct hydrocarbon, and appears to be identical with dipentene (*q. v.*). Strong sulphuric acid acting upon citrene (*d*-limonene), causes polymerisation, the chief product being a colophene (310°–320°) (Bouchardat a. Lafont, *C. R.* 115, 1083).

The oil of *Licari kanali* contains a compound, licareol $C_{10}H_{18}O$, from which a hydrocarbon, licarene $C_{10}H_{16}$, is obtainable by the action of acetic anhydride at 150° (Barbier, *C. R.* 114, 674, and *C. R.* 116, 993, and 1062). This terpene appears to consist of impure *d*-limonene, as it boils at 176°–178°, gives a tetrabromide [103°–104°], forms a nitrosochloride, from which carvoxim [72°] is formed by alcoholic potash; but its specific rotatory power is low, $[\alpha]_D = 7{\cdot}51°$.

3. Sylvestrene occurs in Swedish turpentine (Atterberg, *B.* 10, 1206) and in Russian turpentine (Wallach, *A.* 230, 245), in company with australene and other hydrocarbons of higher boiling-point. (176°–177°). S.G. $\frac{18}{18}$ = ·8510; $\frac{20}{20}$ = ·8470. $[\alpha]_D = +66{\cdot}32$ (Wallach, *A.* 245, 197). The odour of sylvestrene differs from that of pinene and limonene, and resembles the odour of fresh firwood. It forms a liquid monohydrochloride, and a crystalline dihydrochloride [72°], from which the hydrocarbon may be recovered unchanged by heating with aniline. Sylvestrene also gives a nitrosochloride [106°–107°], which, by treatment with alcoholic potash, yields only oily products. The tetrabromide crystallises in monoclinic tables [135°] (Wallach, *A.* 239, 29).

4. Phellandrene. The seeds of *Phellandrium aquaticum* were found by Pesci (*G.* 16, 225) to yield about 2½ p.c. of a volatile oil, consisting chiefly of a dextrorotatory terpene (171°–172°). The same hydrocarbon is contained in the oil of bitter fennel, *Fœniculum vulgare* (Wallach, *A.*

239, 40), and in the oil of elemi. Lævo-phellandrene is found, according to Wallach (*A.* 246, 232), in the oil of *Eucalyptus amygdalina.* Phellandrene is characterised by the formation of a nitroso-nitrite $C_{10}H_{16}N_2O_3$. Pesci obtains it by the action of a nitrite and dilute sulphuric acid upon the hydrocarbon. It crystallises in needles [94°], and although obtained from the dextrorotatory hydrocarbon it rotates the plane of polarisation to the left. $[\alpha]_D = -183{\cdot}5°$ (Pesci). By reducing agents this compound is converted into a base $C_{10}H_{16}(NH_2)_2$ (209°–214°). Ammonia converts it into nitrophellandrene $C_{10}H_{15}NO_2$ and an acid.

5. **Dipentene**, formerly called terpilene or terpinylene. As already stated, this compound is produced when equal quantities of dextro- and lævo- limonenes are mixed together (see *Pentylenes*). It is formed by heating isoprene to a temperature of about 300°. It is also the chief constituent of 'isoterebenthene,' formed by the action of heat on lævo-pinene. It occurs among the products of the destructive distillation of caoutchouc. Dipentene is also produced, together with terpinene, terpinolene, and terpineol, by the action of sulphuric acid or phosphoric acid on terpin, or by the action of sulphuric acid on the pinenes under certain conditions (Armstrong a. Tilden, *C. J.* November, 1879). It is also formed from the dihydrochloride [50°], whether made from pinene or limonene, either by the action of heat upon the chloride alone (Tilden, *B.* 12, 1133) or by boiling it with a mixture of sodium acetate and acetic acid, or with alcohol and aniline (Wallach). The products thus obtained were formerly supposed to consist of a single hydrocarbon, to which the name 'terpilene' was given. The hydrocarbons known as cinene and cajeputene formed from cineol and cajeputol respectively also consist of dipentene. Dipentene occurs ready formed in the volatile oil of the camphor tree, also in oil of elemi and in Russian and Swedish turpentines (Wallach, *A.* 227, 296, &c.).

Dipentene boils at about 176°, and has a pleasant smell of lemons. It combines with bromine forming a tetrabromide [124°], and unites with 2HCl forming a chloride [50°], from which it may be regenerated by methods given above. It is to be noted, however, that in all cases more or less isomeric change occurs, and the hydrocarbon, whether reproduced by heat alone or by the action of aniline, always contains terpinene and terpinolene, beside cymene and a small quantity of a paraffinoid hydrocarbon (Tilden a. Williamson, *C. J.* 63, 292). The nitrosochloride $C_{10}H_{16}NOCl$ yields an inactive carvoxim $C_{10}H_{14}NOH$ [93°] (*A.* 245, 267). A mixture of equal volumes of dextro- and lævo-limonene behaves in many respects as though it were a distinct hydrocarbon, as it was supposed to be previously to Wallach's researches. Thus the tetrabromide melts at 124°, while the limonene compound melts at 104°. The inactive isonitrosodipentene or carvoxim, melting at 93°, is formed by mixing together equal quantities of lævo-carvoxim [72°] from dextro-limonene and dextro-carvoxim [72°] from lævo-limonene. The resulting compound gives, by Raoult's freezing-point method, a molecular weight corresponding to the simple formula $C_{10}H_{15}NO$ (Wallach, *A.* 246, 230).

Certain derivatives of dipentene exist in two optically inactive forms. When *d*-limonene-nitrosochloride, prepared from either dextro- or lævo-limonene, is warmed with an alcoholic solution of piperidine, a mixture of two crystallisable nitrolamines is formed in each case, as follows:

NITROLPIPERIDINES $C_{10}H_{16}NONC_5H_{10}$, FROM LÆVOLIMONENE:

(α) [93°–94°] Rhombic, from alcohol. $[\alpha]_D = -67{\cdot}60°$. Hydrochloride dextrorotatory.
(β) [110°–111°]. Monoclinic. $[\alpha]_D = +60{\cdot}18°$. Hydrochloride almost inactive.

FROM DEXTROLIMONENE:

(α) [93°–94°]. Rhombic. $[\alpha]_D = +67{\cdot}95°$. Hydrochloride lævorotatory.
(β) [110°–111°]. Monoclinic. $[\alpha]_D = -60{\cdot}48°$. Hydrochloride (?).

When the two α-piperidine bases [93°–94°] are dissolved in petroleum-spirit, and the solutions mixed, an inactive nitrolamine [154°] is at once precipitated. A second inactive compound [152°] is formed by mixing the β-piperidine bases (Wallach, *A.* 252, 123). Similar results have been obtained by the employment of aniline and benzylamine. The salts of the bases thus produced possess a rotatory power opposite in direction to that of the free base. No method is at present known of producing from limonene active addition-compounds with two molecules of hydracid. With excess of hydrogen chloride the same inactive dipentene dihydrochloride [50°] is always obtained. The corresponding dihydriodide seems to crystallise in two forms differing slightly in melting-point (Wallach, *A.* 239, 13).

6. **Terpinene.** (180° about). This compound is formed, together with dipentene, by the action of acids upon pinene and terpin, &c. It is said to occur in oil of cardamoms (Ev. Weber, *A.* 238, 98). Terpinene has not been obtained in an absolutely pure state, but is characterised by forming a nitrosonitrite $C_{10}H_{16}N_2O_3$ [155°] (Wallach, *A.* 239, 33). The tetrabromide is fluid, and it yields no crystallisable hydrochloride. The nitrosonitrite by the action of bases yields nitrolamines $C_{10}H_{15}{<}\begin{smallmatrix}NOH\\NH_2\end{smallmatrix}$ [116°–118°], $C_{10}H_{15}{<}\begin{smallmatrix}NOH\\NHC_6H_5\end{smallmatrix}$ [130°–131°], &c. (*A.* 241, 315).

7. **Terpinolene.** (185° about). This hydrocarbon is formed along with dipentene and terpinene by the action of acids upon pinene, &c.

With hydrogen chloride and hydrogen bromide terpinolene unites to form the dipentene dihydrochloride [50°] and dihydrobromide [64°]. It forms an optically inactive tetrabromide which crystallises in monoclinic tables [116°] but is gradually converted at ordinary temperatures into a porcelain-like mass.

8. **Fenchene.** A liquid isomeride of camphor (190°–193°), obtained from oil of fennel, is treated with alcohol and sodium, by which it is reduced to the alcohol $C_{10}H_{17}OH$, a colourless crystalline compound. By treating this with phosphoric chloride the chloride $C_{10}H_{17}Cl$ is formed, and from this, by heating with aniline, fenchene $C_{10}H_{16}$ (158°–160°) may be obtained. Fenchene is optically inactive. It differs from other terpenes in resisting the action of nitric acid unless heated (Wallach, *A.* 263, 149).

Synopsis of Terpenes and their Chief Derivatives.

Boiling-points approximately stated. Rotatory power +, −, or 0.

Pinene (156°)	Limonene (176°)	Dipentene (176°)	Sylvestrene (175°)	Phellandrene (170°)	Terpinene (180°)	Terpinolene (185°)	Fenchene (160°)
+ and −	+ and −	±	+	+ and −	0	0	0
$C_{10}H_{16}HCl$ saturated [125°]	$C_{10}H_{16}HCl$ unsaturated liquid	$C_{10}H_{16}HCl$ unsaturated liquid	$C_{10}H_{16}HCl$ liquid	—	—	—	$C_{10}H_{16}HCl$ liquid
$C_{10}H_{16}2HCl$ [50°]	$C_{10}H_{16}2HCl$ [50°]	$C_{10}H_{16}2HCl$ [50°]	$C_{10}H_{16}2HCl$ [72°]	—	—	—	—
$C_{10}H_{16}Br_2$ [170°]	$C_{10}H_{16}Br_4$ [104°]	$C_{10}H_{16}Br_4$ [124°]	$C_{10}H_{16}Br_4$ [135°]	—	$C_{10}H_{16}Br_4$ liquid	$C_{10}H_{16}Br_4$ [116°]	$C_{10}H_{16}Br_2$ liquid
$C_{10}H_{16}NOCl$ [103°]	$C_{10}H_{16}NOCl$ four isomerides [100° to 106°]	$C_{10}H_{16}NOCl$ [101°–102°]	$C_{10}H_{16}NOCl$ [106°]	$C_{10}H_{16}N_2O_3$ [102°]	$C_{10}H_{16}N_2O_3$ [155°]	—	—
$C_{10}H_{16}{<}\begin{matrix}NO\\NHC_7H_7\end{matrix}$ [122°]	$C_{10}H_{16}{<}\begin{matrix}NO\\NHC_7H_7\end{matrix}$ [93°]a	$C_{10}H_{16}{<}\begin{matrix}NO\\NHC_7H_7\end{matrix}$ [109°]a	$C_{10}H_{16}{<}\begin{matrix}NO\\NHC_7H_7\end{matrix}$ [71°]	—	$C_{10}H_{16}N_2O_3$ [137°]	—	—
$C_{10}H_{15}NO$ [132°]	$C_{10}H_{14}N.OH$ [72°]	$C_{10}H_{14}NOH$ [93°]	—	—	—	—	—

Isoterpenes.

Camphenes $C_{10}H_{16}$. Pinene monohydrochloride [125°] was formerly described under the name 'artificial camphor,' from its resemblance to camphor in appearance and to a certain extent in odour. This compound is remarkably stable, but may be decomposed by heating with sodium stearate or benzoate, with potassium acetate, with alcoholic potash, or, better, with a mixture of sodium acetate and alcoholic soda (Brühl, *B.* 25, 147). The resulting hydrocarbon is a camphene [51°–52°] (160°), dextro- or lævo-rotatory or inactive according to the nature of the hydrochloride used and the reagent employed, though the exact conditions which determine the production of one or other are scarcely known (Riban, *A. Ch.* [5] 6, 353).

Camphene is also formed from bornyl chloride by the action of alcoholic potash (Riban), by the action of water and magnesia (Kachler, *A.* 197, 86), or by heating with aniline to the boiling-point of the latter (Wallach, *A.* 230, 234); it is also formed from camphor chloride and from pinene hydrochloride by the action of sodium (Montgolfier, *C. R.* 89, 102). In the last case it is accompanied by a liquid hydrocarbon (170°), $C_{10}H_{20}$, which behaves like a paraffin, and is probably identical with a liquid obtained by the action of hydrogen iodide on turpentine (Berthelot), also by the action of iodine (Armstrong a. Gaskell, *B.* 12, 1756) and by the action of sulphuric acid on turpentine (Armstrong, *B.* 12, 1759).

Camphene is also formed by the action of strong sulphuric acid on turpentine, and constitutes the characteristic ingredient in the liquid formerly known as 'terebene' (Armstrong a. Tilden, *C. J.* 1879, 733).

Camphene closely resembles camphor in appearance and even somewhat in odour. It is soluble in alcohol, ether, and benzene, and crystallises in leaflets from a concentrated solution. It is incapable of combining with bromine, but it forms a compound [157°] with hydrogen chloride, which is distinguished from pinene hydrochloride by its instability, being rapidly decomposed by water with reproduction of camphene (Riban, *C. R.* 80, 1330). It is also dissociated into camphene and hydrogen chloride when volatilised (Ehrhardt, *C. N.* 54, 239). Camphene hydrochloride is said to be identical with bornyl chloride (Kachler a. Spitzer, *A.* 200, 340; *v.* also Brühl, *B.* 25, 160). Camphene does not combine with nitrosyl chloride. In contact with bromine it is slowly attacked, forming an oily monobromo- derivative (230°–240°).

Oxidised by chromic liquor, camphene yields camphor, dextro-, lævorotatory or inactive according to the character of the camphene.

By the action of phosphorus pentachloride on camphene, and subsequent treatment of the mass with an alkaline solution, salts of two phosphonic acids are formed (Marsh a. Gardner, *C. J.* 65, 35).

When camphene is heated to about 300° it is converted into liquid products which seem to include dipentene, but have not been sufficiently investigated.

Homologues of camphene.

Ethyl-camphene obtained by the conjoint action of sodium and ethyl iodide upon camphor monochloride $C_{10}H_{15}Cl$, is a colourless mobile liquid having a smell like turpentine (197·9° – 199·9°, bar. 742·1 mm.). **Isobutyl-camphene** is also a liquid (228°–229°, bar. 750·4 mm.) (Spitzer, *B.* 11, 1817).

Sesquiterpenes $C_{15}H_{24}$.

Oils of clove, calamus, cascarilla, patchouli, and cubebs contain a hydrocarbon of this composition (Gladstone, *C. J.* 1872), as also do the oils of galbanum, and savin and 'huile de cade,' a kind of tar made by distillation of the wood of *Juniperus oxycedrus* (Wallach, *A.* 238, 81). The hydrocarbon obtained from cade or cubebs (274°–275°) (S.G. $\frac{15}{15}$ = ·921) forms the following crystalline compounds: $C_{15}H_{24}2HCl$ [117°–118°], $C_{15}H_{24}2HBr$ [124°–125°], $C_{15}H_{24}2HI$ [105°–106°]. The hydrocarbon, especially when partially resinified by exposure to the air, gives the following characteristic colour reaction: dissolved in chloroform or glacial acetic acid and then shaken up with a few drops of strong sulphuric acid, the liquid assumes an intense green and then blue colour, which, when heated, passes into red (Wallach). An attempt to prepare from isoprene a polymeride of the composition $C_{15}H_{24}$ proved unsuccessful (Wallach).

Conimene $C_{15}H_{24}$, a liquid (264°) having a pleasant odour, is obtained from the incense resin (*Icica heptaphylla*) of British Guiana (Stenhouse a. Groves, *C. J.* 1871, i. 175).

Polyterpenes $C_{20}H_{32}$, *&c.*

This group includes (1) the constituents of certain natural essential oils; (2) products of artificial polymerisation of terpenes; and (3) caoutchouc and guttapercha.

1. Oleo-resin or so-called 'balsam' of copaiba (*Copaifera Langsdorffii* and other species) is a mixture of a resin with an oil (250°–260°). The latter unites with water and absorbs hydrogen chloride, with production of a deep violet colour but no crystalline hydrochloride. A similar hydrocarbon is obtained from Gurjun balsam or 'wood oil,' the product of various species of *Dipterocarpus* growing in the East, and from other essential oils.

2. When turpentine oil and other terpenes are heated for some time to about 300°, or treated with concentrated sulphuric or phosphoric acid or other agents, a large part of the hydrocarbon undergoes polymerisation. The name 'colophene' was given by Deville to the less volatile portions of the product obtained in this manner from French turpentine, apparently under the impression that it was closely related to the oil obtained by distillation of resin. Resin-oil, however, contains oxygen, and exhibits quite different characters.

Colophene is a yellowish viscid fluid, usually fluorescent, which begins to boil at about 300°, but the distillation even under reduced pressure is attended by decomposition. The boiling-point continually rises, and even at a temperature approaching dull redness a viscid residue is left which on cooling becomes nearly solid (Armstrong a. Tilden, *C. J.* Nov. 1879). The portions which distil at 300° and upwards appear to consist of saturated compounds, for they absorb mere traces of hydrogen chloride. By the action of antimony trichloride upon turpentine a solid, $C_{40}H_{64}$, is formed. This combines with hydrogen chloride to form two compounds $C_{40}H_{64}HCl$, and $C_{40}H_{64}2HCl$ (Riban, *C. R.* 1874, 389).

3. Caoutchouc *v.* vol. i. p. 677. For further information concerning the products of its decomposition by heat *v.* Pentinenes (vol. iii. p. 807) and Dipentene (*supra*).

Guttapercha, *v.* vol. ii. p. 658.

Caoutchouc is formed from isoprene by polymerisation, which sometimes occurs spontaneously under circumstances not fully understood (Tilden, *C. N.*, May 1892).

Oxidised compounds connected with terpenes.

A considerable number of oxidised compounds are known which are evidently closely connected with the terpenes, and in many cases directly derivable from them. Some of these, as, for example, borneol and camphor, occur as natural products in essential oils; others, such as terpin, are the products of the addition of water to a terpene, or, like camphor and some of its isomerides, may be formed from terpenes by oxidation. These compounds are enumerated in the following table, together with the hydrocarbons with which they are presumably immediately connected.

Hydrocarbons	Alcohols	Glycols	Ketones (?)
Cymene $C_{10}H_{14}$ (ii. 361)	Carveol $C_{10}H_{15}OH$ (i. 711)	—	Carvol $C_{10}H_{14}O$ (i. 711)
Pinene $C_{10}H_{16}$ (*v. supra*)	Myristicol and absinthol (*v. infra*)	Sobrerol $C_{10}H_{16}(OH)_2$ (*v. infra*)	Sobrerone (pinol) $C_{10}H_{16}O$ (*v. infra*)
Dipentene $C_{10}H_{16}$ (*v. supra*)	Terpineol $C_{10}H_{17}OH$ (*v. infra*)	Terpin $C_{10}H_{18}(OH)_2$ (*v. infra*)	—
—	Cineol $C_{10}H_{17}OH$ (ii. 187). Syn. Eucalyptol, cajeputol	—	
Fenchene $C_{10}H_{16}$ (*v. supra*)	Fencheol $C_{10}H_{17}OH$ (*v. infra*)	—	Fenchone $C_{10}H_{16}O$ (*v. infra*)
Camphene $C_{10}H_{16}$ (*v. supra*)	Borneol $C_{10}H_{17}OH$ (i. 542)	Camphene glycol $C_{10}H_{16}(OH)_2$ (*v. infra*)	Camphor $C_{10}H_{16}O$ (i. 669)
—	Geraniol $C_{10}H_{17}OH$ (ii. 609)	—	Pulegone $C_{10}H_{16}O$ (*v. infra*)
—	Linalool $C_{10}H_{17}OH$ (iii. 146)	—	Puleone $C_{10}H_{16}O$ (*v. infra*)
—	—	—	Tanacetone or Thujone $C_{10}H_{16}O$ (*v. infra*)
Menthene $C_{10}H_{18}$ (iii. 202)	Menthol $C_{10}H_{19}OH$ iii. 203)	—	Menthone $C_{10}H_{18}O$ (iii. 204)
Dihydrocamphene $C_{10}H_{18}$ (*v.* Decinene, ii. 367)	—	—	—
Tetrahydrocamphene $C_{10}H_{20}$ (*v.* Decylene, ii. 369, *et infra*)	—	—	—

Cymene $C_{10}H_{14}$ (176°); ii. 361.

Dipentene $C_{10}H_{16}$ (176°); *v. supra.*

Fenchene $C_{10}H_{16}$ (160°); *v. supra.*

Camphene $C_{10}H_{16}$ (160°); *v. supra.*

Menthene $C_{10}H_{18}$ (167°); iii. 202.

Dihydrocamphene $C_{10}H_{18}$ *v.* DECINENE, ii. 367. The liquid produced, together with the solid monohydrochloride, by passing hydrogen chloride into pinene, yields when treated with sodium a mixture from which a liquid hydrocarbon $C_{10}H_{18}$ (148°-149°), having a smell of oranges, may be separated by fractionation, &c. (Bouveault, *C. R.* 116, 1067).

Tetrahydrocamphene $C_{10}H_{20}$ (DECYLENE, ii. 367). A liquid obtained by the action of hydrogen iodide and phosphorus upon oil of turpentine (Berthelot) and another (160°) by action of phosphonium iodide on turpentine (Baeyer) have this composition. The same formula is ascribed by Armstrong (*B.* 12, 1758) to a liquid (160°-170°) obtained by the action of iodine upon oil of turpentine and upon camphor, also by the action of sulphuric acid upon turpentine. All these products are insoluble in strong sulphuric acid, and resemble the paraffins in chemical characters.

Carveol $C_{10}H_{15}.OH$ (219°); i. 711.

Terpineol $C_{10}H_{17}.OH$. [35°]. (215°-218°). Wiggers, *A.* 33, 358; 57, 247; List, *A.* 67, 362; Tilden, *C. J.* 33, 247, and 35, 286; Wallach, *B.* 18, 618, Ref.; Kannonikoff a. Flawitzky, *J. pr.* [2] 32, 497; Bouchardat a. Voiry, *C. R.* 104, 996. Dextro- and lævo-terpineol are obtained by the action of alcoholic sulphuric acid upon *d*- and *l*-pinene respectively, or inactive by distilling terpin with very dilute sulphuric or hydrochloric acid. Terpineol as thus obtained is a viscous liquid, having an odour of white lilac. By fractional distillation under reduced pressure a portion is obtained (130°-135° at 40 m.m.), which may be crystallised by cooling to −50°, or by the introduction of a crystal of the same. These crystals melt at 30°-32°, and boil undecomposed at 218° (Bouchardat a. Voiry, *C. R.* 104, 996). Terpineol treated with sodium evolves hydrogen, but in consequence of its viscosity the action soon ceases. Contact with dilute acids converts terpineol into terpin hydrate. Hydrogen chloride and iodide react to form $C_{10}H_{18}Cl_2$ [50°] and $C_{10}H_{18}I_2$ [77°] respectively. Potassium hydrogen sulphate at 200° produces dipentene. Terpineol unites with two atoms of bromine, but excess of bromine gives rise to dipentene tetrabromide. With phenyl cyanate it yields phenyl-terpinyl-urethane $C_6H_5.NH.CO.OC_{10}H_{17}$ [110°]. These and other reactions have been repeated by Wallach, using crystallised terpineol (*A.* 275, 103). Terpineol oxidised by permanganate yields a substance $C_{10}H_{20}O_3$ [121°-122°], which probably has the constitution of an oxyterpin $C_{10}H_{17}(OH)_3$. Further oxidised by means of chromic acid this yields a crystalline compound $C_{10}H_{16}O_3$ [62°-63°] (Wallach, *A.* 275, 145).

Cineol $C_{10}H_{18}O$ (176°); ii. 187. Cineol appears to contain no hydroxyl, since it is not acted upon by metallic sodium nor by benzoyl chloride at 120°. It is also unaffected by hydroxylamine and by phenylhydrazine. Hence it appears to be neither an alcohol nor a ketone. Its relation to terpineol (*infra*) is shown by the fact that when heated with alcohol and sulphuric acid cineol is converted into terpinene and terpinolene: also that terpineol, and therefore also terpin, are partly converted into cineol by prolonged heating with phosphoric acid. Cineol oxidised by permanganate of potassium yields the potassium salts of carbonic, oxalic, and cineolic acids, with a small quantity of acetic acid. Cineol yields 45 p.c. of its weight of cineolic acid. This compound forms well-defined anhydrous crystals, which dissolve in 70 pts. of water at 15°, and in 15 pts. at 100°. They melt with decomposition at 196°-197°.

Calcium cineolate $C_{10}H_{14}CaO_5.4H_2O$ is soluble in cold water, but is completely precipitated by boiling the aqueous solution. Silver cineolate $C_{10}H_{14}Ag_2O_5.H_2O$ is soluble in both water and alcohol, but cannot be crystallised. Ethyl cineolate $C_{10}H_{14}(C_2H_5)_2O_5$, obtained by passing hydrogen chloride gas into an alcoholic solution of the acid, is a colourless liquid (155° under 11-12 mm.). By dry distillation cineolic acid yields cineolic anhydride, water, carbon dioxide, and a liquid which appears to consist of a monobasic acid (*A.* 246, 265).

Fencheol $C_{10}H_{17}.(OH)$. Fenchyl alcohol [40°-41°]. (201°). (Wallach, *A.* 263, 143; 272, 99-125). S.G. $\frac{40}{0}$ ·933 (W.). $[\alpha]_D = \pm 10{\cdot}36$ (W.). Dextro- and lævo-fenchyl alcohols are obtained by the reduction with sodium and alcohol of lævo- and dextro-fenchones respectively. Concentrated HNO_3 oxidises *l*-fenchyl alcohol to *d*-fenchone. PCl_5 gives rise to fenchyl chloride $C_{10}H_{17}Cl$ (84°-86° at 14 mm.).

Borneol $C_{10}H_{17}.OH$, i. 522.

Geraniol $C_{10}H_{17}.OH$, ii. 609.

Linalool $C_{10}H_{17}.OH$, iii. 146. Linalool is said to be convertible into the isomeric geraniol by treatment with acetic anhydride, and saponifying the resulting ester with alcoholic potash (Bouchardat, *C. R.* 116, 1253).

Menthol $C_{10}H_{19}(OH)$, iii. 203.

Terpin $C_{10}H_{18}(OH)_2$ [104°-105°]. (258°) (Wiggers, *A.* 33, 358; 57, 247; Tilden, *C. J.* 33, 247; 35, 286; Wallach, *A.* 230, 225-272). Terpin is best known in the form of its hydrate $C_{10}H_{20}O_2.H_2O$ [116-117°], a beautifully crystalline compound which on heating to 100° loses water and leaves terpin as a vitreous mass. Terpin hydrate is readily obtained by shaking turpentine oil with alcohol acidified with sulphuric or nitric acid (Flawitzky, *B.* 12, 1022; Tilden, *C. J.* 33, 247; 35, 286), and leaving the liquid to evaporate. It is an optically inactive, saturated compound, slightly soluble in boiling water, soluble in alcohol and crystallising in rhombic prisms (Rammelsberg, *P.* 63, 570; Maskelyne, *P. M.* 1879). It possesses the characters of a glycol and with hydrogen chloride yields dipentene dihydrochloride [50°]. Boiled with water containing a mere trace of mineral acid, terpin dissolves with production of terpineol and water.

Camphene glycol $C_{10}H_{16}(OH)_2$. [192°] (G. Wagner, *B.* 23, 2311).

Formation.—By the oxidation of camphene in benzene solution with a 1 p.c. solution of $KMnO_4$ (*l.c.*).

Properties.—Colourless prismatic needles (from benzene) very readily soluble in ether, alcohol, CS_2, and chloroform. Exhibits the same phenomenon as camphor when thrown on water. Sublimes when heated above 100°. Melts when warmed with water, but only dissolves in it with difficulty. Heated with acetic anhydride in a closed tube at 120°, the greater part loses water, only a small portion being converted into the acetic ester. Treatment with dilute HCl results in the loss of 1 mol. of H_2O, giving rise to a solid body, $C_{10}H_{16}O$, isomeric with camphor, which reduces ammoniacal $AgNO_3$ and reacts with hydroxylamine.

Carvol $C_{10}H_{14}O$ (228°), *v.* i. 711.

Fenchone $C_{10}H_{16}O$. [5°–6°]. (192°–193°) (Wallach, *A.* 263, 130; 272, 102). S.G. ^{19} ·9465 (W.). R_A 44·23 (W.). $[\alpha]_D$ + 71·70 and − 66·94.

Occurrence.—Dextro-fenchone is present in fennel oil, the fraction boiling between 190° and 195° consisting almost exclusively of the ketone, together with traces of anethol; derived from Thuja oil, fenchone possesses lævorotatory optical properties. *D-* and *l-*fenchone form a series of derivatives which bear to one another a relation similar to that subsisting between the two tartaric acids, and the analogy extends to the formation of racemic modifications when equal proportions of the two classes of derivatives are mixed together.

Preparation.—The fraction of fennel oil boiling between 190° and 195° is treated with concentrated HNO_3, the ketone remaining unattacked. After being freed from acid and distilled in a current of steam, the dry oil is cooled, and the fenchone crystallises out.

Reactions.—With bromine in the cold, an addition compound is formed, substitution taking place if the mixture becomes heated. P_2O_5, P_2S_5, and PCl_5 have the same action upon fenchone as upon camphor. Fenchone is dissolved by cold concentrated HCl, being thrown out of solution on warming. HNO_3 has but little action in the cold, but in a sealed tube at 120° HCN is formed (*A.* 263, 134). $KMnO_4$ oxidises fenchone to a mixture of oxalic, acetic, and dimethyl-malonic acids. *D-* and *l-*fenchone yield *d-* and *l-*fenchyl alcohols respectively on reduction with Na and alcohol (*v. Fencheol*). On heating *d-* and *l-*fenchone with ammonium formate, *l-* and *d-*fenchylamines respectively are formed. Fenchone does not react with phenyl-hydrazine or with alkaline sulphites, but both varieties form oxims [161°] with hydroxylamine.

*d-*Fenchon-oxim $C_{10}H_{16}NOH$ [161°] (240°) loses water on treatment with dilute H_2SO_4, an unsaturated dextrorotatory nitrile (218°) being formed.

*l-*Fenchon-oxim $C_{10}H_{16}NOH$ [161°] behaves in a similar manner on treatment with dilute H_2SO_4. The resulting nitrile yields with potash a lævorotatory *α*-isoxim $C_9H_{15}.CONH_2$ [114°–115°] which is readily converted by dilute H_2SO_4 into the *β*-isoxim [136°–137°].

Camphor $C_{10}H_{16}O$ (i. 669).

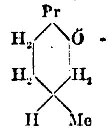
Menthone $C_{10}H_{18}O$ (206°) (iii. 204).

Pulegone $C_{10}H_{16}O$. (130°–131° under 60 mm.). (Beckmann a. Pleissner, *A.* 262, 1; Wallach, *A.* 272, 122; Semmler, *B.* 25, 3515). S.G. ^{22} ·9323 (B. a. P.); R_A 45·55 (B. a. P.); $[\alpha]_D$ 22·89 (B. a. P.). Pulegone is the chief constituent of Spanish oil of pennyroyal (*Mentha pulegium*). It is a dextrorotatory colourless liquid, having an odour of peppermint, and rapidly becoming yellow on exposure to the air.

Reactions.—With HBr it combines forming a lævorotatory ($[\alpha]_D = -33·8$) addition compound $C_{10}H_{16}O.HBr$ [40·5°]. When heated with ammonium formate, Wallach (*A.* 272, 123) failed to obtain a base isomeric with fenchylamine and thujonamine, a mixture of bases being formed. Slow oxidation with $KMnO_4$ gives rise to acetone and *β*-methyl-adipic acid [84·5°]. Rapid oxidation with the same reagent yields a *γ*-valero-lacton-*γ*-acetic acid (Semmler, *B.* 25, 3516). Pulegone combines with hydroxylamine to form pulegonoxim $C_{10}H_{19}NO_2$ [157°]. The oxim contains one molecule of H_2O more than camphoroxim. It is lævorotatory ($[\alpha]_D - 83·4$) and forms a hydrochloride [117°–118°], a benzoyl ester [137°–138°], and an acetyl ester [149°]. On heating its hydriodide pulegonamine $C_{10}H_{18}O.NH$ is formed.

Pulegone hydrobromide $C_{10}H_{16}O.HBr$ [40·5°] is lævorotatory; it forms an oxim [38°] which becomes converted on standing into normal pulegonoxim [157°]. Pulegone hydrobromide, on treatment with moist silver or lead oxide, loses HBr, pulegone being regenerated. Distillation with zinc dust gives rise to an oil which resembles menthone in every respect but the melting-point of its oxim (85° instead of 59°).

Constitution.—From the results of oxidation experiments carried on under various conditions with $KMnO_4$ Semmler (*B.* 25, 3519) attributes to pulegone the constitution:



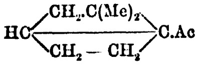
Puleone is the name given to a compound isomeric with camphor, obtained by Barbier (*B.* 25, 110*c*), from pennyroyal oil, described as boiling at 222°–223°, and possessing the following physical properties: S.G. ·9482; ^{23} ·9293; $[\alpha]_D$ + 29·15. Its oxim $C_{10}H_{16}.NOH$ is an oil (170° under 48 mm.) yielding a liquid anhydride $C_{10}H_{15}N$ on treatment with dilute H_2SO_4. Chromic acid mixture oxidises it to carbonic, acetic, and propyl-succinic [89°–91°] acids.

Tanacetone $C_{10}H_{16}O$ (195°–196°; 84·5 at 13 mm.), identical with the thujone of Wallach (*A.* 272, 109; Bruylants, *B.* 11, 450; Semmler, *B.* 25, 3343, 3519; Wallach, *l.c.*). S.G. $\frac{20}{20}$ ·9126 (S.). R_A 44·54 (S.).

Tanacetone occurs in tansy, sage, wormwood, and thuja oils. It has ketonic properties, and possesses an optical rotatory power amounting to + 38° 30′ in a 2-dcm. column.

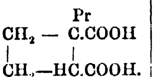
Reactions.—Sodium in alcoholic solution reduces it to tanacetyl alcohol (92·5° at 13 mm.). With alkaline hypobromite it yields bromoform and tanacetogen-dicarboxylic acid (113·5° at 15 mm.). Oxidised with $KMnO_4$ it yields tanacetocarboxylic acid, which exists in two modifications, the *α* and *β* thujaketonic acids of Wallach (*l.c.*), [75°–76°] and [78°–79°] respectively. Heated with ammonium formate, it gives tanacetylamine (198°–199°), the same body being formed when tanacetoxim (see below) is reduced with sodium and alcohol. The hydrochloride of this base on dry distillation yields tanacetene (172°–175°), a hydrocarbon of the formula $C_{10}H_{16}$, identical with Wallach's thujene. Tanacetone reacts with hydroxylamine to form tanacetoxim $C_{10}H_{16}.NOH$ [51·5°] (135°–136° at 22 mm.), which yields tanacetylamine on reduction, while treatment with dilute alcoholic H_2SO_4 converts it into a cymidine (Pr:NH_2:Me:1:3:4), which gives carvacrol with nitrous acid. Tanacetophorone $C_8H_{12}O$ (89°–90° at 13 mm.). R_A 37·6. When tanacetogen-dicarboxylic acid (produced by the action of NaBrO upon tanaceto-carboxylic acid) is heated with soda-lime, tanacetophorone is formed. It has ketonic properties, and combines with hydroxylamine.

Constitution.—Semmler (*B.* 25, 3519) suggests for tanacetone and tanacetogen-dicarboxylic acid the formulæ



Tanacetone.

and

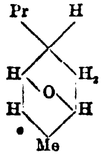


Tanacetogen-dicarboxylic acid.

Sobrerone $C_{10}H_{16}O$. *Pinol.* (183°–184°) (Wallach, *A.* 253, 254; Armstrong, *C. J. Proc.* 1890, 100). S.G. ^{20} ·953 (W.); μ_D 1·469 (W.). Sobrerone is obtained from the mother-liquors accumulated in the preparation of pinene nitrosochloride; also by boiling sobrerol with dilute H_2SO_4 (Armstrong, *l.c.*).

Reactions.—It combines readily with Br to form a dibromide [94°], from which, on treatment with alcoholic potash, sobrerone is regenerated. Sobrerone and its dibromide yield terebic acid [175°–176°] on oxidation with $KMnO_4$. HNO_3 produces the same result. It forms a nitroso-chloride [103°] which, by the action of bases, is readily converted into nitrolamines, *e.g.* sobrerone-nitrol-piperidine [154°] and sobrerone-nitrol-benzyl-amine [133°–134°]. The dibromide $C_{10}H_{16}O.Br_2$ [91°] (143°–144° at 11 mm.) yields on treatment with alcoholic potash, in addition to sobrerone, its glycol-ether $C_{10}H_{16}O(OC_2H_5)_2$ [52°–53°]. Sobrerone-glycol-diacetate is easily obtained by heating the dibromide to 150° with lead acetate in glacial acetic acid solution. When heated at 100° for three hours with formic acid, sobrerone dibromide is converted into pinene.

Constitution.—Its behaviour towards bromine and nitrosyl chloride and its molecular refraction indicate the existence of one ethylene linking, while its indifference towards acid chlorides, hydroxylamine, phenylhydrazine and H_2S render it probable that the O- atom is united to two different C- atoms. From these facts, and from its behaviour on oxidation, Wallach (*A.* 253, 259) assumes the constitution



Sobrerol $C_{10}H_{18}O_2$. [150°] (Sobrero, *C. R.* 33, 66; Armstrong, *C. J. Proc.* 1890, 100; *C. J.* 59, 315). Sobrerol is obtained by oxidising French and American turpentines in sunlight. It occurs in two optically active forms, both melting at 150°, and on allowing a mixed solution to crystallise inactive sobrerol [131°] separates out. When boiled with dilute H_2SO_4 it loses 1 mol. of H_2O, sobrerone—identical with Wallach's pinol—being formed.

Eucalyptol $C_{10}H_{18}O$ (176°) (Jahns, *B.* 17, 2941; Bouchardat a. Voiry, *C. R.* 106, 663). Identical with cineol, spicol, cajeputol, and terpan (B. a. V.).

Myristicol $C_{10}H_{16}O$ (224°) (Wright, *B.* 6, 1320; Gladstone, *C. J.* 23, 147; 25, 1; Brühl, *B.* 21, 471). S.G. ^{22} ·9446 (G.). R_A 46·42 (G.). Myristicol is a dextrorotatory alcohol, obtained from the ethereal oil of nutmeg, *Myristica aromatica.* It yields a chloride with PCl_5, and is converted into cymene by the action of $ZnCl_2$.

Absinthol $C_{10}H_{16}O$ (217°) (Beilstein a. Kupffer, *B.* 6, 1183; Wright, *l.c.* 1320; Gladstone, *C. J.* 45, 241; Brühl, *B.* 21, 471). S.G. $\frac{23}{23}$ ·9128 (G.). R_A 44·62 (G.). Absinthol is obtained from oil of wormwood, and is dextrorotatory. It is converted by $ZnCl_2$ and P_2S_5 into cymene. In what form the oxygen exists is at present unknown.

Constitution of the terpenes.

I. Pinene. The following facts must be taken into consideration:

1. Dry pinene combines with one molecule of hydrogen chloride to form a saturated compound, from which hydrogen chloride is withdrawn with difficulty, the resulting hydrocarbon being a solid camphene. Moist pinene combines with 2HCl, yielding dipentene-dihydrochloride. This also is saturated. The formation of both these compounds is undoubtedly attended by isomeric change, inasmuch as pinene cannot be recovered from either of them; but on removal of the elements of hydrogen chloride a new hydrocarbon results.

2. Pinene seems to combine with two atoms or with four atoms of bromine, according to the method of operating. By adding bromine to a cooled solution of pinene in carbon tetrachloride, Wallach has obtained a crystalline dibromide $C_{10}H_{16}Br_2$ [170°]. The yield is, however, very small, about 7 p.c. of the hydrocarbon employed (*A.* 264, 1). By shaking up a solution of pinene in chloroform, with an excess of sodium hypobromite, acidified with hydrochloric acid, so as to liberate the bromine, and immediately afterwards determining the unabsorbed excess of bromine, Tilden obtained results which pointed to the union of the terpene with four atoms of bromine. The combination is, however, very unstable, and hydrogen bromide is soon evolved (*C. J.* 53, 882). Schtschukaroff finds that a chloroform solution of pinene takes up, *in the dark*, four atoms of bromine; but the bromide formed is unstable, and quickly gives off hydrogen bromide, thus $C_{10}H_{16}Br_4 = HBr + C_{10}H_{15}Br_3$. (*B.* 23, 432, Ref.; *J. pr.* 47, 191–6).

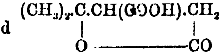
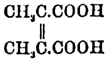
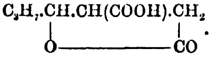
3. Pinene combines with NOCl to form a saturated compound which is not an oxim but a nitroso- compound, and yields up the NO.Cl by the action of aniline, with liberation of an optically inactive pinene.

4. By addition of two atoms of bromine to pinene, and subsequently heating the product

alone, or, better, with aniline (Oppenheim, *B.* 5, 629), cymene is formed.

5. In contact with slightly diluted mineral acids, or when heated above its boiling-point, pinene is gradually converted into an optically inactive mixture of dipentene with terpinene, terpinolene, and polymerised terpene ('colophene').

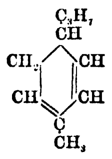
6. When heated to a temperature short of visible redness, pinene yields a considerable quantity of isoprene C_5H_8, together with a notable amount of *metâ*-xylene.

7. Pinene submitted to oxidation yields about 1 p.c. of its weight of *p*-toluic or terephthalic acid. This is perhaps due to the presence of a little cymene. It must, however, be remembered that the oxidising agent usually employed is either nitric acid or acidified chromic liquor, and hence that the pinene is first changed into dipentene or one of the other hydrocarbons referred to above (5). When nitric acid is used oxalic acid is the most abundant product, accompanied by terebic acid  $\begin{array}{l}(CH_3)_2C.CH(COOH).CH_2\\ \quad | \qquad\qquad\qquad\qquad |\\ \quad O\text{———————}CO\end{array}$ and dimethylfumaric acid  $\begin{array}{l}CH_3C.COOH\\ \quad\ \| \\ CH_3C.COOH\end{array}$ (Otto a. Beckurts, *B.* 18, 826). By treatment with chromate and sulphuric acid pinene yields much acetic acid, together with some terebic acid and terpenylic acid  $\begin{array}{l}C_3H_7.CH.CH(COOH).CH_2\\ \quad | \qquad\qquad\qquad\qquad |\\ \quad O\text{———————}CO\end{array}$

8. Natural pinene rotates the plane of polarisation to the right or to the left. It therefore must be supposed to contain an asymmetric atom of carbon.

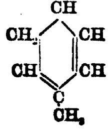
In order to epitomise these facts many formulæ have been proposed. The most important fall under two classes—namely, those in which pinene is represented as a dihydrocymene, and those in which a cross- or para-linkage is assumed.

Of the former class, the first example is the formula given many years ago by Oppenheim (*B.* 5, 98)—

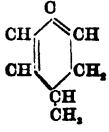


This kind of formula is now attributed with greater probability to limonene, and it must be remarked that of the possible formulæ of this type there are only four which contain an asymmetric carbon atom and *iso*-propyl.

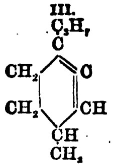
I.



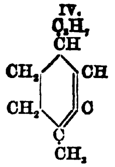
II.



III.



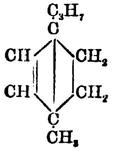
IV.



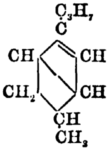
It has been shown that cymene, with which pinene is closely connected, contains *iso*- and not normal propyl (Widman, *B.* 24, 439). Hence pinene and its isomerides are believed also to be isopropyl compounds.

Formulæ containing cross- or para- linkages have been proposed as follows:—

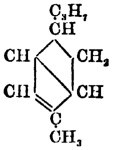
Kannonikoff (*J. pr.* 32, 517) V.



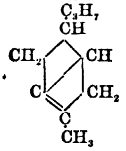
Wallach (*A.* 239, 49) Collie (*B.* 25, 1108) VI.



Wallach (*B.* 24, 1539) VII.



Wagner (*B.* 24, 2187) VIII.



II. **Limonene.**—1. Dry limonene combines with one molecule of hydrogen chloride, but unlike the hydrochloride derived from pinene the resulting compound is optically active and is not saturated, as it combines with halogens, with nitrosyl chloride, and, in the presence of moisture, with a second molecule of hydrogen chloride (Wallach, *A.* 270, 188). Limonene in the presence of water or alcohol readily yields dipentene dihydrochloride [50°], identical with the product formed from pinene. The dihydrochloride is optically inactive.

2. Limonene unites with four atoms of bromine, forming a crystalline tetrabromide.

3. Limonene unites with one molecule of nitrosyl chloride. The product, of which two (stereo?) isomerides occur, gives the reactions of an oxim.

4. Limonene readily yields abundance of cymene identical with that which is obtained from pinene (Oppenheim, *B.* 5, 628).

5. Limonene is polymerised by heat much less readily than pinene, and is not convertible into camphene.

6. Limonene vapour at a low red heat yields isoprene in the same way as pinene.

7. Limonene oxidised by nitric acid or by chromate yields oxalic, acetic, terebic or terpenylic acids according to circumstances, usually without any trace of toluic or terephthalic acid.

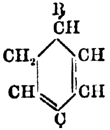
8. Limonene is dextro- or lævo-rotatory. A

mixture of equal volumes of the active hydrocarbons constitutes dipentene, which, on account of its peculiarities, quite different from those of its components, was long regarded as a distinct hydrocarbon.

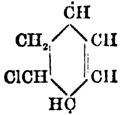
The formula which agrees best with the characters of limonene is either I. or II. given above (see *Pinene*).

In both of these there is an asymmetric carbon atom, and as the mono-hydrochloride is optically active while the dihydrochloride is inactive, these compounds will probably be represented by the following formulæ:—

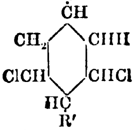
Limonene



Monohydrochloride

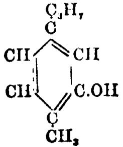


Dihydrochloride

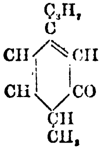


Limonene nitrosochloride deprived of the elements of hydrogen chloride yields a compound which has been identified with carvoxim. If the following formulæ be assumed for carvacrol and carvol, the interrelation of these compounds is obvious.

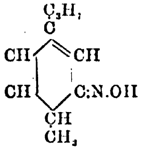
Carvacrol



Carvol

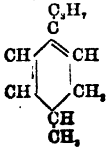


Carvoxim

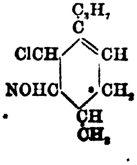


The corresponding formula for limonene should be No. II., but if that correctly represents the constitution of the hydrocarbon, the production of the nitrosochloride, or of the oxim from it, must be attended by isomeric change involving a re-distribution of the hydrogen and of the double linkages. Thus:—

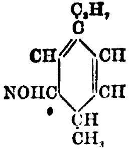
Limonene



Nitrosochloride

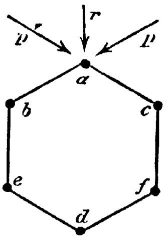


Oxim

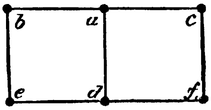


The oxim is optically active.

The very ready conversion of pinene into dipentene (=limonene) is a point of considerable importance, and it appears probable that the products formed by the action of heat and acid oxidising agents are in reality derived, not directly from pinene, but from the isomeric hydrocarbon into which it is first converted. The splitting up of pinene by heat into isoprene has been regarded (Wallach, *A.* 239, 48; Collie, *B.* 25, 1111) as supporting the formulæ already given VI. and VII., in which a para- or cross linkage is adopted. But remembering that isoprene is converted by polymerisation, not back again into pinene, but into dipentene, this evidence is of little importance. On the other hand, the difficulties involved in the assumption of a cross link in a cycloid of six carbon atoms are very considerable. In any closed ring of carbon atoms, the stability of the ring is easily accounted for upon simple mechanical principles. For if we consider six carbon atoms situated at the angles of a regular hexagon, and each attracted to its two neighbours on either side, whatever be the forces of attraction between them the resultant of those forces will have the effect of urging each carbon atom toward the centre of the figure. Thus, if the carbon atom *a* is attracted towards the carbon atom *b* with a force represented by *p*, and towards *c* with a force represented by *p'*, in the figure, the resultant of these two pressures will be *r*, which acts towards the centre; and so with each of the five other atoms.

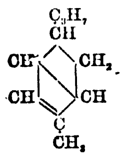


This conception is, of course, independent of any hypothesis concerning the fourth unit of valency, and the formula has no reference to the well-known 'centric' formula. The modern hypothesis according to which the carbon atom is supposed to be situated at the centre of a regular tetrahedron while the radicles with which it is united are placed at the angles of the same supplies no distinction between the force and the direction of the unit of affinity. The difference of specific volume observed between carbon compounds of the aromatic and fatty series seems to indicate that carbon atoms in the former are more closely united together, but it appears that no compounds are known in which the specific volume of carbon differs very greatly from its normal value. Hence it appears probable that the carbon atom, in uniting with other atoms, preserves a nearly constant distance from them, and in the figure above to suppose that *a* is combined with *d* as firmly as with *b* or *c* requires the assumption that a carbon atom is capable of acting through a distance twice as great in one case as in another. If this is possible, and we imagine the force of attraction between *a* and *d* to be as great as between *a* and *b* or *c*, then, unless *c* acts upon *e* and *b* acts upon *f* at the same time with the same force the figure will be changed from the hexagon to a double square.

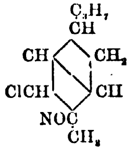


A compound of this kind would be incapable of many of the changes which are characteristic of pinene, and a second cross linkage between *c* and *e*, or between *b* and *f*, would be impossible. Hence the following formulæ, which are attributed by Wallach to nitrosopinene and pinylamine cannot be accepted even if a single diagonal is allowed in the formula of pinene.

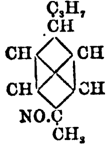
Pinene



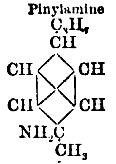
Nitrosopinene hydrochloride



Nitrosopinene

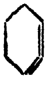


Pinylamine

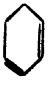


Formulæ III. and IV. now remain to be considered. So far as the writer is aware, formulæ of this type have not been proposed for any of the terpenes. Nevertheless there is much to be said in favour of an expression of this kind for a compound so unstable as pinene, which appears to be incapable of withstanding the action of heat or of contact with any reagent without isomeric change. For example, the conversion of pinene into dipentene, terpinene, and terpinolene may be explained with the minimum amount of hypothesis by the following formulæ, in which the tendency towards the conversion of an unsymmetrical into a symmetrical molecule is clearly shown. The question as to the relative positions of the methyl and propyl groups is left open.

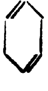
Pinene



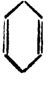
Dipentene



Terpinene or Terpinolene

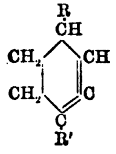


Terpinolene or Terpinene

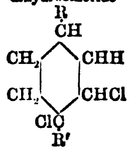


The conversion of pinene into dipentene through the dihydrochloride is readily shown.

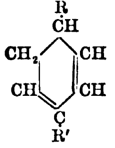
Pinene



Dipentene dihydrochloride

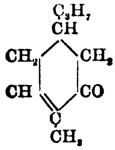


Dipentene

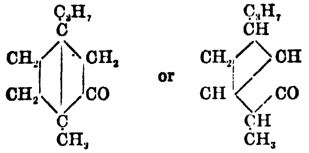


Such a formula for pinene also explains the extreme instability of its tetrabromide.

III. Camphene. Camphene behaves towards all reagents—such as bromine and nitrosyl chloride—as a saturated compound, but with hydrogen chloride it unites, forming a compound which in external appearance resembles pinene monochloride, but differs from that compound by its instability.' When camphene is oxidised by chromic acid it yields camphor, but when treated with permanganate a glycol is formed. This compound crystallises in odourless small monoclinic prisms, which sublime at temperatures above 100° (192° ca.). Its most characteristic property is seen in its reaction with dilute acids, whereby water is separated and a compound isomeric with camphor formed. This reaction appears to indicate the existence of one ethylenic bond in camphene (G. Wagner, *B.* 23, 2307). Brühl (*B.* 25, 160) also finds, as the result of his latest determinations of the molecular refraction and dispersion of camphene, that this hydrocarbon contains one ethylenic linkage. Wallach (*B.* 24, 1555) upon other grounds appears to hold the same view. Camphene is, however, so closely connected with camphor that the constitution of the latter compound when settled may serve as a guide in determining the constitution of the former. The formula for camphor given by Kekulé (*B.* 6, 931) was based upon the supposed intimacy of its relation to cymene and carvacrol.



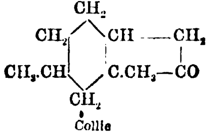
There can be no serious doubt of its character as a ketone, inasmuch as it yields an oxim, though it gives no compound with $NaHSO_3$; but the action of dehydrating agents upon camphor is very complicated, and there can be no doubt that the production of cymene is attended by isomeric change. Armstrong a. Kipping (*C. J.*, Jan. 1893) have shown that among the products of the action of strong sulphuric acid upon camphor there is a considerable quantity of acetyl-orthoxylene (C_6H_2Me.Me.Ac, Me:Me:Ac = 1:2:4). From observation of its molecular refraction Brühl (*B.* 21, 467) suggests a formula containing a para- linkage, either



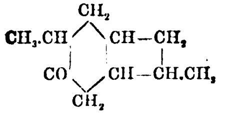
The former of these two formulæ has also been used by Wallach (*B.* 24, 1555). These expressions are equivalent to representing camphor as a derivative of tetramethylene.

A formula of a different character has been suggested by Armstrong a. Miller (*B.* 16, 2260) (*v.* vol. i. p. 670), and another of somewhat similar type by Collie (*B.* 25, 1114):

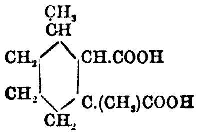
Armstrong



Collie



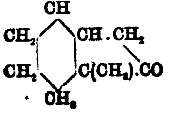
Camphor by oxidation with nitric acid yields camphoric acid in large quantity, and as the characteristic and chief product. Camphoric acid is therefore probably derived from camphor by an operation of a simple kind without constitutional disturbance. The following formula proposed by Collie (*B.* 25, 1116) has been shown to possess a very high degree of probability (Walker, *C. J.*, April 1893):



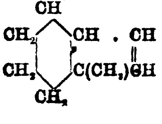
This formula sufficiently accounts for the chief facts concerning camphoric acid, viz. that it is a saturated dibasic acid, which readily yields the anhydride by heating; that it is optically active, and when treated with hydrogen iodide yields tetrahydro- and hexahydro-*m*-xylene.

From this formula are deducible the following formulæ for camphor and camphene:

Camphor



Camphene



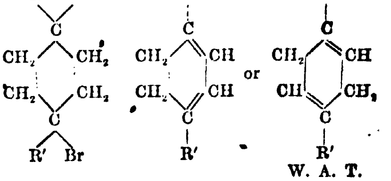
This formula for camphene explains pretty well all its relations, except its derivation from pinene, if either of the formulæ containing a para- linkage be adopted. The chief objections to such formulæ are stated above.

J. Bredt (*B.* 26, 3047) has recently proposed formulæ for camphene, camphor, and camphoric acid, which are derived from a pentamethylene ring.

Synthesis of Terpenes.

Von Baeyer in a series of papers has shown that various dihydro- derivatives of benzene and its homologues may be synthetically produced. Starting with succino-succinic ester, this compound, by treatment with dilute sulphuric acid, yields diketo-hexamethylene, and this, by reduction with sodium-amalgam, gives the corresponding glycol. This glycol possesses the characters of a sugar, and has been named chinite or quinite (*B.* 25, 1037). It occurs in two isomeric forms, which by treatment with hydrogen bromide yield two dibromohexamethylenes. Both of these by heating with quinoline yield dihydrobenzene (*B.* 25, 1840), a liquid which has nearly the same boiling-point as benzene, but combines with HBr and with Br_4. It also reduces permanganate. By a corresponding series of processes dihydro-*p*-xylene was obtained from dimethyl-succino-succinic ester (*B.* 25, 2122). Dihydro-*p*-xylene (134° circa) smells of turpentine, unites with hydrogen bromide, but forms no crystallisable nitrosite.

In order to produce a dihydrocymene it is necessary to start from the methyl-propyl compound of succino-succinic ester. This compound was obtained by heating the sodium compound of the monopropyl ether with methyl iodide (*B.* 26, 233). Methyl-isopropyl-dihydrobenzene boils at about 174°. It smells like turpentine and resinifies in the air. It decolourises permanganate and unites with bromine, forming an uncrystallisable bromide. Although closely resembling a terpene, however, it is obvious that this hydrocarbon is not identical with any natural terpene known, containing, as it does, no asymmetric carbon. It may be identical with terpinene. The relations of the paradibromohexamethylene, or of its alkyl derivatives, to the corresponding hydrocarbon is shown in the following formulæ (*B.* 25, 1840, 2122):



W. A. T.

TERPENYLIC ACID $C_8H_{12}O_4$. [72°] (Fittig); [58°] (Wallach). Formed, together with terebic acid, by oxidising oil of turpentine and other terpenes with chromic acid mixture (Hempel, *B.* 8, 357; *A.* 180, 77; Fittig a. Krafft, *A.* 208, 71). Formed also by oxidising pinol hydrate [131°] with $KMnO_4$ (Wallach, *A.* 259, 318). Monoclinic prisms (containing aq).

Reactions.—1. Yields acetic acid and CO_2 on further oxidation by *chromic acid*.—2. On *dry distillation* it yields teracrylic acid (218°), a very little oxy-heptoic lactone (212°), and other bodies (Amthor, *J. pr.* [2] 42, 388).—3. Reduced by HI and P to β-isopropyl-glutaric acid (Schryver, *C. J.* 63, 1344).

Salts.—BaA'_2. Amorphous powder, v. e. sol. water. Converted by boiling with baryta into barium diaterpenylate $Ba(C_8H_{13}O_5)_2$ aq, which separates in needles on heating the cold saturated solution and is v. sl. sol. water. On adding an acid the liberated diaterpenylic acid at once changes to its lactone, terpenylic acid.—CuA'_2 *x*aq.—AgA'. Crystalline mass. Silver diaterpenylate $AgC_8H_{13}O_5$ is ppd. by adding $AgNO_3$ to a solution of barium diaterpenylate.

Ethyl ether EtA'. [38°]. (305° i.V.). Monoclinic crystals; $a:b:c = 1{\cdot}051:1:{\cdot}381$; $\beta = 50°\ 58'$. V. sol. alcohol and ether, sl. sol. cold water. Sodium converts it into (α)- and (β)-diterpodilactone $C_{15}H_{22}O_5$.

(α)-Diterpodilactone $C_{15}H_{22}O_5$. [154°]. Formed as above (Fittig, *A.* 256, 113). Long needles (from water), m. sol. alcohol. Yields $CaC_{15}H_{24}O_7$ 6aq, $Ag_2C_{15}H_{24}O_7$, and $BaC_{15}H_{24}O_7$ 6aq crystallising in monoclinic prisms; $a:b:c = {\cdot}935:1:{\cdot}595$; $\beta = 65°\ 54'$, which, when decomposed by HCl and immediately extracted with ether yields (α)-diterpolactonic acid $C_{15}H_{24}O_8$ [160°]. This acid decomposes above 160° into water and its lactone.

(β)-Diterpodilactone $C_{15}H_{22}O_5$. [135°]. A product of the action of Na on terpenylic ether (Fittig, *A.* 256, 122). Needles, m. sol. alcohol. Converted by baryta into (β)-diterpolactonic acid [187°] and (β)-diterpoxylic acid $C_{15}H_{26}O_7$. (β)-diterpolactonic acid forms trimetric crystals; $a:b:c = {\cdot}732:1:{\cdot}259$ and is re-converted by heat into the lactone. (β)-Diterpoxylic acid forms the salts BaA″ 3½aq, CaA″, and Ag_2A''.

(α)-Diterpylic acid $C_{16}H_{22}O_7$. (α)-*Diterpodilactone carboxylic acid.* [216°]. An intermediate product of the action of Na on terpenylic ether. Needles, m. sol. alcohol. Converted by boiling HClAq or by heating above 216° into (α)-diterpodilactone.

TERPILENE *v.* TERPENES.

TERPILENOL $C_{10}H_{18}O$. [c. 32°]. (c. 130° at 50 mm.). S.G. c. ·95. H.C. (inactive) 113,318; (active) 102,923 (Louguinine, *C. R.* 107, 1165). Got by saponification of the terpilene acetates $C_{10}H_{16}HOAc$ or terpilene formates $C_{10}H_{16}CH_2O_2$ by alcoholic potash (Lafont, *A. Ch.* [6] 15, 205). Crystals, insol. water, v. sol. oil of turpentine, alcohol, and ether. Boils with decomposition at 220°. Occurs in several forms varying in their action on polarised light.

Reactions.—1. HCl forms $C_{10}H_{16}2HCl$ [48°], which is inactive even if the terpilenol were active.—2. Alcohol and HNO_3 give $C_{10}H_{22}O_3$ [104°].—3. *Phthalic anhydride* forms terpilene $C_{10}H_{16}$.—4. Ac_2O at 100° forms the acetyl derivative or terpilene acetate.

Acetyl derivative $C_{10}H_{17}OAc$ or $C_{10}H_{16}HOAc$. (220°). S.G. ^{2} ·971. V.D. 6·6. Obtained by heating terpilene with HOAc at 150°. Liquid (Bouchardat a. Lafont, *C. R.* 102, 1555).

Formyl derivative $C_{10}H_{17}O.CHO$. $[\alpha]_D = -69°\ 25'$. S.G. ^{2} ·999. Formed from oil of turpentine and cold formic acid (Lafont, *C. R.* 106, 140). By heating with water at 100° 65 p.c. of the ether is saponified.

TERPIN *v.* TERPENES.

TERPINEOL *v.* TERPENES.

TERPYLONIC ACID $C_9H_{14}O_6$. [135°]. A product of the oxidation of turpentine by chromic acid mixture (Schryver, *C. J.* 63, 1328). Needles, v. e. sol. water, m. sol. ether. Differs from camphoronic acid in electrical conductivity.

TETANINE *v.* PTOMAÏNES.

TETRADECANAPHTHENE $C_{14}H_{28}$. (241° cor.). S.G. ^{2} ·839. Occurs in petroleum from Baku (Markownikoff a. Ogloblin, *J. R.* 15, 339).

***n*-TETRADECANE** $C_{14}H_{30}$. *Diheptyl.* [4·5°]. (253°). S.G. $\frac{5}{4}$ ·775; $\frac{15}{4}$ ·768. Formed by heating myristic acid with HI and P (Krafft, *B.* 15, 1700). Got also by the action of Na on *n*-heptyl iodide (Krafft, *B.* 19, 2223; Sorabji, *C. J.* 47, 37).

Reference.—DI-BROMO-TETRADECANE.

TETRADECENOIC ACID $C_{14}H_{26}O_2$ *i.e.* $C_6H_{13}.CH{:}C(C_5H_{11}).CO_2H$. *Amylhexylacrylic acid.* Formed by the action of alcoholic potash on œnanthol (Perkin, *B.* 15, 2803; 16, 211). Liquid, boiling *in vacuo* at 275° to 280°.

TETRADECENOIC ALDEHYDE $C_{14}H_{26}O$ *i.e.* $CH_3[CH_2]_5CH{:}C(CHO)[CH_2]_4CH_3$. (278°). S.G. $\frac{15}{15}$ ·849. Formed by the action of alcoholic potash or of $ZnCl_2$ on œnanthol (Perkin, *C. J.* 43, 47). Oil, not solid at −20°. Forms crystalline $C_{14}H_{16}ONaHSO_3$. Yields hexoic and heptoic acids on oxidation.

TETRADECENYL ALCOHOL $C_{14}H_{28}O$. (282°). S.G. $\frac{15}{15}$ ·852. Formed by reducing the preceding aldehyde with sodium-amalgam (Perkin, *B.* 15, 2808). It is also a product of the action of sodium-amalgam on a solution of œnanthol in HOAc (Perkin, *C. J.* 43, 68). Oil. May be reduced to $C_{14}H_{30}O$.

Acetyl derivative $C_{14}H_{27}OAc$. (285°–290°). S.G. ^{15} ·868. Combines with Br (2 atoms).

TETRADECINENE $C_{14}H_{26}$ *i.e.* $CMe{:}C.C_{11}H_{23}$. [6·5°]. (134° at 15 mm.). S.G. $\frac{6{\cdot}5}{4}$ ·8064; $\frac{15{\cdot}2}{4}$ ·8000. Formed from tetradecylene bromide and alcoholic potash at 150° (Krafft, *B.* 17, 1372; 25, 2249).

TETRADECOIC ACID $C_{14}H_{28}O_2$ *i.e.* $C_5H_{11}.CH(C_7H_{15}).CO_2H$. (300°–310°). Got by the action of moist Ag_2O on the corresponding aldehyde (Perkin, *C. J.* 43, 74). Liquid, not solid at −10°.

Tetradecoic acid *v.* MYRISTIC ACID.

Reference.—OXYTETRADECOIC ACID.

TETRADECOIC ALDEHYDE $C_{14}H_{28}O$ *i.e.* $C_5H_{11}.CH(C_7H_{15}).CHO$. [30°]. (267°). S.G. $\frac{30}{30}$ ·827. A product of the action of Na on an ethereal solution of œnanthol (Perkin, *C. J.* 43, 71). Tables, v. sol. alcohol. Reduces ammoniacal $AgNO_3$. Yields heptoic, hexoic, and acetic acids on oxidation.

Isomeride *v.* MYRISTIC ALDEHYDE.

***n*-TETRADECYL ALCOHOL** $C_{14}H_{30}O$. [38°]. (167° at 15 mm.). S.G. $\frac{50}{4}$ ·8153. Formed by reducing myristic aldehyde (Krafft, *B.* 16, 1720).

Acetyl derivative $C_{14}H_{29}OAc$. [13°]. (176° at 15 mm.).

Tetradecyl alcohol $C_5H_{11}.CH(C_7H_{15}).CH_2OH$. (270°–275°). S.G. $\frac{15}{15}$ ·8368. Formed by reducing the corresponding aldehyde or the aldehyde $C_{14}H_{28}O$ (Perkin, *B.* 15, 2811; *C. J.* 43, 76). Liquid, solidifying at −10°.

Acetyl derivative $C_{14}H_{29}OAc$. (c. 278°). S.G. $\frac{15}{15}$ ·856. Oil, not solid at −10°.

n-**TETRADECYLENE** $C_{14}H_{28}$ *i.e.* $CH_2{:}CH.C_{12}H_{25}$. [−12°]. (127° at 15 mm.) S.G. $\frac{0}{4}$ ·7852; $\frac{15}{4}$ ·7745. Formed by distilling tetradecyl palmitate at 500 mm. (Krafft, *B.* 16, 3021). Liquid.

Bromide *v.* DI-BROMO-TETRADECANE.

TETRADECYLENE GLYCOL *v. Di-iso*-BUTYL PINACONE.

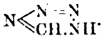
TETRADECYL-MALONIC ACID $C_{17}H_{32}O_4$ *i.e.* $C_{14}H_{29}CH(CO_2H)_2$. [118°]. Formed by boiling its nitrile with alcoholic potash (Hell a. Jordanoff, *B.* 24, 988). White powder (from HOAc), insol. water, v. sl. sol. ether, sl. sol. cold alcohol. At 150°-170° it is split up into CO_2 and palmitic acid.—Ag_2A'': white pp.

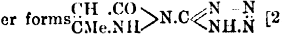
Amide $C_{14}H_{29}.CH(CO_2H)(CONH_2)$. Pearly scales. At c. 140° it yields palmitic amide.

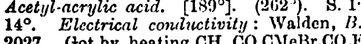
Nitrile $C_{14}H_{29}.CH(CO_2H).CN$. [76°]. Formed by heating *p*-bromo-palmitic ether with alcoholic KCy. Silky plates (from HOAc).

n-**TETRA-ICOSANE** $C_{24}H_{50}$. [51°]. (243° at 15 mm.). S.G. $\frac{76}{4}$ ·763; $\frac{95}{4}$ ·748. Formed by the action of HI and P on $C_{17}H_{35}.CCl_2.C_6H_{13}$ made from the ketone obtained by distilling barium stearate with barium heptoate (Krafft, *B.* 15, 1718).

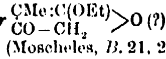
TETRA-ICOSOIC ACID $C_{23}H_{47}.CO_2H$. [72·5°]. Occurs in the soap got by heating carnaüba wax with aqueous NaOH (Stärcke, *A.* 223, 307). Crystalline powder, v. sol. hot alcohol.—PbA'_2. [111°]. Sol. toluene and hot HOAc.

TETRAZOLE  $N{<}\begin{smallmatrix}N=N\\CH.NH\end{smallmatrix}$ [155°]. Formed by treating amido-phenyl-tetrazole carboxylic acid with alkaline $KMnO_4$ followed by HNO_3 (Bladin, *B.* 25, 1412). Plates (from toluene). Reddens blue litmus.

TETRAZYL-HYDRAZINE $NH_2.NH.C{<}\begin{smallmatrix}N-N\\NH.N\end{smallmatrix}$ [199°]. Formed from amido-tetrazotic acid by diazotisation and reduction by $SnCl_2$ (Thiele, *A.* 273, 155). Yellowish crystalline aggregates, v. sol. hot water.—$B''2HCl$. [176°]. Aceto-acetic ether forms  $\begin{smallmatrix}CH\ .CO\\CMe.NH\end{smallmatrix}{>}N.C{<}\begin{smallmatrix}N-N\\NH.N\end{smallmatrix}$ [215°] crystallising in needles.

TETRIC ACID $C_{10}H_{12}O_6$ *i.e.*  $CH_2{:}C(OH).CMe{<}\begin{smallmatrix}O\ .CO\\CO.O\end{smallmatrix}{>}CMe.C(OH){:}CH_2$ (Nef, *A.* 266, 92) or $CH_3.CO.C(CO_2H){:}CH_2$. *Acetyl-acrylic acid.* [189°]. (262°). S. 1·5 at 14°. *Electrical conductivity*: Walden, *B.* 24, 2027. Got by heating $CH_3.CO.CMeBr.CO_2Et$ at 100°, but not by heating the isomeric acid $CH_2Br.CO.CHMe.CO_2Et$ (Nef; *cf.* Pawloff, *B.* 16, 486). Formed by successive action of bromine and alcoholic potash on methyl-acetoacetic ether (Demarçay, *C. R.* 87, 351; 88, 126). Triclinic prisms (from water), v. sol. hot water, alcohol, and ether. Gives a violet-red colour with $FeCl_3$. PCl_5 gives rise to several compounds boiling between 169° and 185° which take up chlorine forming $C_5H_5Cl_5O$ (Pawloff, *Bl.* [2] 45, 181; *C. R.* 97, 99). Demarçay obtained oily $C_4H_4Cl_2O$ (?) which united with Cl and Br forming $C_4H_4Cl_4O$ [48°] and $C_4H_4Cl_2Br_2O$ [67°]. Resinified by dilute HClAq at 150°. Potash-fusion gives formic and propionic acids. Distillation with lime forms methyl ethyl ketone. Sodium-amalgam has no action.

Salts.—$(NH_4)_2A''$. Crystals, v. sol. water.—Na_2A'' 6aq.—K_2A''.—BaA'' 3aq. Needles, v.e. sol. water.—BaA'' 2aq.—$Ba_2(OH)_2A''$. Sl. sol. water.—CaA'' 2aq.—MgA'' 10aq.—ZnA'' aq.—CuA''.—Ag_2A''. Needles, sl. sol. water.

Ethyl ether  $\begin{smallmatrix}CMe{:}C(OEt)\\CO-CH_2\end{smallmatrix}{>}O$ (?). [30°]. (180° at 70 mm.) (Moscheles, *B.* 21, 2607).

Amide $C_5H_7NO_2$. [212°]. Got by heating the acid with alcoholic NH_3.

TETROLE CYANURAMIDE *v. Nitrile of* PYRROLE CARBOXYLIC ACID.

TETROLIC ACID $C_4H_4O_2$ *i.e.* $CH_3.C{:}C.CO_2H$. *Butyrolic acid.* Mol. w. 84. [77°]. (203°). Formed by boiling β-chloro-crotonic acid or β-chloro-iso-crotonic acid with dilute potash (Geuther, *Z.* 1871, 215; Friedrich, *A.* 219, 343; Kahlbaum, *B.* 12, 2338). Formed also by the action of Na and CO_2 on allylene chloride (Pinner, *B.* 14, 1081).

Preparation.—From acetoacetic ether and PCl_5, the product being freed from $POCl_3$ by heating to 115°, mixed with water, and freed from chloro-crotonic acid by distillation with steam. The residue is treated with alcoholic potash (Fittig a. Clutterbuck, *A.* 268, 96; *cf.* Friedrich, *A.* 219, 322).

Properties.—Plates (from ligroïn). May be sublimed. V. e. sol. water, alcohol, and ether. Not reduced by sodium-amalgam to crotonic acid (F. a. C.; *cf.* Aronstein, *B.* 22, 1181). Slightly volatile with steam.

Reactions.—1. Br forms di-bromo-crotonic acid [120°], which is reduced by sodium-amalgam to tetrolic acid. *Bromine* also yields $C_4H_4Br_2O_2$. [97°] (Pinner).—2. HBr forms bromo-crotonic acid [91°].—3. Heated with conc. KOHAq it forms acetone.—4. Fuming HClAq at 15° in a few weeks converts it into β-chloro-crotonic acid [94·5°].—5. Boiling with Na and MeOH yields butyric acid (A.).—6. *Chlorine* forms $C_4H_4Cl_4O_2$. 7. On heating with *iodine* in $CHCl_3$ in sealed tubes it yields di-iodo-crotonic acid (*B.* 26, 843).—8. Split up at 211° into CO_2 and allylene.—9. $KMnO_4$ forms acetic acid.

Salts.—NaA'. Crystalline.—KA' (dried at 100°). Prisms (from alcohol).—NH_4A'.—LiA' aq.—MgA'_2 3aq.—BaA'_2 3aq.—CaA'_2 3aq. Small needles.—ZnA'_2 2aq (Lagermark, *J. R.* 12, 290).—ZnA'_2 2aq (Fittig). Groups of prisms.—CdA'_2 4aq.—PbA'_2 aq. S. 1·5 in 92 p.c. alcohol at 20°.

Chloride C_4H_3OCl. Fuming liquid, carbonised by heat. Quickly decomposed by water (Lagermark, *Bl.* [2] 35, 171).

DI-TETROLUREA *v.* CARBONYL-PYRROL.

TETROLE-URETHANE *v. Ethyl ethyl* of PYRROLE CARBOXYLIC ACID.

TEUCRIN $C_{21}H_{24}O_{11}$ or $C_{21}H_{26}O_{11}$. [230°]. A glucoside occurring in *Teucrium fructicans*, a plant used in Sicily as febrifuge. Extracted by alcohol (Oglialoro, *G.* 9, 440; 13, 498). Slender yellow prisms. Boiling dilute nitric acid forms anisic, tartaric, and oxalic acids. Boiling dilute H_2SO_4 yields glucose and a yellow insoluble residue.

TEWFIKOSE. $[a]_D = 53·1°$. A sugar occurring in the milk of the Egyptian buffalo (*Bos* *bubalus*). Yields glucose on hydrolysis (Pappel a. Richmond, *C. J.* 57, 759), *v.* Sugars.

THALICTRINE. *Macrocarpine.* Occurs in *Thalictrum macrocarpum* (Hanriot a. Doassans, *Bl.* [2] 84, 83). Yellow needles, insol. water, sol. alcohol and ether. Resembles aconitine, but is less poisonous.

THALLIN *v.* Oxy-quinoline.

THALLIUM. Tl. At. w. 203·64. Mol. w. 407·28 as gas at c. 1700° (*v. infra*). Melts at 293·9° (Crookes, *C. J.* 17, 123; *cf.* Lamy, *A. Ch.* [3] 67, 385). Boils at full red heat. S.G. pressed 11·88, cast 11·81, in wire 11·91 (Crookes, *l.c.*; *cf.* Lamy, *l.c.*; Werther, *J. pr.* 91, 385; de la Rive, *C. R.* 56, 588). V.D. 232·7 at 1636°, 203·7 at 1728° (Biltz a. V. Meyer, *B.* 22, 725). S.H. ·0325 (Lamy, *l.c.*); ·0335 (17°–100°) (Regnault, *A. Ch.* [3] 67, 437). C.E. (linear) ·00003021 at 40°, ·00003135 at 50° (Fizeau, *C. R.* 68, 1125). E.C. 5·225 at 0° (Hg at 0° = 1) (Bénoit, *P. M.* [4] 45, 314; *cf.* Matthiessen, *P.* 118, 431). H.C. $[Tl^2,O]=42,240$ (*Th.* 3, 354). Latent heat of fusion c. 1040 for 203·6 g. (Heycock a. Neville, *C. J.* 65, 35). The characteristic green line of the emission spectrum has the wave-length 5347 according to Huggins (*T.* 1864. 139), 5349·6 according to Mascart (*Ann. de l'écol. norm.*, 4, 7 [1867]), and 5349·5 according to Thalén (*Détermin. des long. d'onde des raies métalliques* [Upsala, 1868]). Concerning the emission spectrum of Tl *v.* also Crookes, *Pr.* 12, 536; Nicklès, *C. R.* 58, 132; Kirchoff a. Bunsen, *A.* 155, 230, 366; Lockyer a. Roberts, *Pr.* 23, 344; Liveing a. Dewar, *Pr.* 27, 132; Hartley a. Adeney, *T.* 1884. 104; Becquerel, *C. R.* 99, 376; Wilde, *Pr.* 53, 369.

Historical.—In 1861 Crookes was preparing Se from the flue-dust of a sulphuric acid manufactory at Tinkelrode in the Harz mountains, when on distilling the impure Se he obtained a residue which showed a marked single green line in the spectrum; this line was not known to belong to the spectrum of any element, hence Crookes supposed that the impure Se contained a new element. Crookes isolated the element towards the end of 1861, and called it thallium. (from θαλλός = a green bud) (*v. C. N.* 3, 193, 303). Lamy (*A. Ch.* [3] 67, 385) noticed a new green line in the spectrum of a leaden chamber deposit about the same time as Crookes was investigating the cause of the line he had observed; in 1862 Lamy isolated a specimen of the metal which Crookes had obtained a few months before.

Occurrence. — Never uncombined. Compounds of Tl are widely distributed, but only in very small quantities. The sulphide occurs in minute quantities in many specimens of *copper pyrites* and *iron pyrites* (*v.* Crookes, *C. J.* 17, 112; Lamy, *l.c.*; Wöhler, *A.* 142, 263; Carstanjen, *J. pr.* 102, 65; Gunning, *Ar. N.* 3, 86); also in native sulphur from Lipari and Spain. Compounds of Tl are found in small quantities in many ores of As, Bi and Hg, and in preparations from these ores; also in commercial Se and Te, probably as selenide and telluride (*v.* Crookes, *l.c.*; Röppler, *Am. S.* [2] 35, 420; Herapath, *Ph.* 4, 302; Werther, *J. pr.* 89, 129). Some specimens of *lepidolite* contain small quantities of Tl compounds (*v.* Schrötter, *W. A. B.* 48 (ii.) 734; 50 (ii.) 268). A Swedish mineral called *crookesite* was found by Nordenskjold to contain from 16·3 to 18·55 p.c. Tl as selenide, along with selenides of Cu and Ag (*Bl.* [2] 7, 409). Small quantities of TlCl are found in some mineral springs and in the saline deposits from such springs (*v.* Böttger, *J. pr.* 89, 378; 90, 22; 96, 294). Traces of Tl alum have been found accompanying the double sulphates of Cs, Li, and Rb in *alumite* from the island of Volcano (Cossa, *Acad. dei Lincei* [3] 2). Small quantities of Tl compounds have been noticed in *carnallite*, *sylvine*, and *kainite* (Schramm, *A.* 219, 374). Many specimens of commercial sulphuric and hydrochloric acids contain traces of Tl compounds (*v.* Crookes, *l.c.*).

Formation.—(Crookes, *l.c.*; or *T.* 1872.)—1. By reducing Tl_2CO_3 by fusion with KCN.—2. By electrolysis of Tl_2CO_3 covered with water.—3. By electrolysis of Tl_2SO_4. — 4. By heating $Tl_2C_2O_4$ in a covered crucible.—5. By ppg. by zinc from solution of a thallous salt to which excess of NH_3Aq or NaOHAq has been added.

Preparation.—The most economical source is the flue-dust from sulphuric acid manufactories where pyrites or sulphur containing Tl compounds has been used. Many specimens of flue-dust contain no Tl compounds; in some specimens 8 p.c. Tl has been found, but only in a very few does the quantity amount to ·25 p.c. Tl (Crookes). After having been heated to dull redness, to remove any HCl, the dust is well stirred in wooden tubs with its own weight of boiling water and allowed to settle for 12 hours; the liquid is siphoned off, and the residue is again stirred with boiling water and let settle; the mixed liquids are ppd. by a considerable excess of conc. HClAq; the pp., which is crude TlCl, is well washed on a calico filter and squeezed dry. About 68 lbs. crude TlCl were thus obtained from 3 tons flue-dust (Crookes, *T.* 1872). The crude TlCl is heated with its own weight of pure conc. H_2SO_4 in a Pt dish till all HCl and most of the H_2SO_4 are removed; the $TlHSO_4$ is dissolved in c. 20 times its weight of water, the solution is nearly neutralised by $CaCO_3$, filtered, ppd. by conc. HClAq, and the TlCl so obtained is well washed, and is then boiled for a few minutes with $(NH_4)_2SAq$; the pp. of Tl_2S is filtered off, well washed with water containing H_2S, and dissolved in dilute H_2SO_4Aq; the solution is boiled to remove H_2S, ammonia is added in slight excess, and after boiling the solution is filtered and crystallised; $(NH_4)_2SO_4$, being much more soluble in water than Tl_2SO_4, remains in solution when Tl_2SO_4 crystallises out.

If small quantities of Tl are to be prepared from Tl_2SO_4, the salt is dissolved in c. 20 times its weight of water, the solution is acidulated with H_2SO_4, and electrolysed, Pt electrodes being used. If large quantities of Tl are to be prepared, Tl_2SO_4 is placed in a deep porcelain dish (holding about 4½ litres) and covered with water (c. 3 kilos Tl_2SO_4 are used at a time) and plates of pure zinc are arranged vertically around the sides of the vessel; heat is applied, and the whole of the Tl separates in a few hours as a spongy mass easily detached from the zinc by shaking. The spongy Tl is washed several times, pressed by the fingers, and then fused with KCy in a porcelain crucible to get it into a lamp (for details *v.* Crookes, *l.c.*; *v.* also Gunning, *J. pr.* 105, 343).

Crookes (*l.c.*) gives several methods for preparing pure Tl. If the starting-point is commercial Tl_2SO_4, he recommends to dissolve this salt in water, to saturate the cold solution with pure H_2S, filter, heat to boiling, and pour into boiling, dilute, pure HClAq; to filter while hot, and allow to cool; to wash the TlCl that crystallises out, by decantation, till the washings are free from H_2SO_4, and to purify by re-crystallising twice from water. The TlCl thus obtained is dried, mixed with pure Na_2CO_3, and projected, in small successive portions, into molten pure KCy in an unglazed porcelain crucible; reduction to metal is rapid. After cooling, the contents of the crucible are treated with water, the ingot of Tl is boiled for some time in water, dried, and fused over a spirit lamp (coal-gas should not be used on account of the S compounds in it) in an unglazed porcelain crucible, with free access of air and frequent stirring with a piece of unglazed porcelain, to facilitate oxidation, and the metal is poured into a porcelain mould.

Properties.—A white metal without any tinge of blue; when fused under coal-gas, liquid Tl is exactly like Hg; may be highly polished by rubbing under water; very soft, may be cut with the nail, or scratched by lead. Less tenacious than lead; does not become brittle between −18° and its m.p.; very malleable, Lamy (*A. Ch.* [3] 67, 385) says that plates $\frac{1}{15,000}$ mm. thick can be obtained; can be squeezed, but not drawn, into wire; very inelastic. Tl crystallises very easily in octahedral forms; it crackles like tin when bent; a wire of Tl seems amorphous when prepared, but under water it soon becomes crystalline. Tl quickly tarnishes in air; the film of oxide formed protects the mass of metal. The metal may be kept unchanged for years under water that has been deprived of air (*v.* Böttger, *D. P. J.* 197, 374). Tl melts easily (at 294°) without first becoming pasty; it expands considerably before melting is complete, and contracts much on cooling. Tl boils below white heat; it may be distilled in a current of H. Pieces of the metal may be welded together by pressure at the ordinary temperature. Tl is nearly as diamagnetic as bismuth. Tl gives an intense green colour to a non-luminous flame (*v. infra, Detection*). Heated in air, Tl readily burns to Tl_2O; it combines with S, Se, P, Cl, Br, I, &c., when heated with these elements; it dissolves in solutions of most acids (*v. Reactions*). The compounds of Tl are very poisonous, producing symptoms like those of lead poisoning.

The at. w. of Tl has been determined (1) by ppg. Cl as AgCl from TlCl by $AgNO_3Aq$ (Lamy, *A. Ch.* [3] 67, 385 [1862]; Hebberling, *A.* 134, 11 [1865]); (2) by ppg. I from TlI by $AgNO_3$ (Werther, *J. pr.* 92, 136 [1864]); (3) by converting Tl_2SO_4 into $BaSO_4$ (Lamy, *l.c.*; Hebberling, *l.c.*); (4) by converting Tl into $TlNO_3$ (Crookes, *T.* 1873. 277); (5) by determining S.H. of Tl (Lamy, *l.c.*; Regnault, *A. Ch.* [3] 67, 437 [1862]); (6) by determining V.D. of TlCl (Roscoe, *Pr.* 27, 426).

The mol. w. of Tl in the gaseous state is double the at. w.; in other words, the gaseous molecule is diatomic (Biltz a. Meyer, *B.* 22, 725). Ramsay (*C. J.* 55, 521) determined the depression produced in the vapour pressure of Hg by dissolving Tl in that solvent; assuming that equal volumes of dilute solutions contain equal numbers of molecules, and that the mol. w. of liquid Hg is 200, the results obtained by R. indicated the molecule of Tl dissolved in Hg to be monatomic.

Tl is distinctly a metallic element; no compounds have been isolated wherein Tl certainly forms part of the negative radicle, although there are indications of the existence of such compounds (*v.* THALLIUM DIOXIDE, p. 680); the compounds which $TlBr_3$, $TlCl_3$, and TlI_3 form with alkali halides *may* contain Tl in the negative radicles. Tl is the last element in the odd-series family of Group III.; this family comprises Al, Ga, In, and Tl. The element Tl also shows marked resemblances to the alkali metals; and in its physical properties it is more like lead than any other element. The position assigned to Tl by the periodic classification of the elements clearly indicates the relations between this element and other elements. The relations of Tl (III.–11) to Al (III.–3) should be similar to those of Hg (II.–11) to Mg (II.–3), and also similar to those between Pb (IV.–11) and Si (IV.–3). The resemblances between the compositions and properties of the oxides of Hg and Mg on the one hand, and of the oxides of Pb and Si on the other hand, are shown only in the highest oxides of these elements: there is Hg_2O but no Mg_2O, there is PbO but no SiO; HgO and MgO are basic, PbO_2 and SiO_2 are feebly acidic. Nevertheless Hg and Pb form lower oxides than HgO and PbO_2; these lower oxides, Hg_2O and PbO, are basic; Hg_2O feebly, and PbO strongly, basic. Hence it is likely that the resemblances between the oxides of Tl and Al will be shown in the highest oxides. This supposition is confirmed; Tl_2O_3 and Al_2O_3 are basic, forming salts M_2X_3, where X = the radicle of a dibasic acid; these oxides are more basic than PbO_2 and SiO_2, but less basic than HgO and MgO. As Hg and Pb form lower oxides than HgO and PbO_2, and these lower oxides are more basic than HgO and PbO_2 so Tl will likely form an oxide lower than Tl_2O_3 and this oxide will be more basic than Tl_2O_3; Tl forms the strongly basic oxide Tl_2O. Then consider the position of Tl in series 11. Consider the oxides of the members of this series: the lower oxides Hg_2O, PbO, and Bi_2O_3 are basic; the higher oxides HgO, PbO_2, and Bi_2O_5 pass from basic (HgO) to feebly acidic (PbO_2 and Bi_2O_5); therefore it is probable that the higher oxide of Tl will be less basic than HgO, but that it will not be acidic; Tl_2O_3 is a feebly basic oxide.

If the chlorides of series 11 are considered, the position of Tl in III.–11 is seen to be justified: HgO gives $HgCl_2$, which can be gasified unchanged, PbO_2 gives $PbCl_4$, which is very easily decomposed by heat, no chloride corresponding with Bi_2O_5 has been isolated; therefore Tl_2O_3 will probably give a chloride more stable towards heat than $PbCl_4$, but less stable than $HgCl_2$. $TlCl_3$ is decomposed by heating to c. 80° into TlCl and Cl. Hg_2O gives HgCl, PbO gives $PbCl_2$, and Bi_2O_3 gives $BiCl_3$, and these chlorides can all be gasified unchanged; therefore the chloride of Tl corresponding with Tl_2O will probably not be decomposed by heat; TlCl has been gasified unchanged. The relations between the elements Hg, Tl, Pb, Bi, and Mg, Al, Si may be summarised in the expressions Tl : Hg : Pb = Al : Mg : Si; and Tl : Hg = Pb : Tl = Bi : Pb. (For a further working out of the relations of Tl, *v.* Mendeléeff, *C. N.* 1880. 2; *v.* also ALKALIS, METALS OF THE, vol. i. p. 114; and EARTHS, METALS OF THE, vol. ii. p. 424.) The atom of Tl is monovalent in the gaseous molecule TlCl; the V.D. of no other compound of Tl has been determined.

Reactions and Combinations.—1. Exposed to *air* or *oxygen*, a film of Tl_2O is at once formed; when heated in air or O to somewhat below redness (c. 300°) Tl burns to Tl_2O_3, and at a higher temperature this gives Tl_2O and O (Lamy, *A. Ch.* [3] 67, 385). Moist *ozone* acts on Tl giving TlO_3H_3.—2. A compact piece of Tl does not decompose boiling *water*, decomposition begins at a red heat; but spongy Tl, as ppd. by zinc, dissolves in water forming TlOHAq.—3. Tl dissolves in solutions of most *acids*, forming thallous salts Tl_2X, where X = 2Cl, $2NO_3$, SO_4, &c.—4. Tl combines with *sulphur* and *selenion* (*v. sulphides* and *selenides*).—5. Forms alloys with many *metals* (*v. alloys*).—6. Forms compounds with *antimony* and *arsenic* (*v. antimonide* and *arsenide*).—7. A phosphide is formed by heating Tl in vapour of *phosphorus* (*v. phosphide*).—8. Combines with *chlorine*, *bromine*, and *iodine*, when heated with these elements (*v. chlorides*, *bromides*, and *iodides*).—9. Tl ppts. the *noble metals*, also *copper*, *lead*, and *mercury* from solutions of salts of these metals (Reid, *C. N.* 12, 242).

Detection and Estimation.—Tl is best detected by the intense green colour which the metal and its compounds give to the non-luminous flame of the Bunsen lamp; according to Lamy (*l.c.*) $\frac{1}{50,000}$ mgm. can be detected by the use of the spectroscope; if induction sparks are used it is said that $\frac{1}{80,000,000}$ mgm. can be detected (Cappel, *P.* 139, 628). Tl is generally estimated as TlI or Tl_2SO_4; it can also be determined volumetrically by $KMnO_4Aq$ (Willm, *Z.* 1863. 479).

Thallium, alloys of. Several alloys of Tl were prepared by Carstanjen in 1867 (*J. pr.* 102, 62) by heating the metals together. Many of the alloys are soft, and most of them readily tarnish in the air; the alloy with $\frac{1}{4}$ pt. Sb is fairly hard; and those with Bi and Pb, Bi and Cd, and Bi and Sn are hard and brittle. Alloys are described with Al, Sb, Cd, Cu, Pb, Mg (*v.* also Mellor, *C. N.* 19, 245), Hg (*v.* also Crookes, *l.c.*, and Regnauld, *C. R.* 64, 60), K, Na, and Zn; also with Bi and Cd, Bi and Pb, and Bi and Sn.

Thallium, antimonide of. A hard, grey, crystalline solid was obtained by fusing together Tl and Sb in the ratio Tl : Sb; with cold dilute H_2SO_4Aq the substance gave off SbH_3 (Carstanjen, *l.c.*).

Thallium, arsenide of. Carstanjen (*l.c.*) obtained a white, crystalline, soft substance by fusing Tl and As in the ratio Tl : As; with cold acids AsH_3 was formed.

Thallium, bromides of. The compounds TlBr and $TlBr_3$ have been isolated, and also two compounds the simplest formulæ of which are Tl_2Br_3 and $TlBr_2$. As none of the bromides has been gasified, the formulæ are not necessarily molecular; but from the analogy of TlCl, the formula TlBr probably represents the composition of the gaseous molecule of this compound.

THALLOUS BROMIDE TlBr. (*Thallium monobromide.*) Tl reacts very slowly with Br. Thallous bromide is obtained, as a white pp., by adding HBrAq or solution of a bromide to solution of a thallous salt; almost insoluble in water (Willm, *A. Ch.* [4] 5, 28). TlBr melts at 458° to a brownish-yellow liquid, which solidifies to a yellow solid (Carnelley, *C. J.* 33, 278). Thomsen gives H.F. [Tl,Br] = 41,290 (*Th.* 3, 354).

THALLIC BROMIDE $TlBr_3$. (*Thallium tribromide.*) Prepared by adding Br to TlBr suspended in water until solution is effected, and evaporating *in vacuo*. $TlBr_3$ forms a yellow crystalline solid; it is very deliquescent, becoming gradually brown and giving off Br. Very soluble in water, also in alcohol. Reduced to TlBr by SO_2Aq and other reducing agents (Willm, *l.c.*). Thomsen gives H.F. $[Tl,Br^3,Aq] = 56,450$ (*Th.* 3, 354). $TlBr_3$ combines with NH_3 to form $TlBr_3.3NH_3$; a white solid that gives off NH_3 and Br at 100°, and when more strongly heated leaves TlBr (W., *l.c.*). Also combines with NH_4Br and KBr, forming $TlBr_3.NH_4Br$ and $TlBr_3.KBr.2aq$ (W., *l.c.*; Nicklès, *C. R.* 58, 537). Rammelsberg (*P.* 146, 597) described $2TlBr_3.3KBr.3aq$.

THALLIUM DIBROMIDE $TlBr_2$ (or $TlBr.TlBr_3 = Tl_2Br_4$). Obtained in long, yellow, needles by adding TlBr to boiling $TlBr_3Aq$, in the ratio $TlBr{:}TlBr_3$, and cooling. Not decomposed at 100°; water forms $TlBr_3Aq$ and Tl_2Br_3 (*v. infra*) (W., *l.c.*).

THALLIUM SESQUIBROMIDE Tl_2Br_3, or $TlBr_3.3TlBr = Tl_4Br_6$. (*Thallo-thallic bromide.*) Orange-red hexagonal leaflets; obtained by adding HBrAq to a mixture of a thallous and a thallic salt in solution; also by adding TlBr to $TlBr_3Aq$, or by adding a little water to $TlBr_2$ ($3TlBr_2 + Aq = Tl_2Br_3 + TlBr_3Aq$) (W., *l.c.*).

Thallium, chlorides of. Tl and Cl combine to form at least four compounds: TlCl, Tl_2Cl_3, $TlCl_2$ and $TlCl_3$.

THALLOUS CHLORIDE TlCl. Mol. w. 239·01. Melts at 427° (Carnelley, *C. J.* 33, 277). Boils at 708°–719° (C. a. Williams, *C. J.* 33, 284). S.G. 7·02, after fusion (Lamy, *J.* 15, 184). V.D. at 830° to 1025° = 117·8 (Roscoe, *Pr.* 27, 426). S. ·19 at 0°, ·27 at 16°, ·28 at 16·5°, 1·6 at 63° (Hebberling, *A.* 134, 15). H.F. [Tl,Cl] = 48,580; [Tl,Cl,Aq] = 38,480 (*Th.* 3, 354).

Formation.—1. By heating Tl in Cl, keeping the Tl in excess.—2. By boiling powdered Tl in HClAq, and dissolving the film of TlCl that forms in much boiling water.—3. By adding SO_2Aq to $TlCl_3Aq$.

Preparation.—HClAq, or solution of a chloride, is added to the solution of a thallous salt; the white curdy pp. that forms is washed with cold water, dissolved in a large quantity of boiling water, and the salt that separates as the solution cools is purified by two or three recrystallisations from boiling water (Crookes, *C. J.* 17, 112).

Properties and Reactions.—A white, crystalline solid; resembling $PbCl_2$, but separating from solution in hot water in smaller and less shining crystals than $PbCl_2$. Becomes slowly violet coloured when exposed to light (Hebberling, *A.* 134, 15). Melts at 427° to a clear yellow liquid, which solidifies to a white crystalline mass. Very slightly soluble in water (*v. supra*); less soluble in water containing a little HCl; insoluble in alcohol; insoluble in ammonia; soluble in hot Na_2CO_3Aq, KOHAq, or Na_2SO_4Aq. Hot conc. *sulphuric acid* forms Tl_2SO_4 and HCl; *oxidisers* such as ClAq, *aqua regia*, $KMnO_4$Aq and HClAq, form $TlCl_3$, Tl_2Cl_3, or $TlCl_2$ (*v.* these chlorides). TlCl is reduced to Tl by *zinc and sulphuric acid*, also by adding *aluminium* to TlClAq at 90° (Cossa, *Acad. dei Lincei* [3] 2). Fusion with *sodium hydrogen sulphate* produces Tl_2SO_4 (Krause, *D. P. J.* 217, 323; Nietzki, *D. P. J.* 219, 262).

Combinations.—1. With *platinic chloride* to form $2TlCl.PtCl_4$ ($= Tl_2PtCl_6$); obtained, as a pale-yellow, crystalline powder, by mixing solutions of TlCl and $PtCl_4$; this salt is extremely insoluble in water, one part dissolving in 15,585 parts water at 15°, and in 1948 parts boiling water (Crookes, *l.c.*).—2. With *mercuric chloride*, to form $TlCl.HgCl_2$; white lustrous needles, separating from a hot solution of TlCl in $HgCl_2$Aq; all $HgCl_2$ is removed at 200° (Carstanjen, *J. pr.* 102, 141; Jörgensen, *J. pr.* [2] 6, 82).—3. With *ferric chloride* to form $3TlCl.FeCl_3$; small red prisms; obtained by adding TlCl to a hot solution of $FeCl_3$ in HClAq, and crystallising the red pp. from hot conc. HClAq; decomposed to its constituent salts by water (Wöhler, *A.* 144, 350).—4. With *chromic chloride*, to form $3TlCl.CrCl_3$ (*v.* Neumann, *A.* 244, 328).—5. According to Lepierre a. Lachaud (*C. R.* 113, 196), a conc. solution of *chromium trioxide* reacts with TlCl to form small red prisms of $CrO_3.TlCl$ [$CrO_2(OTl)Cl$], which are decomposed by water to TlCl and CrO_3Aq.

THALLIC CHLORIDE $TlCl_3$. Mol. w. not certainly known; from analogy of $AlCl_3$, $GaCl_3$, and $InCl_3$, the formula $TlCl_3$ is probably molecular.

Formation.—1. By heating TlCl with hot *aqua regia* and evaporating the solution in Cl (Willm, *A. Ch.* [4] 5, 28).—2. By dissolving freshly ppd. TlO_3H_3 in HClAq, adding HNO_3Aq, and evaporating in Cl.—3. By heating TlCl at its melting-point in Cl; it is doubtful whether the product is pure $TlCl_3$, or contains also $TlCl_2$ or Tl_2Cl_3 (Lamy, *l.c.*).

Preparation.—Cl is passed into water containing TlCl in suspension until a little of the solution ceases to give a turbidity with $PtCl_4$Aq; excess of Cl is removed by a stream of CO_2, and the solution is evaporated *in vacuo*. Crystals of $TlCl_3.H_2O$ separate, which lose water at c. 40° (Werther, *J. pr.* 91, 385).

Properties and Reactions.—The hydrate forms large colourless prisms; the dehydrated salt is a white crystalline solid. Werther (*l.c.*) also obtained a hydrate $2TlCl_3.15H_2O$ from a solution of $TlCl_3$ prepared as described. Cl begins to be given off at c. 50° to 60°; at 100° a mixture of TlCl and chlorides intermediate between TlCl and $TlCl_3$ remains (Werther, *l.c.*; Lamy, *l.c.*). $TlCl_3$ is very deliquescent; it dissolves very easily in water. Thomsen gives $[Tl,Cl^3,Aq] = 89,250$ (*Th.* 3, 354). On diluting a conc. aqueous solution considerable quantities of TlO_3H_3 and HClAq are formed. Reducing agents, such as SO_2, form TlCl.

Combinations.—1. With *ammonia* to form $TlCl_3.3NH_3$ (Willm, *A. Ch.* [4] 5, 28). A white, crystalline powder. Obtained by passing NH_3 over $TlCl_3$; by adding an alcoholic solution of NH_3 to $TlCl_3$ suspended in absolute alcohol; or by boiling TlO_3H_3 with conc. NH_4ClAq, ppg. by NH_3Aq, washing with alcoholic ammonia, then with absolute alcohol, and drying *in vacuo*. The compound is unchanged in air; water forms NH_4ClAq and Tl_2O_3; when heated NH_3, NH_4Cl, and N are given off and TlCl remains. Dissolves in HClAq, forming $TlCl_3.3NH_4Cl$.—2. With *ammonium chloride* to form $TlCl_3.3NH_4Cl$; obtained by adding NH_4Cl to a solution of TlO_3H_3 in HClAq, and evaporating *in vacuo*; large, white, quadratic crystals, probably with $2H_2O$ (Rammelsberg, *P.* 146, 597; *v.* also Nicklès, *J. Ph.* [4] 1, 25).—3. Compounds with *potassium chloride*, *cæsium chloride*, and *rubidium chloride*, $TlCl_3.3MCl.xaq$, have been obtained (*v.* Rammelsberg, *l.c.*, also *W.* 16, 709; Godeffroy, *Zeit. des allgemein. österr. Apothekerver.* 1880 No. 9; Neumann, *A.* 244, 348; Willm, *l.c.*). Neumann (*l.c.*) also describes a compound of $TlCl_3$ with *beryllium chloride*.—4. Willm (*l.c.*) describes a compound with *cupric chloride*, $2TlCl_3.CuCl_2$.—5. According to Nicklès (*C. R.* 58, 537) $TlCl_3$ forms a compound with *ether and hydrochloric acid*, to which he gives the composition $TlCl_3.Et_2O.HCl.H_2O$; it is described as a yellow fuming liquid.

THALLIUM DICHLORIDE $TlCl_2$ (or $TlCl.TlCl_3 = Tl_2Cl_4$). Lamy (*A. Ch.* [3] 67, 402) obtained a yellow, slightly hydroscopic, easily fusible solid, to which he assigned the composition $TlCl_2$, by heating Tl and TlCl in a stream of Cl so that the product always remained liquid, and allowing to cool when saturated; the substance gave off Cl, and Tl_2Cl_3 remained.

THALLIUM SESQUICHLORIDE Tl_2Cl_3; or $TlCl_3.3TlCl = Tl_4Cl_6$. (*Thallothallic chloride.*) Formed by heating dry $TlCl_3$ somewhat above 100° as long as Cl is given off; the brown liquid cools to a clear yellow, crystalline mass (Lamy, *l.c.*, p. 403). Also formed by the direct combination of Cl with molten Tl (L., *l.c.*); also by ppg. a solution containing a thallous and a thallic salt by HClAq (Willm, *l.c.*). Also obtained by dissolving Tl or TlCl in *aqua regia*, evaporating, heating till Cl ceases to be given off, and crystallising from water slightly acidified with *aqua regia* (Lamy, *l.c.*; Crookes a. Church, *C. N.* 8, 1). According to Werther (*J. pr.* 91, 390) the product of this reaction, dried at 100°, is a mixture of compounds of TlCl and $TlCl_3$, besides Tl_2Cl_3. Tl_2Cl_3 crystallises in yellow, hexagonal leaflets; unchanged in air; melting between 400° and 500° to a dark-brown liquid that solidifies with much contraction, forming a yellowish mass with S.G. 5·9 (Lamy, *l.c.*). Very slightly soluble in water; S. ·26 at 15°, ·29 at 17°, 1·9 at 100° (Crookes; Hebberling, *A.* 134, 21). The solution is said to show the reactions both of thallous and thallic compounds. Heated above 500° Cl is given off; heating in H_2S produces Tl_2S, S, and HCl (Hebberling, *l.c.*). Heating in NH_3 produces TlCl, NH_4Cl, and N (Crookes a. Church, *C. N.* 8, 1). Tl_2Cl_3 reacts with KOHAq to form TlO_3H_3, TlCl, and KCl.

OTHER THALLO-THALLIC CHLORIDES. According to Werther (*J. pr.* 91, 390), two compounds

besides Tl_2Cl_3 are obtained by evaporating TlCl in *aqua regia*, heating till Cl ceases to be given off, crystallising from water slightly acidified with *aqua regia*, and drying at 100°. To these compounds W. gives the formulæ $3TlCl.4TlCl_3 = Tl_7Cl_{15}$ and $TlCl.15TlCl_3 = Tl_{16}Cl_{46}$.

Thallium, cyanide of; *v.* vol. ii. p. 347.

Thallium, ferrocyanide of; *v.* vol. ii. p. 337.

Thallium, fluorides of. Only one fluoride of Tl has been isolated with certainty; there are indications of the existence of another.

Thallous fluoride TlF. Formula probably molecular, from analogy of TlCl. Prepared by dissolving Tl_2CO_3 in HFAq, evaporating to dryness, heating gently to remove HF, and crystallising from water; forms white, lustrous, regular octahedra (Büchner, *J. pr.* 96, 404). TlF is also said to be formed as a white sublimate by heating Tl_2O in HF gas (Kuhlmann, *C. R.* 58, 1037). Sol. in water; S. = 80 at 15°, and increases with increase of temperature; solution in water has alkaline reaction; somewhat sol. in alcohol. A *hydrate* $TlF.H_2O$ forms in monoclinic crystals by evaporating a solution of Tl_2O or Tl_2CO_3 in HFAq; it is deliquescent, and acts on glass (Kuhlmann, *l.c.*; Willm, *A. Ch.* [4] 5, 5). A *compound with fluorhydric acid*, $TlF.HF = TlHF_2$, is obtained by evaporating a solution of TlF in HFAq over H_2SO_4. Decomposed above 100° to TlF and HF. V. sol. water; S. = 100 at ordinary temperature; the solution has an acid reaction (Büchner, *l.c.*).

Thallic fluoride. By digesting TlO_3H_3 with HFAq, and also by adding HFAq to $Tl(NO_3)_3Aq$, Willm (*A. Ch.* [4] 5, 5) obtained a dark olive-green solid, becoming brown when heated, and melting to an orange-yellow liquid that became white on cooling, insoluble in water and in cold HClAq. This substance was probably thallic fluoride, or perhaps a thallo-thallic fluoride; no analyses are given.

Thallium, hydride of. Herapath (*Ph.* 4, 302) supposed that a compound of Tl and H existed; but Crookes (*C. J.* 17, 132) failed to obtain any compound either by the interaction of an acid with Tl–Zn alloy, or by heating Tl in a stream of H; the escaping H burnt with a green flame, but this was found to be due to particles of Tl carried by the stream of H.

Thallium, hydroxides of. Tl forms three compounds with O and H, namely, TlOH, TlO_2H (or TlO.OH), and TlO_3H_3.

Thallous hydroxide TlOH. (*Hydrated thallous oxide* $Tl_2O.H_2O$.) Mol. w. not known with certainty. Thomsen (*Th.* 3, 354) gives H.F. $[Tl,O,H] = 56,915$; $[Tl^2,O,H^2O] = 45,470$; $[Tl^2O,H^2O] = 3,230$.

Formation.—1. By dissolving Tl in water containing air, and evaporating.—2. By decomposing Tl_2SO_4Aq by BaOAq, filtering, and evaporating.—3. By the interaction of CaOAq and $Tl_2C_2O_4Aq$.—4. By dissolving Tl_2O in water and evaporating.

Preparation.—1. Tl ppd. by zinc is allowed to oxidise in warm, moist air, and the oxide is dissolved in boiling water; these operations are repeated till a saturated hot solution is obtained, and this solution is evaporated a little, filtered from any Tl_2CO_3 that may have separated, and allowed to crystallise (Crookes, *C. J.* 17, 132).—2. Tl_2SO_4Aq is mixed with the proper quantity of BaOAq, and the solution, filtered from $BaSO_4$, is crystallised *in vacuo*; this method is tedious, and there is much difficulty in getting rid of all BaO.—3. Thin plates of Tl are suspended over a shallow dish containing absolute alcohol, within a bell-jar from which air has been exhausted, and pure O is passed into the jar, the temperature being kept at 20°–25°; after several hours or days, C_2H_5TlO is formed as an oil in the dish; excess of alcohol is removed by heating to 100°; a little water is added, whereby TlOH is ppd.; the pp. is drained, and exposed to warm dry air till all water and alcohol are removed (Lamy, *A. Ch.* [3] 67, 385).

Properties and Reactions. — Pale-yellow, prismatic crystals. At 100° in air, or *in vacuo* over H_2SO_4 at the ordinary temperature, the crystals become black from formation of Tl_2O, without altering their crystalline form. Easily soluble in water; Thomsen (*Th.* 3, 354) gives $[TlOH,Aq] = -3,155$. The solution in water resembles KOHAq and NaOHAq in its properties; it is strongly alkaline, absorbs CO_2, ppts. heavy metals as hydroxides or oxides, feels soapy to the touch, stains the skin, neutralises acids, &c. The solution absorbs a little O on heating; when evaporated to dryness and the residue re-dissolved, a little Tl_2O_3 generally remains.

Thallic hydroxides. Two thallic hydroxides are known, TlO.OH and TlO_3H_3.

I. *Monohydrated thallic oxide*, $TlO.OH = Tl_2O_3.H_2O$. Mol. w. not known with certainty.

Formation.—1. By ppg. $TlCl_3Aq$ by alkali and drying at 100° (Lamy, *A. Ch.* [3] 67, 385).—2. By passing ozonised air through TlOHAq (Schönbein, *J. pr.* 93, 35).—3. By the action of H_2O_2Aq on Tl; according to Weltzien (*A.* 138, 129) a mixture of TlOH and TlO.OH is thus obtained.—4. Various oxidisers—*e.g.* $KMnO_4Aq$, hypochlorite solutions, &c.—convert TlOH into TlO.OH (Schönbein, *l.c.*).—5. By electrolysing a neutral or ammoniacal solution of $Tl_2(SO_4)_3$ or $Tl(NO_3)_3$; the hydroxide separates on the positive (Pt) electrode (Flemming, *J. Z.* 1869. 292).

Preparation.—$TlCl_3Aq$ is ppd. by a slight excess of KOHAq or NH_3Aq, the pp. is thoroughly washed, and dried at 100° (Lamy, *A. Ch.* [3] 67, 397; Crookes, *C. J.* 17, 132; Werther, *J. pr.* 91, 388). The air-dried pp. has the composition TlO.OH (Carnelley a. Walker, *C. J.* 53, 88).

Properties and Reactions.—A brown powder; insoluble in water and dilute alkali solutions. Heated to c. 60° begins to lose water; completely dehydrated at 115°, according to Werther (*J. pr.* 91, 385), but the residue contains some Tl_2O, as well as Tl_2O_3 (*cf.* Birnbaum, *A.* 138, 133). According to Carnelley a. Walker (*C. J.* 53, 88), dehydration is complete at 230°, and the residue is Tl_2O_3, which is stable to 360°. Dissolves in HClAq, forming $TlCl_3$; in conc. acid Cl is given off and some TlCl is produced. Dissolves in dilute H_2SO_4Aq; with conc. acid some O is given off. Dissolves in SO_2Aq, As_2O_3Aq, hot tartaric acid solution, and boiling oxalic acid solution, in each case forming a salt of Tl_2O. TlO.OH dissolves in warm conc. NH_4ClAq, giving off NH_3 and forming $TlCl_3.3NH_3$; on adding water Tl_2O_3 is ppd. as a black powder (Willm, *A. Ch.* [4] 5, 5).

II. *Trihydrated thallic oxide*, $TlO_3H_3 = Tl_2O_3.3H_2O$. Formed, as light-brown, lustrous,

microscopic, hexagonal plates, by dissolving TlO.OH in molten KOH, fusing for some time, cooling, washing with hot water, then with alcohol, and drying at 100°. Insoluble in water. Not decomposed at 340°; soluble in dilute acids (Carnegie, *C. N.* 60, 113).

Thallium, iodides of. Tl combines directly with I. At least two compounds are known: TlI and Tl_2I_3; TlI_3, and probably one, or perhaps more than one, other compound of TlI and TlI_3, seem also to exist.

Thallous iodide TlI. (*Thallium monoiodide.*) Mol. w. not known with certainty, but formula TlI is probably molecular from analogy of TlCl.

Formation. — 1. By heating together Tl and I in the ratio Tl:I.—2. By adding KIAq to solution of a thallous salt.

Preparation.—KIAq is added to a dilute solution of a thallous salt, and the yellow pp. is thoroughly washed with water and dried at 100° (Lamy, *A. Ch.* [3] 67, 405; Crookes, *C. J.* 17, 137).

Properties and Reactions.—A citron-yellow powder; melts at 439° (Carnelley, *C. J.* 33, 278), and boils at 800°-806° (C. a. Williams, *C. J.* 33, 284). S.G. 7·072 at 15·5°, after fusion 7·0975 at 14·7° (Twitchell, *Clarke's Table of Spec. Grav.* [2nd edit.] 35). Very slightly soluble in water. Determinations of solubility vary considerably; Werther (*J. pr.* 92, 130) says that 1 pt. requires 20,000 pts. water to dissolve it at 15°, and Crookes (*l.c.*) gives solubility as 1 in 4450 of water at 15° (*v.* also Hebberling, *A.* 134, 16). Crookes says TlI is somewhat more soluble, Hebberling says it is decidedly less soluble, in KIAq than in water.

When heated to c. 190° TlI becomes red, and when it melts a red liquid is formed which solidifies to a red crystalline mass having the composition TlI (Hebberling, *l.c.*, p. 18); the red variety is also obtained by crystallising from hot KOHAq (Willm, *A. Ch.* [4] 5, 28); also by crystallising from hot $KC_2H_3O_2Aq$ (Werther, *l.c.*). The red form of TlI is produced by adding KIAq to a warm conc. solution of a thallous salt (Hebberling, *l.c.*, p. 16). Red TlI crystallises in octahedral forms (W., *l.c.*). The red variety slowly changes on keeping to the yellow form.

When freshly ppd. yellow TlI is exposed to the sun's rays it becomes green and crystalline without any change in composition. The green variety of TlI is somewhat more soluble in hot water than the yellow form; it crystallises from hot water in green microscopic crystals that are very refractive. The green variety changes slowly to the yellow on keeping; the change is hastened by heating in water containing I or KI, but not by heating with pure water. When strongly heated, green TlI becomes red (*v.* Knösel, *B.* 7, 576, 893).

TlI is decomposed by warm HNO_3Aq, with separation of I. It is dissolved, without I being separated, by ClAq or *aqua regia*; Willm (*l.c.*) supposes that an iodochloride is formed. Fusion with KCN produces Tl (Werther, *l.c.*).

Thallic iodide TlI_3. This compound has not been isolated with certainty. By treating Tl with an ethereal solution of I, Nicklès (*C. R.* 58, 537) obtained a brown liquid from which brown needles gradually separated. These crystals may have been TlI_3; no analyses are given.

Double salts of TlI_3 with alkali iodides have been prepared by digesting TlI with solutions of I and alkali iodides in ether; these salts have the composition $TlI_3.MI.xH_2O$, where $M = NH_4$ and K (*v.* Nicklès, *J. Ph.* [4] 1, 25; Willm, *A. Ch.* [4] 5, 5; Rammelsberg, *P.* 146, 597). A compound $TlI_3.CuI_2.4NH_3$ is described by Jörgensen (*J. pr.* [2] 6, 82).

Thallium sesqui-iodide Tl_2I_3 or $TlI_3.3TlI = Tl_4I_6$. (*Thallothallic iodide.*) Black, lustrous needles; insoluble in water, slightly soluble cold alcohol, decomposed by boiling alcohol; decomposed slowly at ordinary temperature, quickly on heating; obtained by long-continued heating yellow TlI with excess of IAq (Knösel, *B.* 7, 576, 893).

Other thallo-thallic iodides. By evaporating a solution of TlI in HIAq, in presence of I, at 70°, small, brown, rhombic, crystals were obtained by Jörgensen (*l.c.*). The composition of the crystals is represented by J. as $6TlI.TlI_3$, or perhaps $5TlI.TlI_3$. The same compound is said to be obtained by digesting TlI with an ethereal solution of I. Heating to c. 100° drives off I, and leaves yellow TlI; boiling alcohol, and also KIAq, withdraws I, forming TlI.

Thallium, oxides of. Two oxides have been isolated, Tl_2O and Tl_2O_3; there is evidence in favour of the existence of a third oxide, probably TlO_2.

Thallous oxide Tl_2O. (*Thallium monoxide.*) Mol. w. not known with certainty. $[Tl^2,O] = 42,240$ (*Th.* 3, 354). Prepared by heating Tl in air to not above 100° (to prevent formation of Tl_2O_3); also by heating TlOH to 100° out of contact with air; also by heating Tl_2O_3 to full redness. A black powder; melting at c. 300° to a dark-yellow liquid, which acts on glass, forming a silicate of Tl. Tl_2O absorbs moisture from the air, forming TlOH; it dissolves easily in water, forming a strongly alkaline solution of TlOH (*v.* Thallous hydroxide, p. 678). Soluble in absolute alcohol, forming $C_2H_5.OTl$, a colourless, heavy oil (S.G. 3·55); this oil is decomposed by a little water with separation of TlOH (*v.* Thallous hydroxide, *Preparation*, No. 3, p. 678). (Crookes, *C. J.* 17, 128; Lamy, *A. Ch.* [3] 67, 385). Tl_2O is reduced to Tl by heating to redness in H, or in CO, or with Mg (Winkler, *B.* 23, 788).

Thallic oxide Tl_2O_3. Mol. w. not known with certainty. Prepared by ppg. a thallic salt with KOHAq or NH_3Aq, washing the pp. thoroughly, drying, and heating it to c. 260° (Crookes, *l.c.*, p. 132). Also formed by burning Tl in air to a little below redness; at a lower temperature the product is chiefly Tl_2O, and at a full red heat Tl_2O_3 is decomposed to Tl_2O and O (Lamy, *l.c.*). Tl_2O_3 is also formed by passing an electric current (from a couple of Grove cells) through neutral Tl_2SO_4Aq, using Pt electrodes; Tl deposits on the negative electrode, and Tl_2O_3 forms, as a brown cake, on the positive electrode; the H_2SO_4Aq formed should be neutralised from time to time by NH_3Aq (Crookes, *l.c.*). For other methods of formation *v.* Wöhler (*A.* 146, 263, 375), and Willm (*A. Ch.* [4] 5, 19). Tl_2O_3 is a brownish-black solid; insoluble in water Melts at c. 760° (?) (Carnelley a. O'Shea, *C. J.*

45, 409). Gives off O at a full red heat, forming Tl_2O. Dissolves in hot H_2SO_4Aq, forming Tl_2SO_4Aq and giving off O. Soluble cold HClAq, forming $TlCl_3Aq$, and some TlCl with evolution of Cl. Takes fire in dry H_2S, forming Tl_2S_3 (Carstanjen, *J. pr.* 102, 65). A mixture of Tl_2O_3 and S takes fire when struck (Böttger, *J. pr.* 90, 27). Reduced by heating in H or CO to Tl_2O, and then to Tl. Tl_2O_3 absorbs NH_3 when heated in that gas; no definite compound has been isolated. For compounds with H_2O *v.* THALLIC HYDROXIDES, p. 678).

THALLIUM DIOXIDE (?TlO_2). When a rapid stream of Cl is passed into conc. KOHAq, holding freshly ppd. TlO.OH in suspension, a violet-coloured solution is obtained; mineral acids added to this solution form thallous salts, and give off O, or Cl with HClAq. Carstanjen (*J. pr.* 101, 55) supposed the violet solution to contain a thallate of potassium. Piccini (*G.* 17, 450) obtained a violet pp. by adding $Ba(NO_3)_2Aq$ to the violet solution; analyses of this pp. were not satisfactory, but the results indicated that an oxide of Tl of the composition TlO_2 is formed by the method described. Piccini says that the same violet solution is obtained by electrolysing 30 p.c. KOHAq, using a plate of Tl as anode; also by digesting 1 pt. KOH with 4 pts. KClO, in water, and adding Tl_2SO_4.

Thallium, phosphide of. No compound of Tl and P has been isolated with certainty. According to Crookes (*C. J.* 17, 135), the black substance formed by passing P hydride into ammoniacal Tl_2SO_4Aq is a phosphide of Tl. Carstanjen (*J. pr.* 102, 80) failed to obtain a phosphide by reducing Tl_3PO_4 by C or H, or by heating the elements together. Flemming (*Bl.* [2] 10, 35) noticed that a thin, black coating formed on molten Tl when pieces of P were thrown on to it; by heating solution of a thallous salt with P in a sealed tube, he obtained a black solid, perhaps a phosphide, and also a phosphite and hydride of P (*cf.* Willm, *A. Ch.* [4] 5, 5).

Thallium, platino-cyanide of; *v.* vol. ii. p. 345.

Thallium, salts of. Two series of salts are formed by replacing the H of acids by Tl; thallous salts, Tl_2X, and thallic salts, Tl_2X_3, where $X = SO_4$, CO_3, $2NO_3$, $2IO_3$, $\frac{2}{3}PO_4$, &c. The chief thallous salts of oxyacids are *arsenates*, *carbonates*, *chlorate* and *perchlorate*, *chromate*, *dichromate* and *trichromate*, *dithionate* and *trithionate*, *hypophosphite*, *iodate* and *periodate*, *molybdates*, *nitrate*, *phosphates*, *selenite* and *selenates*, *silicates*, *sulphates* and *sulphite*, *tellurate*, *thiosulphate*. The principal thallic salts are *arsenate*, *iodate* and *periodate*, *nitrate*, *phosphates*, *sulphates* (*v.* CARBONATES, NITRATES, SULPHATES, &c.). Several double salts of both series are also known.

Thallium, salts of oxyacids of. No compounds of this kind have been isolated with certainty, but there is evidence in favour of the existence of salts of the hypothetical thallic acid, probably analogous to plumbates (*v.* THALLIUM DIOXIDE, *supra*).

Thallium, selenides of. Tl_2Se has been isolated; another selenide, perhaps Tl_2Se_3, probably exists.

THALLOUS SELENIDE Tl_2Se. Mol. w. not known. Obtained by fusing the elements together in the ratio 2Tl:Se (Willm, *A. Ch.* [4] 5, 5; Carstanjen, *J. pr.* 102, 79); also by ppg. Tl_2CO_3Aq by H_2Se (Kuhlmann, *Bl.* [2] 1, 330). A grey, lustrous, crystalline solid; melting at c. 340° (Kuhlmann, *l.c.*). Dissolves in H_2SO_4Aq and HClAq, giving off H_2Se.

THALLIC SELENIDE (?Tl_2Se_3). By fusing the elements together in the ratio 2Tl:3Se, Carstanjen (*l.c.*) obtained greyish-black prismatic crystals, resembling Sb; not acted on by dilute H_2SO_4Aq; decomposed by hot conc. H_2SO_4, with separation of Se and evolution of SO_2. The composition of this substance has not been determined.

Thallium, silicofluoride of, Tl_2SiF_6. Obtained by dissolving Tl_2CO_3 in H_2SiF_6Aq, and evaporating. Colourless, regular, octahedra (Werther, *J. pr.* 91, 385). According to Kuhlmann (*Bl.* [2] 1, 330), the crystals are $Tl_2SiF_6.H_2O$. Easily soluble in water. Volatile without decomposition, according to Kuhlmann (*l.c.*).

Thallium, sulphides of. Tl_2S and Tl_2S_3 have been isolated, and also probably more than one compound of these two sulphides.

THALLOUS SULPHIDE Tl_2S. Mol. w. not known.

Formation.—1. By fusing the elements together in the ratio 2Tl:S (Carstanjen, *J. pr.* 102, 76).—2. By ppg. an alkaline solution of a thallous salt by H_2S.—3. By ppg. slightly acidified Tl_2SO_4Aq by H_2S (Hebberling, *A.* 134, 11).—4. By heating an alkaline solution of a thallous salt with $Na_2S_2O_3$ (C., *l.c.*).

Preparation.—A cold, fairly conc., aqueous solution of Tl_2SO_4 is acidulated with a trace of H_2SO_4Aq, and saturated with H_2S, and the bluish-black pp., consisting of microscopic crystals, is washed with H_2SAq and dried over H_2SO_4 (Hebberling, *l.c.*).

Properties and Reactions.—Prepared by ppn. from slightly acidulated Tl_2SO_4Aq, Tl_2S forms very minute, blue-black, lustrous tetrahedra; prepared by heating together Tl and S it is a black, crystalline, brittle solid; prepared by ppn. from alkaline solutions it is a black amorphous solid. When the amorphous solid is dried, and strongly heated, it melts, and solidifies on cooling to a black crystalline mass. After melting, S.G. is 8·0 (Lamy, *J.* 15, 185). H.F. $[Tl^2,S] = 21,660$ (*Th.* 3, 354). Moist ppd. Tl_2S oxidises in air to Tl_2SO_4. On long continued heating Tl_2S is completely decomposed (Lamy, *l.c.*). Tl_2S is insoluble in solutions of alkalis, alkali sulphides, carbonates, and cyanides; it dissolves readily in H_2SO_4Aq and HNO_3Aq, and less readily in HClAq. By ppg. from a very dilute solution of a thallous salt, and dialysing, Winssinger (*Bl.* [2] 49, 452) obtained a reddish-brown aqueous solution of colloidal Tl_2S.

Combination.—By passing H_2S into Tl_2SO_4Aq containing As_2O_3Aq, and acidulated with dilute H_2SO_4Aq, Gunning (*Ar. N.* 3, 86) obtained a red pp. of $Tl_2S.As_2S_3$; the same compound was obtained by mixing a solution of As_2S_3 in NH_3Aq with an ammoniacal solution of a thallous salt. Heat decomposes the compound into its constituent sulphides; alkali solutions dissolve out As_2S_3, leaving Tl_2S.

THALLIC SULPHIDE Tl_2S_3. Obtained as a black, amorphous, easily fusible, solid, by melting Tl with excess of S, and removing uncombined S by heating out of contact with air (Carstanjen, *J. pr.* 102, 65). Below 12° Tl_2S_3 is hard and brittle; above 12° it is so soft that it may be drawn out like pitch. It dissolves in warm dilute H_2SO_4Aq without separation of S. Strecker (*J. pr.* [2] 2, 162) obtained a lustrous, brown-black pp. by passing H_2S into a solution of a thallic salt mixed with sodium tartrate and excess of NH_3Aq, followed by boiling; this pp. was Tl_2S_3 according to Strecker. When H_2S is passed into an aqueous solution of a thallic salt, the pp. is a mixture of Tl_2S and S. Tl_2S_3 *combines with potassium and sodium sulphides*, forming $Tl_2S_3.K_2S$ and $Tl_2S_3.Na_2S$. These compounds are obtained by fusing together 1 pt. Tl_2SO_4, 6 pts. S, and 9 pts. K_2CO_3 or Na_2CO_3, and washing the fused mass with water. The K compound is more stable than the compound of Na; when heated it melts, and then gives off S, leaving K_2S and Tl_2S; it is not changed by water or alkali solutions, but is decomposed by mineral acids (*v.* Schneider, *A.* 135, 215; *cf.* Krüss, *B.* 19, 2738). These compounds may be regarded as $KTlS_2$ and $NaTlS_2$, that is, as salts of a hypothetical thio-thallic acid.

THALLO-THALLIC SULPHIDES. By adding $(NH_4)_2SAq$ to a solution of Tl_2Cl_3, a black pp. is obtained which is more fusible than Tl_2S, and after melting solidifies to large greyish-black prisms. This pp. contains Tl and S. Similar substances are formed by heating together Tl_2S and Tl_2S_3, and by melting Tl with more S than 2Tl:S, and less than 2Tl:3S; Carstanjen (*J. pr.* 102, 65) gave the formulæ $5Tl_2S.3Tl_2S_3 = Tl_{16}S_{14}$, and $Tl_2S.Tl_2S_3 = TlS$ to compounds obtained in this way. By heating $Tl_2S_3.Na_2S$ (*v. supra*) with water, Schneider (*A.* 135, 215) obtained a compound to which he gave the formula $Tl_2S.2Tl_2S_3 = Tl_6S_7$.

Thallium, sulphocyanide of; *v.* vol. ii. p. 352.

Thallium, thiosalts of. The compounds of Tl_2S_3 with K_2S and Na_2S may be regarded as K and Na thiothallates (*v.* THALLIC SULPHIDE, *supra*).
M. M. P. M.

THALLIUM ETHIDE TlEt. Has not been obtained in the free state.

Ethylo-chloride $TlEt_2Cl$. S. 2·76 in the cold; 3·37 at 92°. S. (alcohol) ·33 at 78°. Formed from $TlCl_3$ and $ZnEt_2$ in ether (Hartwig, *A.* 176, 257). Scales (from water), explodes feebly at 190°, yielding TlCl. Reacts with silver salts forming: $TlEt_2NO_3$, S. 5·67 at 70°, exploding at 236°.—$(TlEt_2)_2SO_4$, S. 65·4 in the cold; 87·3 at 90°; exploding at 205° and converted by BaI_2 into $TlEt_2I$, S. ·1, exploding at 195°.—$(TlEt_2)_3PO_4$, S. 23·7 in the cold; 20·7 at 75°, exploding at 189°.—$TlEt_2OAc$ crystallising in needles [212°] (245°), exploding if rapidly heated.

Ethylo-hydroxide $TlEt_2OH$. S. 15·1 in the cold; 8 at 88°. Formed from $(TlEt_2)_2SO_4$ and baryta. Silky needles (from water). More sol. cold than hot water, forming an alkaline solution. Does not unite with CO_2, but forms the above salts with other acids.

THAPSIC ACID $C_{16}H_{30}O_4$. [124°]. Obtained from the root-bark of *Thapsia garganica*. The bark is extracted with ether, which leaves on evaporation an amber-coloured resin. The resin dissolves in potash with evolution of heat, and the solution, on acidification, yields a neutral resin, *n*-octoic acid and thapsic acid. The alkaline solution on standing deposits potassium thapsate (Canzoneri, *G.* 13, 514). White scales (from alcohol), nearly insol. water and benzene, sol. alcohol and ether.

Salts.—$K_2A''xaq$. Prisms.—BaA'' (dried at 120°). Crystalline pp.—Ag_2A'': amorphous.

Anhydride $C_{16}H_{28}O_3$. [71°]. Crystalline powder (from benzene).

Anilide $C_{16}H_{28}O_2(NHPh)_2$. [163°].

THEBAÏNE $C_{19}H_{21}NO_3$. [193°]. S.G. 1·3. $[\alpha]_j = -219°$ in 97 p.c. alcohol at 15°; $= -230°$ in $CHCl_3$; S. (ether) ·7 at 10°; S. (isoamyl alcohol) 1·67 in the cold; S. (benzene) 5·27 in the cold (Kubly, *J.* 1866, 823). Occurs in opium to the extent of about ·6 p.c. (Pelletier, *J. Ph.* 21, 569; Couerbe, *A. Ch.* [2] 59, 155; Kane, *A.* 19, 9; Anderson, *A.* 86, 179; Hesse, *B.* 3, 367; *A.* 153, 47; 176, 196). Prepared by treating the aqueous extract of opium with Na_2CO_3 or lime, exhausting the filtrate with ether, agitating the ether with dilute acetic acid, and pouring the acid liquid into dilute KOHAq. The pp. is collected after 24 hours, warmed with dilute alcohol and dilute HOAc is added till just acid. The alcohol is evaporated off at 50°, papaverine and narcotine removed by filtration, and thebaïne acid tartrate ppd. by adding powdered tartaric acid to the filtrate. The tartrate is re-crystallised from water (Hesse, *A. Suppl.* 8, 262). Thebaïne may also be obtained by adding NaOAc to a solution of the hydrochlorides of the opium alkaloids, allowing to stand, filtering, evaporating, again filtering, and adding sodium salicylate. After 24 hours thebaïne salicylate crystallises (Plugge, *Ar. Ph.* [3] 24, 993; 25, 343).

Properties.—Colourless leaflets (from dilute alcohol) or prisms (from conc. alcohol). Tasteless. Alkaline in reaction. Very poisonous. Begins to sublime at 135°; at 160° the sublimate contains needles, cubes, and prisms (Blyth). V. sol. alcohol and chloroform. Ppd. by alkalis and alkaline carbonates, the pp. being slightly soluble in NH_3Aq and lime-water. Conc. H_2SO_4 gives a deep-red solution. Boiling dilute H_2SO_4 converts it into thebenine and thebaïcine. Hot conc. HClAq at 90° yields MeCl and morphothebaïne (Howard, *B.* 17, 527). HIAq gives MeI (2 mols.) (Howard a. Roser, *B.* 19, 1597). Bromine-water forms $C_{19}H_{20}BrNO_3$, a flocculent pp. converted by excess of Br into $C_{19}H_{20}Br_3NO_3$, a yellow pp. Solutions of its salts give a pp. of the dichromate on adding $K_2Cr_2O_7$.

Salts.—$B'HCl$ aq. Large trimetric prisms. S. 6·3 at 10°. $[\alpha]_j = -168·32 + 2·33p$. —$B'_2H_2PtCl_6$ 2aq. Amorphous pp., quickly changing to orange prisms. Decomposed by boiling water (O. De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2C_2O_4$ 6aq. S. 1·03 at 10°.—$B'H_2C_2O_4$aq. S. 2·3 at 20°.—$B'C_4H_6O_6$aq. Prisms, very soluble in hot alcohol. S. ·77 at 20°.—Meconate $B'_2C_7H_4O_7$ 6aq. White prisms (from alcohol).—$B'_4H_4FeCy_6$ (Plugge, *Ar. Ph.* [3] 25, 793).

Methylo-iodide B'MeI. Crystallises from alcohol in prisms (containing EtOH), m. sol. water.

Ethylo-chloride B'EtCl. Needles.

Ethylo-iodide B'EtI. Needles (from alcohol) (Howard, *B.* 17, 527).

Benzylo-chloride $B'C_7H_7Cl$. Crystals.

Morpho-thebaïne $C_{17}H_{17}O_3N$ [191°]. Obtained by heating thebaïne with strong aqueous HCl or

HBr, MeCl (or EtCl) being split off; the yield being 50 p.c. of the thebaïne. Yellowish crystals. Soluble in alcohol, ether, and benzene, sparingly in water. It dissolves in H_2SO_4 to a colourless solution.

Salts.—B'HCl. Small glistening crystals, sol. water, insol. alcohol.—B'HBr: fine silky needles.—$B'HNO_3$ 2aq: small white crystals, v. sol. water and alcohol.—$B'_2H_2SO_4$ 7aq: small crystals, v. sol. water, insol. alcohol. The **oxalate** is a sparingly soluble amorphous pp. The **picrate** is a yellow pp. which melts under water. Insoluble pps. are produced with potassium ferrocyanide, ammonium molybdate, $HgCl_2K_2I_2$, $K_2Cr_2O_7$, and bismuth-potassium iodide.

Acetyl derivative $C_{17}H_{18}AcO_3N$. [183°]: glistening plates (Howard, *B.* 17, 529).

Ethylo-iodide B'EtI. Crystallises from acetic acid.

Methylo-iodide B'MeI. Dimetric tables, insol. alcohol, sol. HOAc.

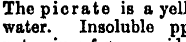
Benzylo-chloride $B'C_7H_7Cl$. Needles, m. sol. water, sl. sol. alcohol (Howard a. Roser, *B.* 19, 1596).

Thebenine $C_{19}H_{21}NO_3$. Formed by boiling thebaïne with HClAq (S.G. 1·04) (Hesse, *A.* 153, 69). Amorphous. Insol. benzene and ether, sl. sol. boiling alcohol. Conc. H_2SO_4 forms a blue solution. V. sol. KOHAq.—B'HCl 3aq. S. 1. Plates.—$B'_2H_2HgCl_4$ 2aq. Very long efflorescent prisms.—$B'_2H_2SO_4$ 2aq. Plates, insol. cold water. —$B'H_2C_2O_4$ aq. Prisms, sl. sol. hot water.

Thebaïcine. Formed by boiling thebaïne or thebenine with conc. HClAq (Hesse). Yellow amorphous pp., insol. ether, benzene, and water, sl. sol. hot alcohol, v. sol. KOHAq. Conc. H_2SO_4 forms a dark-blue solution. The salts are resinous.

Theïne *v.* CAFFEÏNE.

THEOBROMINE $C_7H_8N_4O_2$ *i.e.*


$\mathrm{CO}<\begin{matrix}\mathrm{NMe.C:CH.NMe}\\ \mathrm{N{=\!=}C.NH.CO}\end{matrix}$. Mol. w. 180. *Di-methyl-xanthine.* S. ·062 at 17°; ·7 at 100°. S. (alcohol) ·02 at 17°; ·2 at 78°. S. (ether) ·006 in the cold; ·17 at 35°. S. (boiling $CHCl_3$) 1. Occurs in the seeds of *Theobroma cacao* to the extent of 1·3 to 4·6 p.c. (Woskresensky, *A.* 41, 125; Glasson, *A.* 61, 335; Keller, *A.* 92, 71; Rochleder, *A.* 71, 9; 79, 124; Strecker, *A.* 118, 151). Formed by heating the lead salt of xanthine $C_5H_2PbN_4O_2$ (4 pts.) with MeI (5 pts.) for twelve hours at 130° (Fischer, *B.* 15, 454; *A.* 215, 311). Prepared by ppg. the aqueous extract of the seeds with lead acetate, filtering, removing excess of lead by H_2SO_4, adding $MgCO_3$, evaporating to dryness, and extracting with alcohol (Dragendorff, *Ar. Ph.* [3] 12, 1). Got also by freeing cacao from oil by pressure, adding slaked lime, and extracting with 80 p.c. alcohol (Schmidt a. Pressler, *A.* 217, 287).

Properties.—Minute trimetric crystals, sl. sol. hot water, alcohol, and ether. Tastes bitter. At 184° it begins to sublime; at 170° (Blyth) or 290° (S. a. P.) it yields a crystalline sublimate. Very slowly attacked by pure HNO_3 (Franchimont, *R. T. C.* 6, 223). Not attacked by boiling KOHAq. Its salts are more or less easily decomposed by water. Ammoniacal $AgNO_3$ gives a gelatinous pp. which dissolves on warming, and deposits, on boiling, crystalline $C_7H_7AgN_4O_2$ (Strecker). Theobromine is ppd. by sodium phosphotungstate (Wolfram, *C. J.* 36, 406; *Fr.* 18, 346).

Reactions.—1. Yields methyl-parabanic acid on oxidation by CrO_3.—2. $KClO_3$ and HClAq at 50° yield methyl-alloxan and methyl-urea (Fischer, *A.* 215, 304). Chlorine-water yields amalic acid.—3. Will not combine with MeI to form a methyloiodide. But in presence of dilute alcoholic KOH it reacts with MeI, forming caffeïne, even in the cold; better at 100°. But the reaction is never complete, some theobromine being decomposed.—4. Conc. HCl has no action below 200°. At 250° it decomposes it, producing formic acid, carbonic acid, ammonia, methylamine and sarcosine, $C_7H_8N_4O_2 + 6H_2O = 2CO_2 + NMeH_2 + 2NH_3 + C_3H_7NO_2 + CH_2O_2$; the NH_3 and $NMeH_2$ occur in the proportion indicated by the formula (Schmidt, *A.* 217, 298). Boiling aqueous $Ba(OH)_2$ effects in 40 hours the same decomposition.—5. HNO_3 forms CO_2, methyl-parabanic acid and methylamine, but no ammonia.

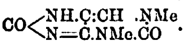
Salts.—B'HCl aq. Rosettes of needles.—B'HBr aq. Tables. — $B'_2H_2PtCl_6$ 4aq. — $B'_2H_2PtCl_6$ 5aq. — $B'HAuCl_4$. — B'_2HNO_3. — B'HOAc.—$B'_2H_2I_8$. Nearly black prisms, decomposed by alcohol (Jörgenssen, *Z.* [2] 5, 675).—$B'HAg(NO_3)_2$. Silvery needles, v. sl. sol. water.—$C_7H_7AgN_4O_2$ 1½aq.—$Ba(C_7H_7N_4O_2)_2$ (dried at 105°). Got by adding theobromine to baryta-water (Maly a. Andreasch, *M.* 4, 379). Needles (from hot water).

Bromo-theobromine $C_7H_7N_4O_2Br$. From theobromine and bromine (Fischer, *A.* 215, 305). Crystalline powder. Sl. sol. hot water. Sol. HCl, but reppd. by water. Sol. aqueous NaOH, not in NH_3. Does not give an ethoxy- derivative with alcoholic KOH (unlike bromo-caffeïne). After warming with ammonia it gives with ammoniacal $AgNO_3$ a silver salt that can be converted by EtI into bromo-ethyl-theobromine $C_7H_6EtN_4O_2Br$, whence alcoholic KOH forms eth-oxy-ethyl-theobromine $C_7H_6EtN_4O_2(OEt)$ [153°] as needles. Boiling HCl converts this into EtCl and oxy-ethyl-theobromine $C_7H_6EtN_4O_2(OH)$, whence bromine and alcohol form the di-ethyl derivative of tri-oxy-di-hydro-ethyl-theobromine $C_7H_6EtN_4O_2(OH)(OEt)_2$ [152°]. This body on treatment with hot dilute HCl gives methylamine and apo-ethyl-theobromine (?); and with chlorine at −10° forms hypo-ethyl-theobromine $C_7H_9N_3O_3$ [142°].

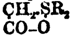
Methyl-theobromine is CAFFEÏNE.

Ethyl-theobromine $C_7H_7EtN_4O_2$. [above 270°]. Formed from $C_7H_7AgN_4O_2$ and EtI (Philips, *B.* 9, 1308). Small crystals, m. sol. hot water. Weak base.

THEOPHYLLIN $C_7H_8N_4O_2$ *i.e.*


$\mathrm{CO}<\begin{matrix}\mathrm{NH.C:CH\ .NMe}\\ \mathrm{N{=}C.NMe.CO}\end{matrix}$. [264°]. Occurs in alcoholic extract of tea, from which it may be separated by means of its Ag salt (Kossel, *B.* 21, 2164). Monoclinic tables (containing aq, v. e. sol. warm water and very dilute ammonia. May be sublimed. When evaporated with chlorine-water it yields a scarlet residue, which is coloured violet by NH_3Aq. MeI converts its Ag salt into caffeïne. $KClO_3$ and HClAq yield di-methyl-alloxan.

Salt.—$AgC_7H_7N_4O_2\frac{1}{2}aq$. Amorphous pp., which may be crystallised from NH_3Aq.

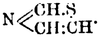
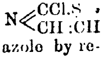
THETINES. A name given by Crum-Brown and Letts to compounds of the form $CO_2H.CH_2.SR_2.OH$ or their anhydrides  $\begin{array}{l}\mathrm{CH_2{-}SR_2}\\ \mathrm{CO{-}O}\end{array}$ where R is a hydrocarbon radicle; *v.* DI-ETHYL-THETINE and DI-METHYL-THETINE.

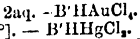
THEVETIN $C_{54}H_{84}O_{24}3aq$. [170°]. S. ·8 at 14°. $\alpha = -85\cdot5°$. A poisonous glucoside occurring in the kernels of *Thevetia nereïfolia* (Blas, *J.* 1868, 768; De Vrij, *R. T. C.* 3, 167; Warden, *Rh.* [3] 12, 417). Crystalline powder, v. sol. hot water and alcohol, insol. ether. Sol. acids and alkalis. Lævorotatory. Conc. H_2SO_4 gives a dirty-brown colour. Decomposed by boiling dilute HClAq into glucose and theveresin $C_{48}H_{76}O_{17}2aq$, a white powder [140°], v. sl. sol. cold water, sol. alkalis.

THIACETIC ACID *v.* THIO-ACETIC ACID.

THIALDINE $C_6H_{13}NS_2$ *i.e.* $\mathrm{NH}\!<\!\begin{array}{l}\mathrm{CHMe.S}\\ \mathrm{CHMe.S}\end{array}\!>\!\mathrm{CHMe}$. Mol. w. 163. [43°]. Formed by passing H_2S for four hours into a solution of aldehyde-ammonia (1 pt.) in water (15 pts.), and a little NH_3Aq (Wöhler a. Liebig, *A.* 61, 2; Hofman, *A.* 103, 93; Brusewitz a. Cathander, *J. pr.* 98, 315). Monoclinic crystals (from ether-alcohol). May be distilled with steam. V. sl. sol. water, v. sol. alcohol, v. e. sol. ether. Boiling dilute H_2SO_4 forms thio-acetic aldehyde. $KMnO_4$ forms $CH_3.CH(SO_3K)_2$ (Guareschi, *B.* 11, 1384, 1692). Boiling $AgNO_3Aq$ forms aldehyde. MeI in ether forms crystalline $C_6H_{13}MeNS_2I$ (Hofmann, *A.* 103, 93). I in KI forms amorphous $(CHMe)_2S_4$ (Fassbender, *B.* 20, 460).

Salts.—B'HCl. Prisms, v. sol. water.—B'HBr.—B'HI.—$B'HNO_3$.—$B'H_2SO_4$. Prisms.—$B'H_3PO_4$ aq. Needles, v. sol. water.

THIAZOLE  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH.S}\\ \mathrm{CH{:}CH}\end{array}$. (116·8° cor.). S.G. $\frac{17}{4}$ 1·1979; $\frac{17}{17}$ 1·1998. Formed by the action of boiling alcohol on the diazo-compound of amido-thiazole, obtained from di-chloro-di-ethyl oxide and thio-urea (Hantzsch a. Popp, *B.* 21, 2582; *A.* 250, 274). Formed also from  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{CCl.S}\\ \mathrm{CH{:}CH}\end{array}$, and the corresponding μ-bromo-thiazole by reduction with zinc-dust and HOAc (Schatzmann, *A.* 261, 12). Mobile liquid, very volatile, hygroscopic, and highly refractive. Miscible with water, alcohol, and ether. Insol. KOHAq. Smells like pyridine. Neutral in reaction.—**Salts.**—$B'_2H_2PtCl_6$ 2aq.—$B'HAuCl_4$. [250°].—$B'C_6H_3N_3O_7$. [151°].—$B'HHgCl_3$. [104°].—$B'HgCl_2$. [204°]. Crystalline pp., sl. sol. water.

μ-Amido-thiazole  $\mathrm{N}\!<\!\begin{array}{l}\mathrm{C(NH_2).S}\\ \mathrm{CH{=}CH}\end{array}$. *Thiazoline. Thiazylamine.* [90°]. Formed by the action of chloro-acetic aldehyde on thio-urea (Traumann, *A.* 249, 36). Prepared by boiling $CH_2Cl.CHCl.OEt$ (1 pt.) with thio-urea (1 pt.) and water (5 pts.). Yellowish plates, sl. sol. water, alcohol, and ether. Strong base.—B'HCl aq. Needles.—$B'_2H_2PtCl_6$. Yellow tables.

Acetyl derivative. [203°]. Needles.

THIAZOLE-TRIAZOLE (so called) $\mathrm{CH}\!<\!\begin{array}{l}\mathrm{S{-}C{:}N}\\ \mathrm{CH.N.N}\end{array}\!>\!\mathrm{CH}$. Formed by the action of HClAq on methyl-nitroso-imido-thiazoline (Näf, *A.* 265, 123). Liquid, v. sol. water. Alkaline; reduces Fehling's solution. Nitrous acid reproduces nitroso-methyl-imido-thiazoline.—B'HCl 2aq. [220°]. Needles.—B'HBr 2aq.

THIENONE is DI-THIENYL KETONE.

DITHIENYL $C_8H_6S_2$ *i.e.* $C_4H_3S.C_4H_3S$. [83°]. (266° cor.). Formed on passing thiophene through a red-hot tube (Nahnsen, *B.* 17, 789, 2197). Plates (from alcohol). Conc. H_2SO_4 gives a reddish-brown solution with deep-green fluorescence. On warming with isatin and H_2SO_4 it gives a violet-blue colour.

Sulphonic acid $C_8H_5S_2(SO_3H)$. Got by heating with H_2SO_4 (20 pts.) at 100°. Yields a crystalline BaA'_2 aq.

Reference.—HEXA-BROMO-DITHIENYL.

THIENYL-ACETIC ACID $C_4H_3S.CH_2.CO_2H$. [76°]. Formed from $C_4H_3S.CH(OH).CO_2H$ [115°], HIAq, and P (Ernst, *B.* 19, 3281). Crystalline, sol. hot water, alcohol and ether.—$Ba'A_2$ (dried at 130°). Crystals.—AgA': pp.

Reference.—OXY-THIENYL-ACETIC ACID.

THIENYL-ACRYLIC ACID $C_7H_6SO_2$ *i.e.* $C_4H_3S.CH{:}CH.CO_2H$. [138°]. Formed by boiling thiophenic aldehyde with NaOAc and Ac_2O (Biedermann, *B.* 19, 1855). Needles (from water), sol. hot water and alcohol. $FeCl_3$ gives an amorphous orange pp.—AgA': white pp.

THIENYLAMINE *v.* AMIDO-THIOPHENE.

THIENYL-BROMO-ETHANE *v.* BROMO-THIENYL-ETHANE.

THIENYL-BROMO-ETHYLENE *v.* BROMO-THIENYL-ETHYLENE.

THIENYL BROMO-METHYL KETONE $C_4H_3S.CO.CH_2Br$. *ω-Bromo-acetothienone.* Formed by adding Br (2 at.) to thienyl methyl ketone (1 mol.) dissolved in CS_2 (Brunswig, *B.* 19, 2891). Pungent yellow oil, may be distilled *in vacuo*. V. sol. alcohol and ether. Solidified by cold. Alcoholic NH_3 forms a deep-blue colour. Oxidised to (α)-thiophenic acid [126·5°]. Aniline yields $C_4H_3S.CO.CH_2NHPh$ [80°].

Thienyl di-bromo-methyl ketone $C_4H_3S.CO.CHBr_2$. [c. 0°]. Formed from thienyl methyl ketone and Br. Pungent oil, almost insol. ligroïn.

(β)-THIENYL-CARBINOL $C_4H_3S.CH_2OH$. (207° cor.). Formed by shaking (β)-thiophenic aldehyde with aqueous potash (Biedermann, *B.* 19, 639). Liquid. HCl forms $C_4H_3S.CH_2Cl$, a pungent oil boiling with partial decomposition at 175°.

THIENYL CHLORO-ETHANE *v.* CHLORO-THIENYL-ETHANE.

THIENYL-CHLORO-ETHYLENE *v.* CHLORO-THIENYL-ETHYLENE.

(α)-THIENYL CHLORO-METHYL KETONE $C_4H_3S.CO.CH_2Cl$. [47°]. (259° cor.). Formed by chlorination of thienyl methyl ketone (Peter, *B.* 18, 539). Pungent white crystals. Yields (α)-thiophenic acid on oxidation.

THIENYL-ETHYL-AMINE C_6H_9NS *i.e.* $C_4H_3S.CHMe.NH_2$. (186°). Got by reducing the oxim of thienyl methyl ketone in alcoholic solution by adding sodium-amalgam and HOAc (Goldschmidt a. Schulthess, *B.* 20, 1700). Liquid, sol. water. Absorbs CO_2 from the air.—B'HOAc. Needles, v. e. sol. water.

Benzoyl derivative. [95°]. Needles.

THIENYL ETHYL KETONE $C_4H_3S.CO.C_2H_5$. *Propiothienone.* (228° cor.). Formed from propionyl chloride, thiophene, and $AlCl_3$ (Krekeler, *B.* 19, 677). Liquid. Hot conc. H_2SO_4 forms propionic and thiophene (*a*)-sulphonic acids Chromic acid mixture yields (*a*)-thiophenic acid

Oxim $C_4H_3S.CEt{:}NOH$. [56°].

THIENYL DIETHYL PHOSPHINE $(C_4H_3S)PEt_2$. (225°). Formed from thienyl-chloro-phosphine and $ZnEt_2$ in ether (Sachs, *B.* 25, 1517).

Ethylo-iodide $(C_4H_3S)PEt_3I$.

Methylo-iodide $(C_4H_3S)PEt_2MeI$. [122°]. White powder, v. sol. water insol. ether.

THIENYL-GLYCOLLIC ACID *v.* Oxy-thienyl-acetic acid.

(*a*)-THIENYL-GLYOXYLIC ACID $C_6H_4SO_3$ aq *i.e.* $C_4H_3S.CO.CO_2H$. [91°]. Formed by oxidising thienyl methyl ketone with alkaline $KMnO_4$ (Peter, *B.* 18, 537; Biedermann, *B.* 19, 637; Bradley, *B.* 19, 2115). Formed also, together with thiophene (*a*)-carboxylic acid, by oxidation of (*a*)-ethyl-thiophene by alkaline $KMnO_4$. Crystals (containing aq, possibly as $C_4H_3S.C(OH)_2.CO_2H$), v. sol. warm water. Melts at 59° when hydrated. May be extracted by ether, from its aqueous solution. If a drop of crude benzene, followed by H_2SO_4, be added to its solution in HOAc, a brown colour is formed, which on addition of more H_2SO_4 passes through blue-green, green, violet, red, and bluish-violet to blue.

Reactions.—1. On heating it splits up into CO_2 and thiophenic aldehyde.—2. On heating with di-methyl-aniline and $ZnCl_2$ it yields the leuco-base of a green dye $C_4H_3S.CH(C_6H_4NMe_2)_2$.—3. PCl_5 forms thiophenic chloride.

Salts.—BaA'_2 aq. Slender efflorescent needles, v. sol. water.—CaA'_2 2aq.—CuA'_2 2aq.—ZnA'_2 2aq.—AgA' aq: amorphous pp., probably $C_4H_3S.C(OH)_2.CO_2Ag$.

Methyl ether MeA'. [28·5°].

Ethyl ether EtA'. (265° uncor.). Oil.

Amide $C_4H_3S.CO.CO.NH_2$. [88°]. Needles, almost insol. water, v. sol. alcohol and ether.

Oxim $C_4H_3S.C(NOH).CO_2H$. [146°]. (Hantzsch, *B.* 24, 48). Slender white needles. Exhibits Liebermann's reaction (Bradley, *B.* 19, 2119).—$BaA'_2\,1\frac{1}{2}$aq.—AgA': amorphous pp.—MeA' [105°]. Converted by NaOMe and MeI into liquid $C_4H_3S.C(NOMe).CO_2Me$.—EtA'. [123°]. Needles.

Acetyl derivative of the oxim. [87°].

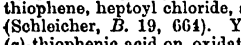
Phenyl-hydrazide $C_4H_3S.C(N_2HPh).CO_2H$. [165°]. Deep-yellow needles (from ether).

Reference.—Nitro-thienyl-glyoxylic acid.

THIENYL HEXYL KETONE $C_{11}H_{16}SO$ *i.e.* $C_4H_3S.CO.C_6H_{13}$. (304° cor.). Formed from thiophene, heptoyl chloride, and $AlCl_3$ in ligroïn (Schleicher, *B.* 19, 664). Yellow oil, yielding (*a*)-thiophenic acid on oxidation. Conc. H_2SO_4 forms thiophene (*a*)-sulphonic and heptoic acids.

Oxim [49°]. Crystals (from alcohol).

THIENYL-INDOLE $C_{12}H_9NS$ *i.e.*


$C_6H_4{<}\begin{matrix}CH\\NH\end{matrix}{>}C.C_4H_3S$. [162°]. Formed by heating the phenyl-hydrazide of thienyl methyl ketone with $ZnCl_2$ (Brunck, *A.* 272, 201). Light-yellow needles, insol. water, v. sol. ether, m. sol. alcohol. Colours pine-wood, moistened with HCl, bluish-violet. Yields $C_{12}H_3Br_6NS$ [278°] and $C_6H_5CH(C_{12}H_8NS)_2$ [245°].—$B'C_6H_3N_3O_7$ [187°]. Dark red plates, v. sol. alcohol.

Nitrosamine $C_{12}H_8(NO)NS$. [241°].

DI-THIENYL KETONE $(C_4H_3S)_2CO$. [88°]. (326° uncor.). Formed from thiophene, $COCl_2$, and $AlCl_3$. Obtained also by distilling calcium *a*-thiophenate (Gattermann, *B.* 18, 3012). Needles or plates, sol. alcohol.

Phenyl-hydrazide [137°].

THIENYL MERCAPTAN $(C_4H_3S).SH$. (166°). Got by reducing thiophene (*a*)-sulphinic acid with zinc and HClAq (Biedermann, *B.* 19, 1616). Got also in small quantity from succinic acid and P_2S_5 (V. Meyer a. Neure, *B.* 20, 1757). Stinking oil, volatile with steam.—$AgS.C_4H_3S$.

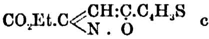
Acetyl derivative $(C_4H_3S).SAc$. (231°).

Methyl ether $(C_4H_3S)SMe$. (186°).

DI-THIENYL METHANE $C_9H_8S_2$ *i.e.* $CH_2(C_4H_3S)_2$. (267°). Got by adding H_2SO_4 to a solution of thiophene and methylal in HOAc (Peter, *B.* 17, 1345). Oil, smelling like oranges. Volatile with steam. Gives a red colour with isatin and H_2SO_4.

(*a*)-THIENYL METHYL KETONE C_6H_6SO *i.e.* $C_4H_3S.CO.CH_3$. *Acetothienone.* (213° cor.). S.G. $\frac{24}{24}$ 1·167. Formed from thiophene, AcCl, and $AlCl_3$ (Peter, *B.* 17, 2643; Biedermann, *B.* 19, 636; Bradley, *B.* 19, 2115). Formed also from $C_4H_3(HgCl)S$ and AcCl (Volhard, *A.* 267, 178). Liquid, smelling like acetophenone. Gives a blue colour with isatin and H_2SO_4. Oxidised by $KMnO_4$ to (*a*)-thienyl-glyoxylic and thiophenic acids. Mercuric chloride and NaOAc form the compound $(CH_3.CO.C_4H_3S)HgCl_2$ crystallising in white needles. Oxalic ether (1 mol.) and NaOEt give $C_4H_3S.CO.CH_2.CO.CO_2Et$ [42°], which forms large yellow crystals, converted by boiling alcoholic hydroxylamine hydrochloride into the compound

$C_4H_3S.C{<}\begin{matrix}CH{:}C.CO_2Et\\N\ .\ O\end{matrix}$ or


$CO_2Et.C{<}\begin{matrix}CH{:}C.C_4H_3S\\N\ .\ O\end{matrix}$ crystallising in colourless needles [48°] (Angeli, *B.* 24, 232).

Oxim $C_6H_6S(NOH)$. [112°].

Phenyl-hydrazide $C_6H_6S(N_2HPh)$. [96°].

Reference.—Bromo-, Chloro-, Iodo-, and Nitro-thienyl methyl ketone.

THIENYL PHENYL - AMIDO - METHYL KETONE $C_4H_3S.CO.CH_2.NHPh$. [80°]. Formed by mixing $C_4H_3S.CO.CH_2Br$ with aniline in alcohol (Brunswig, *B.* 19, 2892). Plates. Yields a nitrosamine $C_4H_3S.CO.CH_2.NPh(NO)$ [81°], and acetyl derivative $C_4H_3S.CO.CH_2.NPhAc$ [142°].

THIENYL PHENYL KETONE $C_4H_3S.CO.C_6H_5$. [55°]. (c. 300°). Formed by the action of $AlCl_3$ on a mixture of thiophene and BzCl (Comey, *B.* 17, 790). Formed also by heating $C_4H_3(HgCl)S$ with BzCl at 100° (Volhard, *A.* 267, 179). Long needles (from dilute alcohol), insol. water. Gives a blue colour on heating with isatin and H_2SO_4. Yields thiophene and benzoic acid on heating with soda-lime.

Oxims $C_4H_3S.CPh{:}NOH$. Hydroxylamine forms two stereo-isomeric (?) oxims [93°] and [114°] (Hantzsch, *B.* 23, 2332; 24, 59).

THIENYL-PHENYL-METHANE $CH_2Ph.C_4H_3S$. (265°). Formed by the action of H_2SO_4 on a mixture of thiophene and benzyl alcohol dissolved in HOAc (Peter, *B.* 17, 1346). Liquid with fruity smell, volatile with steam. Gives a red colour with isatin and H_2SO_4.

Thienyl-di-phenyl-methane $CHPh_2.C_4H_3S$. [63°]. (330°-340°). Formed from thiophene, di-phenyl-carbinol, and P_2O_5 (Levi, *B.* 19, 1624).

Plates (from alcohol) or needles (from ligroïn), v. sol. HOAc, alcohol, and ether. Crystallises from cold benzene in needles $C_{17}H_{14}SC_6H_6$ [48°].

THIENYL ISOPROPYL KETONE $C_4H_3S.CO.CHMe_2$. (232° cor.). Formed from isobutyryl chloride, thiophene, and $AlCl_3$ (Krekeler, *B.* 19, 675). Liquid. Yields (*α*)-thiophenic acid on oxidation. Fuming H_2SO_4 reacts with formation of the sulphonic acid $C_4H_2(SO_3H)S.CO.CHMe_2$, which yields the salts BaA'_2, PbA'_2xaq, and is converted by phenyl-hydrazine into $C_4H_2(SO_3N_2H_4Ph)S.C(N_2HPh).CHMe_2$, crystallising from hot water in plates.

Oxim $C_4H_3S.C(NOH).CHMe_2$. [108°]. Pearly plates (from dilute alcohol).

THIENYL STYRYL KETONE *v.* STYRYL THIENYL KETONE.

THIENYL DISULPHIDE $(C_4H_3S)_2S_2$. [56°]. Formed by atmospheric oxidation of a solution of thienyl mercaptan in alcoholic NH_3 (Meyer a. Neure, *B.* 20, 1757). Needles.

THIENYL SULPHOCYANO - METHYL KETONE $CH_2(SCy).CO.C_4H_3S$. [88°]. Formed from $CH_2Br.CO.C_4H_3S$ and KSCy in alcohol (Brunswig, *B.* 19, 2893). Plates (from ether), sl. sol. water and ligroïn, m. sol. alcohol.

DI-THIENYL-THIOPHENE $C_4SH_2(C_4SH_3)_2$. [147°]. (357°). V.D. 8·6. One of the products of the passage of benzene and sulphur-vapour through a red-hot tube (Renard, *C. R.* 112, 49). Yellowish needles (from alcohol), m. sol. benzene. H_2SO_4 forms a rose-coloured solution, turned violet and finally blue on heating. Fuming H_2SO_4 at 120° forms a trisulphonic acid, which yields $(C_{12}H_5S_3(SO_3)_3)_2Ca_3$ as an amorphous powder, v. sol. water. Fuming HNO_3 at 160° forms $C_{12}H_8S_2O_4$ [313°], crystallising in white plates, v. sl. sol. benzene. Br forms $C_{12}H_5Br_3S_3$ [282°], and amorphous $C_{12}H_8Br_6S_3$.

THIENYL TOLYL KETONE $C_{12}H_{10}SO$ *i.e.* $C_6H_4Me.CO.C_4H_3S$. Formed from *o*-toluic chloride, thiophene, and $AlCl_3$ (Ernst, *B.* 19, 3279). Oil. Yields an oily oxim.

THIO-. This prefix is employed to denote the replacement of O by S. Most inorganic salts of thio- acids are described under the heading of the oxy-salts; thus *thio-carbonates* are described under CARBONATES. In some cases thio- salts are described under the heading of the characteristic element of the salts: *thio-arsenates* are to be found under ARSENIC. Certain thio -salts are described under headings placed in their strictly alphabetical position; for instance, THIOSULPHATES. *Thiocyanides* are described as SULPHOCYANIDES.

The following addition should be made to the sub-article THIO-OXYORTHOPHOSPHATES (p. 147). By heating metallic chlorides or sulphides with excess of P_2S_5 Glatzel has prepared a number of *tetrathio-oxyorthophosphates, i.e.* salts of the hypothetical acid H_3PS_4 (*Zeit. für anorg. Chemie*, 4, 186). These salts are crystalline—generally green to black in colour; they are burnt in air, giving off SO_2; some are decomposed to sulphides and P_2S_5, but the mercuric and arsenic salts distil unchanged when heated out of contact with air. These salts are insol. in dilute acids; they are decomposed by strong acids. G. isolated the thiophosphates of Sb, As, Bi, Cd, Cu(ous), Fe(ous), Pb, Mn, Hg(ic), Ni, Ag, Tl, Sn(ous), and Zn; he could not obtain the salts of Ca, K, Na, or Sr.

M. M. P. M.

THIOACETAMIDE $CH_3.CS.NH_2$. [108°]. Formed from acetonitrile and H_2S (Bernthsen, *A.* 192, 46), and from acetamide and P_2S_5 (Hofmann, *B.* 11, 340). Monoclinic plates, v. sol. water and alcohol, m. sol. ether. HgO forms HgS. $AgNO_3$ gives Ag_2S. $CuSO_4$ and $Pb(OAc)_2$ give, on boiling, CuS and PbS. $HgCl_2$ forms a crystalline compound. α-bromo-acetoacetic ether forms $CH_3.C(NH).S.CH_2.CO.CH_2.CO_2Et$ [94°], and finally $S{<}\begin{matrix}CMe{:}N\\CH{:}C.CH_2.CO_2Et\end{matrix}$ (239°), the ether of methyl-thiazyl-acetic acid [121°] (Steude, *A.* 261, 36). The ether melting at 94° is converted by warming with water into the compound $CH_3.CO.S.CH_2.CO.CH_2.CO_2Et$ (155° at 15 mm.), whence H_2SO_4 forms an acid $C_6H_8SO_2$ [168°].

THIO-ACETIC ACID C_2H_4SO *i.e.* $CH_3.CO.SH$. Mol. w. 76. (93°). S.G. ^{10} 1·074. Prepared by distilling acetic acid with P_2S_5 (Kekulé, *A.* 90, 311; Ulrich, *A.* 109, 272; Kekulé a. Linnemann, *A.* 123, 273). Obtained also from AcCl and KSH (Jacquemin a. Vosselmann, *J.* 1859, 354), by heating lead acetate with $Na_2S_2O_3$ (Fröhde, *Z.* 1866, 543), and by the action of KSH on an alcoholic solution of PhSAc (Kekulé, *Z.* [2] 3, 196). Colourless liquid, turning yellow on keeping. Smells like acetic acid and H_2S. Not solid at −17°. M. sol. warm water, v. sol. alcohol and ether. Violently attacked by fuming HNO_3. PCl_5 yields AcCl, $PSCl_3$ and HCl. Its neutral solutions give pps. with $AgNO_3$ and $HgCl_2$, which quickly turn black. Molten $ZnCl_2$ forms $CMe{:}S_3{:}CMe$ [225°], which may be crystallised from hot alcohol (Bongartz, *B.* 19, 2182). HCl passed into a mixture of thio-acetic acid and benzoic aldehyde forms $(CH_3.CO.S)_2CHPh$ [148°], crystallising from hot ether in slender needles.

Salts.—KA'. Crystals, v. sol. water and alcohol.—NaA' ½aq.—BaA'_2 3aq.—SrA'_2 2aq.—CaA'_2 2aq.—PbA'_2. Silky needles (from hot water or alcohol). Quickly decomposes, with separation of PbS.

Methyl ether MeA'. (96°). Formed by heating AcBr with Me_2S at 100° (Cahours, *Bl.* 25, 562; Wallach a. Bleibtreu, *B.* 12, 1062). Formed also from AcCl and $Pb(SMe)_2$ (Obermeyer, *B.* 20, 2920).

Ethyl ether EtA'. (116° i.V.). Formed from AcCl and NaSEt (Saytzeff, *Z.* [2] 4, 642; Beckmann, *J. pr.* [2] 17, 461). Formed also from PhOAc and NaSEt (Seiffert, *J. pr.* [2] 31, 468). Colourless liquid, with alliaceous odour. Oxidised by $AgMnO_4$ to acetic acid and ethane sulphonic acid.

n-Propyl ether PrA'. (136°).

Isopropyl ether PrA'. (126°).

Isobutyl ether CH_2PrA'. (149°).

Anhydride v. ACETYL SULPHIDE.

Thio-acetic acid $CH_3.CS.OH$.

Amide v. THIOACETAMIDE.

Anilide $CH_3.CS.NHPh$. [75°]. Formed from $CH_3.CCl{:}NPh$ and H_2S (Leo, *B.* 10, 2134). Prepared by heating acetanilide with P_2S_5 at 100° (Hofmann, *B.* 11, 339; Jacobsen, *B.* 19, 1071). Yellowish needles (from water). Sol. NaOHAq and reppd. by acids. On oxidation with alkaline K_3FeCy_6 it yields ethenyl-amido-phenyl mercaptan. MeI forms C_8H_8NSMeI or $(CH_3.CS.NPhMe)HI$ [139°], which yields an aqueous solution from which $AgNO_3$ at once ppts. AgI, and which is converted by AgCl into $C_8H_9NSMeCl$, whence $(C_8H_9NSMeCl)_2PtCl_4$ may be got (Bernthsen, *A.* 192, 56). NaOEt forms $CH_3.C(SNa):NPh$, whence MeI yields the ether $CH_3.C(SMe):NPh$ (245°) (Wallach a. Bleibtreu, *B.* 12, 1061; 13, 529), which is decomposed by MeI at 100° into methyl thioacetate and methylaniline. NaOEt and EtBr yield the corresponding $CH_3.C(SEt):NPh$, a heavy oil, insol. alkalis, split up by warm HClAq into thioacetic ether and aniline. 'Ethyl-iso-thioacetanilide' yields $(C_{10}H_{13}NS)_2H_2PtCl_6$.

Methyl anilide $CH_3.CS.NMePh$. [59°]. (290°). Formed from AcNMePh and P_2S_5 (Wallach, *B.* 13, 528). Monoclinic tables, v. sol. alcohol.

o-Toluide $CH_3.CS.NHC_7H_7$. [68°]. Yields $CH_3.C(SEt):NC_6H_4Me$ (262°), an oil which reacts with bases forming amidines and EtSH.

p-Toluide [132°]. Yields oily $CH_3.C(SEt):NC_7H_7$. (273°) (Wallach a. Wüsten, *B.* 16, 147).

Xylidide $CH_3.CS.NHC_6H_3Me_2$. [80°] (G.); [95°] (Jacobsen). Formed by heating acetylxylidine with P_2S_5 on the water-bath (Gudeman, *B.* 21, 2551).

ψ-Cumidide $CH_3.CS.NHC_6H_2Me_3$. [114°]. Prisms (Jacobsen a. Elley, *B.* 22, 907).

(α)-*Naphthalide* $CH_3.CS.NHC_{10}H_7$. [96°]. Tables. Formed from naphthyl-acetamidine and CS_2 (Bernthsen a. Trompetter, *B.* 11, 1760).

(β)-*Naphthalide.* [146°]. Needles or plates (Jacobsen, *B.* 21, 2627). Oxidised by K_3FeCy_6 to $C_{10}H_6{<}\begin{matrix}N\\S\end{matrix}{>}CMe$ [81°].

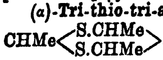
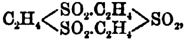
Tri-thio-ortho-acetic acid $CH_3.C(SH)_3$.

Ethyl ether $CH_3.C(SEt)_3$. Formed from mercaptan, $CHCl_3$, and NaOH at 100° (Laves, *B.* 25, 354). Brownish liquid. Oxidised by $KMnO_4$ and H_2SO_4 to the trisulphone.

Benzyl ether $CH_3.C(SC_7H_7)_3$. [46°]. Formed from benzyl mercaptan, $CHCl_3$, and (2 p.c.) NaOHAq (Laves). Crystals, v. sol. $CHCl_3$, m. sol. alcohol.

THIO-ACETIC ALDEHYDE. On passing H_2S into an aqueous solution of aldehyde, crude thioacetic aldehyde separates as an oil, which solidifies at −8°, and then melts at −2°. This oil [V.D. 60 (H = 1)] is a mixture of thioacetic aldehyde and its polymerides, and may be represented, in a state of vapour, as $C_2H_4S + C_6H_{12}S_3$ (Pinner, *B.* 4, 258; Klinger, *B.* 9, 1893; 10, 1877; 11, 1023). On distillation, or on passing HCl through the liquid, it is converted into the polymeric tri-thio-tri-acetic aldehyde.

Tri-thio-tri-acetic aldehyde $C_6H_{12}S_3$. Mol. w. 180. [46°]. V.D. 89·7 (calc. 90) (Hofmann, *B.* 3, 589; *Z.* [2] 6, 699). Formed by passing H_2S into an acid solution of aldehyde (Klinger; *cf.* Weidenbusch, *A.* 66, 152; Crafts, *C. R.* 54, 1279). Formed also from paraldehyde and H_2S. White needles, sol. alcohol and ether. Smells like garlic. $AgNO_3$ added to its alcoholic solution forms crystalline $C_6H_{12}S_3 2AgNO_3$. Chlorine forms ethylidene chloride (Pinner, *A.* 179, 21). $KMnO_4$ oxidises it to $CH_3.CH(SO_3H)_2$ and oxysulphides, including $C_6H_{12}S_3O_6$ [217°], which crystallises from hot water in needles (Guareschi, *A.* 222, 301). Zinc permanganate produces $C_6H_{12}S_3O_6$, which does not melt below 245°, $C_6H_{12}S_3O_2$ [112°–116°], and $C_6H_{12}S_3O_4$ [228°–231°] (*cf.* Baumann, *B.* 26, 2074).

(α)-**Tri-thio-tri-acetic aldehyde** $C_6H_{12}S_3$ *i.e.*  $CHMe{<}\begin{matrix}S.CHMe\\S.CHMe\end{matrix}{>}S$. [102°]. (247°). V.D. 6 (air = 1). Formed by the long-continued action of H_2S on a mixture of equal parts of water, conc. HClAq and aldehyde. Long prisms (from acetone). Reduced by HI to Et_2S_2. Oxidised by $KMnO_4$ to $C_6H_{12}S_3O_4$ [284°] (S. 1 at 100°; ·116 at 20°), and $C_6H_{12}S_3O_6$ or  $C_2H_4{<}\begin{matrix}SO_2.C_2H_4\\SO_2.C_2H_4\end{matrix}{>}SO_2$, which softens at 340° and is converted by MeI into $C_9H_{18}S_3O_6$ [302°]. Yields crystalline $C_6H_{12}S_3AgNO_3$ and $C_6H_{12}S_3 3AgNO_3$.

(β)-**Tri-thio-tri-acetic aldehyde** $C_6H_{12}S_3$. [126°]. (247°). V.D. 6·0. Formed by the action of AcCl or H_2SO_4 on its (α)-isomeride. Prepared by passing H_2S into a mixture of aldehyde (1 pt.) and alcohol previously saturated with HCl (3 pts.) (Baumann a. Fromm, *B.* 22, 2600; 26, 2074). Long needles (from alcohol). Oxidised by $KMnO_4$ to the same sulphones as the (α)-isomeride. Reacts with MeI, yielding SMe_3I. Distillation with Cu forms ψ-butylene. Forms crystalline $C_6H_{12}S_3AgNO_3$ and $C_6H_{12}S_3 3AgNO_3$.

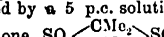
(γ)-**Tri-thio-acetic aldehyde** $C_6H_{12}S_3$. [76°]. (242°). Formed, together with $C_5H_9NS_3$, by boiling thialdine sulphocyanide with water (Marckwald, *B.* 19, 1827; 20, 2817). Needles (from alcohol), insol. water, v. sol. ether and CS_2. Volatile with steam. Sol. conc. H_2SO_4 and reppd. by water. When mixed with EtI (4 pts.) and left for some weeks it suddenly changes to a crystalline mass of the (β)-isomeride. $C_6H_{12}S_3 3AgNO_3$. Plates, v. sol. water. Yields Ag_2S on boiling with alcohol.

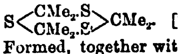
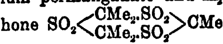
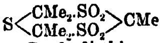
'**Di-thialdehyde thiocarbimide**' $C_5H_9NS_3$. [138°]. Formed as above. Needles, m. sol. ether. Yields $C_5H_9NS_3AgNO_3$ v. sol. water, and $(C_5H_9NS_3)_2PtCl_4$.

Di-thio-acetic orthoaldehyde. *Ethyl ether* $CH_3.CH(SEt)_2$. Formed by passing HCl into a mixture of acetic aldehyde and EtSH (Baumann, *B.* 18, 884). Mobile oil.

THIOACETIC ANHYDRIDE *v.* ACETYL SULPHIDE.

THIO-ACETONE $CH_3.CS.CH_3$. A product of the action of H_2S on acetone, and formed also when $CMe_2(SEt)_2$ is heated above 160° (Baumann a. Fromm, *B.* 22, 2592). Volatile oil, with very persistent and disagreeable smell. Unstable.

Duplo-thioacetone $C_6H_{12}S_2$ *i.e.* $S{<}\begin{matrix}CMe_2\\CMe_2\end{matrix}{>}S$. V.D. 5·08 (calc. 5·11). (184° cor.). Formed by heating acetone with P_2S_5 at 125° (Wislicenus, *Z.* [2] 5, 324; Autenrieth, *B.* 20, 375). Formed also by heating tri-thio-tri-acetone at 200° for some time (Fromm a. Baumann, *B.* 22, 1043). Oil. Its alcoholic solution gives a white pp. with $HgCl_2$. Reduced by sodium-amalgam to isopropyl mercaptan (Spring, *Bl.* [2] 40, 69). Oxidised by a 5 p.c. solution of $KMnO_4$ to the disulphone  $SO_2{<}\begin{matrix}CMe_2\\CMe_2\end{matrix}{>}SO_2$ [220°–225°].

Tri-thio-tri-acetone $C_9H_{18}S_3$ *i.e.*  $S{<}\begin{matrix}CMe_2.S\\CMe_2.S\end{matrix}{>}CMe_2$. [24°]. (130° at 15 mm.). Formed, together with $C_{13}H_{28}S_4$ [171°], by passing H_2S into a cooled mixture of acetone and conc. HClAq (Fromm a. Baumann, *B.* 22, 1037, 2597). Needles (from alcohol); insol. water, v. sol. alcohol and ether. Boils, with much decomposition, at 225°-230°. Gives a white pp. with $HgCl_2$ and a yellow pp. with lead acetate. Potassium permanganate and H_2SO_4 yield the trisulphone  $SO_2<\begin{matrix}CMe_2.SO_2\\CMe_2.SO_2\end{matrix}>CMe_2$ [302°] and  $S<\begin{matrix}CMe_2.SO_2\\CMe_2.SO_2\end{matrix}>CMe_2$ [208°].

Duplo-di-thio-acetone $(Me_2CS_2)_2$. [98°]. (c. 243°). Formed from acetone and yellow ammonium sulphide in the cold (Willgerodt, *B.* 20, 2467). Dimetric crystals, *a*:*c* = 1: ·868, insol. water. Partially decomposed on distillation.

Di-thio-orthacetone. *Di-ethyl ether* $CMe_2(SEt)_2$. *Acetone-ethyl-mercaptol.* (191°). Formed by passing dry HCl into a mixture of acetone (1 pt.) and mercaptan (2 pts.) (Baumann, *B.* 18, 887). Liquid.

Di-phenyl ether $CMe_2(SPh)_2$; *v.* DI-PHENYL-PROPYLIDENE DISULPHIDE.

THIOACETONURAMIC ACID *v.* ACETONYL THIOCARBAMATE.

THIO-ACETOPHENONE $C_6H_5.CS.CH_3$. [119·5°]. Formed by the action of alcoholic ammonium sulphide on acetophenone (Engler, *B.* 11, 930). Colourless leaflets or needles, insol. water, sl. sol. alcohol, v. sol. ether. May be sublimed.

THIO-ACETYL-TOLUIDINE *v.* *Toluide of* THIO-ACETIC ACID.

THIO-ALLOPHANIC ACID. *Ethyl ether* $C_4H_8N_2SO_2$ *i.e.* $NH_2.CO.NH.CO.SEt$. [180°]. Formed by heating urea with Cl.CO.SEt at 80°-90° (Peitzsch a. Salomon, *J. pr.* [2] 7, 477). Pearly needles (from water), v. sl. sol. cold water and alcohol. Aqueous NH_3 at 100° forms biuret and mercaptan. Boiling baryta-water gives allophanic acid and mercaptan. Aniline yields di-phenyl-biuret and mercaptan.

Isoamyl ether $NH_2.CO.NH.CO.SC_5H_{11}$. [176°]. Needles (Schöne, *J. pr.* [2] 32, 251). AcCl yields an acetyl derivative [85°].

Phenyl ether [218°] (Gattermann, *A.* 244, 43).

Isothio-allophanic ether $NH_2.CS.NH.CO_2Et$. [170°-175°]. Formed by the action of thio-urea on $COCl.CO_2Et$ (Peitzsch, *B.* 7, 896). Prisms (from alcohol).

Di-thio-allophanic ether $NH_2.CS.NH.CO.SEt$. Formed from KSCy, alcohol, and HCl (Blankenhorn, *J. pr.* [2] 16, 358). Pearly prisms, insol. cold water, sol. hot ether. Alcoholic NH_3 at 150° forms thio-urea. Baryta-water yields mercaptan, CO_2, and thio-urea.

DI-THIO-AMMELIDE $C_3H_4N_4S_2$ *i.e.* $C_3N_3(NH_2)(SH)_2$. S. ·3 at 100°. Formed by boiling pseudosulphocyanogen $C_3HN_3S_3$ with KSH or ammonium sulphide solution (Jamieson, *A.* 59, 339; Ponomareff, *J. R.* 8, 222). Small needles, nearly insol. cold water, alcohol and ether, v. sol. aqueous ammonium sulphocyanide. Acid in reaction, decomposing carbonates.

Reactions.—1. Yields cyanuric acid when heated with HClAq.—2. NH_3Aq forms melamine $C_3H_6N_6$ by heating in a sealed tube.

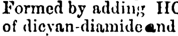
Salts.—$NaHA''1\frac{1}{2}aq$. Tables.—$KHA''2aq$. White prisms, v. e. sol. water and alcohol.—$MgH_2A''_2 6aq$.—$CaH_2A''_2 2aq$.—$BaH_2A''_2 5aq$.—$BaH_2A''_2 6aq$. Monoclinic crystals, sl. sol. cold water.—$SrH_2A''_2 4aq$.—$AgHA''$. Flocculent pp., insol. water.

Methyl ether $C_3N_3(NH_2)(SMe)_2$. [200°]. Formed by heating $C_3N_3(SMe)_3$ with alcoholic NH_3 for five hours at 100° (Hofmann, *B.* 18, 2756). Trimetric tables, v. sl. sol. water, v. sol. alcohol. Boiling conc. HClAq forms MeSH, cyanuric acid, and NH_3.—$B'HAuCl_4$. Needles.

Ethyl ether Et_2A''. [112°]. Formed by heating tri-thio-cyanuric ether with alcohol NH_3 at 180° (Klason, *J. pr.* [2] 33, 298). Trimetric prisms. Converted by acids into ammelide.

Isoamyl ether $(C_5H_{11})_2A''$. [82°].

Di-thio-methyl-ammelide *di-methyl ether* $Cy_3(NHMe)(SMe)_2$. [175°]. Formed by heating $Cy_3(SMe)_3$ with aqueous $NMeH_2$ (Hofmann, *B.* 18, 2761). Needles or prisms (from dilute alcohol).

THIO-AMMELINE $C_3H_5N_5S$ *i.e.*  $C(SH)<\begin{matrix}N.C(NH_2)\\N:C(NH_2)\end{matrix}>N$. S. ·77 at 100° (K.). Formed by adding HCl to an aqueous solution of dicyan-diamide and ammonium sulphocyanide at 100° (Rathke, *B.* 18, 3106; 20, 1059; 23, 1675). Formed also from $C_3N_3(NH_2)_2Cl$ and KSH (Klason, *J. pr.* [2] 33, 296) and by heating ψ-sulphocyanogen with conc NH_3Aq at 100° (Ponomareff, *C. R.* 80, 1384). Needles, sl. sol. hot water, v. sol. acids and alkalis. Yields a canary-yellow pp. on boiling with ammoniacal $CuSO_4$. Conc. HClAq at 130° yields cyanuric acid, H_2S, and NH_3. Ethylene bromide forms crystalline $C_5H_7N_5SHBr$. Conc. NH_3Aq at 200° forms melamine. Boiling NaOHAq yields ammeline. Ammoniacal silver nitrate ppts. $C_3H_4N_5SAg$ and $C_3H_3N_5SAg_2$. Bromine added to a solution of thio-ammeline in HBrAq forms $S_2(C_3N_3(NH_2)_2)_2$, which dissolves in alkalis, and is split up by boiling with acids into ammeline, thio-ammeline, and S.

Salts.—$B'HNO_3$. Needles.—$B'_2H_2SO_4 3aq$.—$B'_2H_2C_2O_4 aq$. Needles, v. sl. sol. cold water.

Methyl ether MeA'. [268°]. Formed by heating tri-methyl tri-thiocyanurate for five hours with conc. alcoholic NH_3 at 160° (Hofmann, *B.* 18, 2757). Tables (from water).—$B'_2H_2PtCl_6$.

Ethyl ether EtA'. [165°].

Isoamyl ether $C_5H_{11}A'$. [178°].

Reference.—TRI-PHENYL-THIO-AMMELINE.

THIO-ANILINE *v.* DI-AMIDO-DI-PHENYL SULPHIDE.

THIOANISOIC ACID (so called) $C_{10}H_{14}SO_4$. Got by boiling anethol with HNO_3 (S.G. 1·1), distilling the product and shaking the fraction 215°-245° with conc. $NaHSO_3Aq$ and some alcohol (Städeler a. Wächter, *A.* 116, 163). Crystalline (containing 2aq), v. e. sol. water, alcohol, and ether.—$NH_4A'aq$.—$NaA'aq$. S. 15 in the cold.—$BaA'_2 3aq$. S. 8·5 in the cold.—$CaA'_2 2aq$.—$MgA'_2 5aq$.—AgA'. Plates, m. sol. water.

THIOBENZAMIDE *v.* *Amide* of THIOBENZOIC ACID.

(*a*)-**THIO-BENZOIC ACID** $C_6H_5.CO.SH$. Mol. w. 138. [c. 24°].

Formation.—1. From BzCl and alcoholic K_2S (Engelhardt a. Latschinoff, *Z.* [2] 4, 353).—2. By boiling EtOBz, PhOBz, and Bz_2O with alcoholic KSH.

Properties.—Yellow oil or white crystalline mass with unpleasant smell, volatile with steam. Decomposed by distillation. V. sol. alcohol and ether. Its solutions, when exposed to air, deposit crystals of Bz_2S_2. Nitric acid also oxidises it to benzoyl disulphide. A neutral solution gives with $CuSO_4$ a greenish-yellow pp., turning bright red; the pp. then containing Bz_2S_2.

Salts.—KA'. Large prisms (from alcohol), v. sol. water.—NaA'.—BaA'_2*x*aq. Laminæ (from alcohol).—PbA'_2.—AgA'. Yellowish-white pp.

Methyl ether C_6H_5.COSMe. (232°). Formed from $Pb(SMe)_2$ and BzCl (Obermeyer, *B.* 20, 2922).

Ethyl ether EtA'. (243°). Formed by the action of BzCl on $Pb(SEt)_2$ in presence of ether (Tütscheff, *Petersb. Acad. Bull.* 5, 295), and got also by boiling AgA' and EtI, and from PhOBz and NaSEt (Seiffert, *J. pr.* [2] 31, 471). Oil, with unpleasant smell, sol. alcohol and ether. Boiling alcoholic KOH forms KOBz and KSEt. Alcoholic KSH yields KSBz and KSEt. Oxidised by $AgMnO_4$ to benzoic and ethane sulphonic acids (Beckmann, *J. pr.* [2] 17, 464).

Isoamyl ether $C_5H_{11}A'$. (271°).

Phenyl ether PhS.Bz. [56°]. Formed from phenyl mercaptan and BzCl (Schiller a. Otto, *B.* 9, 1635). Needles (from benzene).

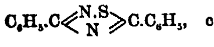
Di-nitro-phenyl ether $C_6H_3(NO_2)_2A'$. [118°]. Formed from (α)-chloro-*m*-di-nitrobenzene, alcoholic KSH, and BzCl (Willgerodt, *B.* 18, 328). Needles (from alcohol).

Benzyl ether C_7H_7A'. [39·5°]. Formed from benzyl mercaptan and BzCl (Otto a. Lüders, *B.* 13, 1285). Triclinic crystals, yielding $PhCH_2.SO_3H$ on oxidation.

p-Tolyl ether C_7H_7A'. [75°] (S. a. O.).

Anhydride v. BENZOYL SULPHIDE.

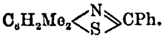
(β)-Thio-benzoic acid C_6H_5.CS.OH. Formed by boiling thiobenzoic aldehyde with nitric acid (S.G. 1·3) (Fleischer, *A.* 140, 234). Needles (containing ½aq), sol. alcohol and benzene. More sol. hot water than benzoic acid. When heated strongly it blackens without melting.—BaA'_2 4aq. Small nodules, v. sol. water and ppd. by alcohol.

Amide $C_6H_5.CS.NH_2$. *Thiobenzamide.* [116°]. Formed by passing H_2S into an alcoholic solution of benzonitrile containing a little NH_3, and heating on a water-bath (Cahours, *C. R.* 27, 329; Bernthsen, *B.* 10, 1241; *A.* 192, 49; Gabriel a. Heymann, *B.* 23, 157). Formed also by heating benzylamine (2 mols.) with S (1 mol.) at 180° (Wallach, *A.* 259, 304). Long needles (from hot water). Decomposed by HgO, yielding HgS and benzonitrile. Sodium-amalgam acting on its alcoholic solution forms amorphous thiobenzoic aldehyde, benzonitrile, benzylamine, and benzoic aldehyde. Iodine added to its alcoholic solution reacts with formation of di-benzenyl-azo-sulphim  $C_6H_5.C{<}\genfrac{}{}{0pt}{}{N.S}{N}{>}C.C_6H_5$, crystallising in long colourless needles [90°] converted by boiling H_2SO_4 into a base $C_{14}H_{14}N_2$ [71°], which yields $B'_2H_2PtCl_6$ (Hofmann, *B.* 2, 645; *B.* 25, 1587; Wanstrat, *B.* 6, 335). Zinc and HCl reduce thiobenzamide in alcoholic solution to benzylamine. Hydroxylamine forms $C_6H_5.C(NOH).NH_2$. Ethylene bromide at 100° forms the compound $C_2H_4(S.C(NH)C_6H_5)_2 2HBr$ [233°] decomposed by boiling water into $C_2H_4(SBz)_2$ (Gabriel a. Heymann, *B.* 24, 783). Chloral (1 mol.) forms, on warming, a compound $C_9H_8Cl_3NSO$ or $C_6H_5.CS.NH.CH(OH).CCl_3$ (?) crystallising in silky plates [104°], sl. sol. water, v. sol. alcohol (Spica, *G.* 16, 182).

Anilide C_6H_5.CS.NHPh or C_6H_5.C(SH):NPh. *Thiobenzanilide.* [102°]. Formed by the action of P_2S_5 (1 pt.) on benzanilide (2 pts.), and by heating phenyl-benzamidine or *s*-di-phenyl-benzamidine CPh(NPh)(NPhH) with H_2S or with CS_2 (Bernthsen, *B.* 11, 503; *A.* 192, 31). Formed also by passing H_2S into a solution of C_6H_5.CCl:NPh in benzene (Leo, *B.* 10, 2133), and from benzophenone oxim and P_2S_5 (Dodge, *A.* 264, 184). Obtained by heating benzyl-aniline (1 mol.) with S (2 at.) at 220° as long as H_2S escapes (Wallach, *A.* 259, 301). Thin prisms (from EtOAc), nearly insol. boiling water, v. sol. alcohol and ether. V. sol. KOHAq. Converted into benzanilide by heating with dry PbO or with alcoholic potash at 150°. Yields benzenyl-*o*-amido-phenyl-mercaptan on dry distillation, on heating with S, and also on treatment in alkaline solution with K_3FeCy_6 (Jacobsen, *B.* 19, 1068). Hydroxylamine yields C_6H_5.C(NOH).NHPh.

o-Toluide $C_6H_5.CS.NHC_6H_4Me$[1:2]. [86°]. Formed by melting $BzNHC_6H_4Me$ with P_2S_5 (Stieglitz, *B.* 22, 3160). Yellow, six-sided prisms (from benzene). Hydroxylamine in alcohol forms, on heating, $C_6H_5.C(NOH).NHC_7H_7$ [147°], crystallising in needles.

p-Toluide. [129°]. Formed in like manner (Müller, *B.* 22, 2405), and also by the action of H_2S on $C_6H_5.CCl:NC_7H_7$ (Leo, *B.* 10, 2134; Pfitzinger a. Gattermann, *B.* 22, 1065), and by heating *p*-tolyl-benzamidine with CS_2 (Bernthsen a. Trompetter, *B.* 11, 1759). Long yellow needles, insol. water, v. sol. alcohol, ether, and NaOHAq.

Xylide $C_6H_5.CS.NHC_6H_3Me_2$. [90°]. Formed by heating the benzoyl derivative of (4,2,1)-xylidine with P_2S_5 (Gudeman, *B.* 21, 2552). Small needles (from alcohol). Oxidised by K_3FeCy_6 to oily  $C_6H_2Me_2{<}\genfrac{}{}{0pt}{}{N}{S}{>}CPh$.

Di-phenyl-amide $C_6H_5.CS.NPh_2$. [151°]. Triclinic crystals (Bernthsen, *A.* 192, 37).

(α) *Naphthalide v.* vol. iii. p. 474.

Di-thio-benzoic Acid C_6H_5.CS.SH. Formed by adding an alcoholic solution of K_2S to $C_6H_5.CCl_3$ (Engelhardt a. Latschinoff, *Z.* [2] 4, 455; Klinger, *B.* 15, 862). Heavy, red oil, v. sol. alcohol and ether. Its dilute ethereal solution is crimson. Resinifies when exposed to air.—PbA'_2. Thin orange-red needles (from alcohol or xylene).—HgA'_2. Golden plates (from alcohol).—AgA'. Brown pp., insol. water and benzene.

References. — OXY-THIO-BENZOIC ACID and AMIDO-THIO-BENZAMIDE.

(α)-THIO-BENZOIC ALDEHYDE C_6H_5.CHS. *Benzylidene sulphide.* Formed by passing H_2S into an alcoholic solution of benzoic aldehyde (Laurent, *A. Ch.* [3] 1, 292; Klinger, *B.* 9, 1895; 15, 863; Böttinger, *B.* 12, 1056), or of hydrobenzamide (Cahours, *C. R.* 25, 457). White amorphous powder, softening at 85°, decomposed at a higher temperature. Insol. water and cold alcohol, v. e. sol. benzene and chloroform. Does not combine with $KHSO_3$ or HCy. Potash-fusion yields benzyl mercaptan. On heating with copper it forms CuS and *s*-di-phenyl-ethylene. Alcoholic KSH on heating forms Ph.CS.SK and di-benzyl disulphide. Thiogly-

sollic acid forms $C_6H_4.CH(S.CH_2.CO_2H)_2$ [124°] (Bongartz, *B.* 21, 479).

(β)-Thio-benzoic aldehyde $(C_6H_5.CHS)_x$. [225°]. Formed from the (α)-isomeride by treatment with AcCl, EtI, or a little iodine in benzene (Klinger, *B.* 10, 1877). Prepared by passing H_2S into a mixture of benzoic aldehyde and alcoholic HCl (Baumann a. Fromm, *B.* 22, 2604). Needles. Crystallises from benzene as $(C_7H_6S)_3C_6H_6$, and gives off its benzene at 130°-140°. V. sol. hot HOAc, m. sol. alcohol. On heating with copper-powder it yields CuS and di-phenyl-ethylene. An oily compound $(C_7H_6S)_2H_2S$ is formed, together with benzyl di-sulphide and di-thio-benzoic acid, by the action of alcoholic KSH on benzylidene chloride (Klinger, *B.* 15, 864). This compound yields benzoic acid on treatment with dilute HNO_3.

(γ)-Thio-benzoic aldehyde C_6H_5CHS. [167°]. Occurs in the benzene mother-liquor in the preparation of the (β)-isomeride (B. a. F.). Small pointed needles, much more sol. benzene and chloroform than the (β)-modification, sl. sol. alcohol and ether. Its crystals do not contain benzene of crystallisation. By adding iodine to its solution in benzene it is changed to the (β)-isomeride.

Thio-benzoic orthaldehyde $C_6H_5.CH(SH)_2$.

Methyl ether $C_6H_5CH(SMe)_2$. Formed by passing HCl into a mixture of benzoic aldehyde and MeSH (Bongartz, *B.* 21, 487). Oil. Oxidised by $KMnO_4$ to $C_6H_5.CH(SO_2CH_3)_2$ [163°].

Ethyl ether $C_6H_5.CH(SEt)_2$. Oil (Baumann, *B.* 18, 885).

p-Bromophenyl ether $C_6H_5.CH(SC_6H_4Br)_2$. [80°]. Silky needles (Baumann, *B.* 18, 885).

Reference.—Nitro-thio-benzoic aldehyde.

THIO-BENZOPHENONE $C_6H_5.CS.C_6H_5$. Formed by heating $CSCl_2$ (5g.) with benzene (25 g.) and $AlCl_3$ (9 g.) (Bergreen, *B.* 21, 337). Reddish-brown oil, v. sol. ether, benzene, and hot alcohol. Decomposed by distillation. Reacts with hydroxylamine, forming $Ph_2C:NOH$ and with phenyl-hydrazine, with production of $CPh_2:N_2HPh$.

Thio-benzophenone $(CSPh_2)_x$. [146·5°]. Formed from CCl_2Ph_2 and K_2S (Engler, *B.* 11, 922). Small white needles. Converted by CrO_3 and HOAc into benzophenone. Does not react with hydroxylamine or phenyl-hydrazine.

THIO-BENZOYL-(α)-NAPHTHYLAMINE *v.* vol. iii. p. 474.

THIOBENZPINACONE $C_{26}H_{22}S_2$ *i.e.* $CPh_2(SH).CPh_2(SH)$ or $CPh_2H.S.S.CPh_2H$. [151°]. Formed from benzophenone by the action of alcoholic ammonium sulphide (Engler, *B.* 11, 922) or P_2S_5 (Japp a. Roschen, *C. J.* 49, 479), and, together with thiobenzophenone, by the action of KSH on $C_6H_5.CCl_2.C_6H_5$ (Behr, *B.* 5, 970). Formed also by the action of alcoholic KSH on $(C_6H_5)_2CHCl$, and of P_2S_5 on di-phenyl-carbinol. Slender needles (from alcohol), v. sol. CS_2. In alcoholic solution it is converted by finely-divided copper into tetra-phenyl-ethane $CHPh_2.CHPh_2$.

THIO-BIURET $C_2H_5N_3OS$. Formed by boiling carbimido-urea ('amidodicyanic acid') with ammonium sulphide (Wunderlich, *B.* 19, 452). Needles (containing aq). Sol. hot water and alkalis, v. sl. sol. ether. Gives a white pp with copper salts. By ammoniacal $AgNO_3$ it is converted back into carbimido-urea.

THIO-BUTYRIC ACID C_4H_8SO *i.e.* $CH_3.CH_2.CH_2.CO.SH$. (130°). Formed by distilling butyric acid with P_2S_5 (Ulrich, *A.* 109, 280). Liquid with disgusting smell, v. sl. sol. water, v. sol. alcohol.—PbA'_2. Small crystals (from hot water).

Thio-isobutyric acid. *Methyl ether* $C_5H_{10}SO$ *i.e.* Pr.CO.SMe. (c. 142°). V.D. 57·5. Formed from $Pb(SMe)_2$ and isobutyryl chloride (Obermeyer, *B.* 20, 2922). Oil.

THIO-ISOBUTYRIC ALDEHYDE PrCHS. (70°-90°). A product of the action of S on isobutyric aldehyde at 180° (Barbaglia, *G.* 18, 85). Oil.

(α)-THIO-CARBAMIC ACID $NH_2.CO.SH$. This acid, set free by adding acids to a solution of its ammonium salt, splits up at once into COS and ammonia. The ammonium salt $NH_2.CO.SNH_4$ is prepared by passing gaseous COS into alcoholic NH_3 (Berthelot, *J.* 1868, 160) or into NH_3Aq at 0° (Schmidt, *B.* 10, 191; Kretzschmar, *J. pr.* [2] 7, 474). It forms colourless crystals, v. e. sol. water, m. sol. alcohol, insol. ether. The dry salt becomes yellow in air, forming ammonium sulphocyanide. The dry salt forms thio-urea when heated in a sealed tube at 135°. Thio-urea is also formed when $Pb(OH)_2$ is added to its cold aqueous solution. HgO forms, in the cold, ammonium cyanate (Fleischer, *B.* 9, 438). Water at 100° forms NH_4SH and $(NH_4)HCO_3$. $FeCl_3$ gives a red liquid, and finally a red pp. (Mulder, *A.* 168, 228).

Methyl ether $NH_2.CO.SMe$. [c 98°]. Formed, together with a small quantity of the (β)-isomeride, by adding HCl to a solution of potassium sulphocyanide in boiling MeOH (Blankenhorn, *J. pr.* [2] 16, 375). Monoclinic prisms (from ether). Decomposed by alcoholic NH_3 into MeSH and urea. Aniline at 100° forms MeSH, *s*-di-phenyl-urea and NH_3.

Ethyl ether $NH_2.CO.SEt$. [102°] (Pinner, *B.* 14, 1083); [108°] (F.). Formed in like manner (B.) and also by passing NH_3 into Cl.CO.SEt (Salomon, *J. pr.* [2] 7, 256) and by the action of EtBr on $NH_2.CO.SNH_4$ (Fleischer, *B.* 9, 991). Plates, v. sol. hot water, alcohol, and ether. Decomposed at 150° into mercaptan and cyanuric acid. P_2O_5 converts it into ethyl sulphocyanide.

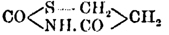
Isoamyl ether $CO(NH_2).SC_5H_{11}$. [107°]. From $CO(SC_5H_{11})Cl$ and NH_3 (Schöne, *J. pr.* [2] 32, 247). Glittering plates (from ether). Sol. hot water, but decomposed by boiling water. Gives amorphous pps., insol. water, alcohol, and ether with $AgNO_3$, $HgCl_2$ and $PtCl_4$.

Reactions.—Alcoholic NH_3 forms urea and amyl mercaptan.—2. Alcoholic KOH forms K_2CO_3, NH_3 and amyl mercaptan.—3. Heated with aniline it forms NH_3, HSC_5H_{11}, and di-phenyl-urea.

(β)-Thio-carbamic acid $NH_2.CS.OH$.

Methyl ether $NH_2.CS.OMe$. [43°]. Formed by the action of alcoholic NH_3 on MeO.CS.SMe or on MeO.CS.SEt (Salomon, *J. pr.* [2] 8, 115).

Ethyl ether $NH_2.CS.OEt$. *Xanthogenamide.* [38°]. Formed by the action of NH_3 on xanthogenic ether EtS.CS.OEt, on MeS.CS.OEt, and on $(EtO.CS)_2S_2$ (Debus, *A.* 72, 1; 75, 121; 82, 253;

Chancel, *J.* 1851, 513; Salomon a. Maintz, *J. pr.* [2] 8, 114). Monoclinic prisms, sl. sol. water, miscible with alcohol and ether. Decomposed on distillation into mercaptan and cyanic acid. Boiling KOHAq resolves it into alcohol and potassium sulphocyanide. P_2O_5 forms ethyl sulphocyanide (Conrad, *J. pr.* [2] 10, 34). Nitrous acid passed into water containing xanthogenamide in solution forms crystalline $C_6H_{10}N_4SO_2$. $CuSO_4$ followed by HClAq ppts. $C_3H_7NOSCuCl$ as a white crystalline powder, nearly insol. water, sol. hot alcohol. Compounds of CuCl with 2, 3, and 4 mols. of xanthogenamide may be obtained. KI added to a boiling alcoholic solution of $(C_3H_7NOS)_3CuCl$ forms crystals of $(C_3H_7NOS)_2CuI$ and $(C_3H_7NOS)_3CuI$. Compounds $(C_3H_7NOS)_2 3CuSCy$ and $C_3H_7NOSCuSCy$ may also be prepared (Debus). Isovaleric aldehyde in presence of HCl and alcohol forms $C_4H_9.CH(NH.CS.OEt)_2$ [108°] (Bischoff, *B.* 7, 1083). *β*-Iodo-propionic acid forms $NH_2.CO.S.CH_2.CH_2.CO_2H$ [147·5°], which yields CaA'_2 3aq, BaA'_2 2aq, and Ag_2A'' (Langlet, *B.* 24, 3849). *β*-Iodopropionic acid and Ac_2O yield sinapano propionic acid  $CO\left\langle\begin{matrix}S \text{---} CH_2\\NH.CO\end{matrix}\right\rangle CH_2$ [159°], v. sol. hot water, converted by HgO into the mercaptide of *β*-thiolactic acid.

Isobutyl ether $NH_2.CS.OCH_2Pr$. [36°]. Tables (from alcohol or ether) (Mylius, *B.* 5, 976; Blankenhorn, *J. pr.* [2] 16, 380).

Isoamyl ether $NH_2.CS.OC_5H_{11}$. Oil (Johnson, *C. J.* 5. 242).

Di-thio-carbamic acid $NH_2.CS.SH$. Mol. w. 93. The ammonium salt $NH_2.CS.SNH_4$ is formed by passing NH_3 (from 150 pts. NH_4Cl) into 95 p.c. alcohol (600 pts.) containing CS_2 (96 pts.) (Mulder a. Bettink, *J. pr.* 103, 178; *cf.* Zeise, *A.* 48, 95; Debus, *A.* 73, 26). It is also formed by heating $(NH_4)_2CS_3$. On gradually adding HClAq to a cooled conc. solution of the ammonium salt the free acid separates as colourless needles, v. sol. water, alcohol, and ether; acid in reaction. An alcoholic solution of the acid gradually decomposes into CS_2 and the NH_4 salt. An aqueous solution of the acid decomposes on heating into H_2S and HCyS. The di-thio-carbamates also split at 100° into H_2S and sulphocyanides. An alcoholic solution of iodine decomposes $NH_2.CS.SNH_4$, forming EtNCS and $EtNH_2$ (Hofmann, *Z.* [2] 5, 671). Ammonic di-thio-carbamate treated with HCl and solution of I gives crystals of the bisulphide $S_2(CS.NH_2)_2$ (Klason, *J. pr.* [2] 36, 62). $FeCl_3$ added to a solution of the NH_4 salt gives a black pp. turned white by excess. $AgNO_3$ gives a yellow pp., turning black. A solution of aldehyde forms carbothialdine $NH_2.CS.SN(C_2H_4)_2$. Benzoic aldehyde, isovaleric aldehyde, and acroleïn form analogous bodies.

Salts.—NH_4A'. Deliquescent lemon-yellow prisms. On heating with KOHAq it forms K_2S, KSCy, and NH_3.—CuA'_2. Yellow powder, insol. water.—PbA'_2. White pp., blackening on boiling with water.—ZnA'_2: white pp.

Ethyl ether $NH_2.CS.SEt$. Mol. w. 121. [42°]. Formed by passing H_2S under pressure into ethyl sulphocyanide at 100° (Jeanjean, *J.* 1866, 501; Salomon a. Conrad, *J. pr.* [2] 10, 29). Trimetric crystals (from ether), insol. water, v. e. sol. alcohol. Alcoholic NH_3 or KOHAq in the cold forms mercaptan and ammonium sulphocyanide.

Isopropyl ether $NH_2.CS.SPr$. [97°]. Trimetric plates (Gerlich, *A.* 178, 82).

Acetyl derivative of the ethyl ether NHAc.CS.SEt. [123°]. Formed by heating thio-acetic acid with ethyl sulphocyanide (Chanlaroff, *B.* 15, 1987). Yellow needles (from alcohol), v. sol. hot water. Decomposed by distillation into thio-acetic acid and ethyl sulphocyanide. Boiling baryta-water forms mercaptan and acetic acid. Hot dilute HClAq forms $NH_2.CS.SEt$.

Isothiocarbamic ether *v.* DI-ETHYL-(*a*)-THIO-CARBONATE. *Amide.*

THIO-CARBAMIDE *v.* THIO-UREA.

THIOCARBAMYL SULPHIDE $C_2H_4N_2S_3$ *i.e.* $(NH_2.CS)_2S$ (?) Very unstable oil, got by adding HCl to its ammonium salt. Quickly decomposes into CS_2, sulphur, H_2S, and ammonium sulphocyanide. The **ammonium salt** $C_2H_2(NH_4)_2N_2S_3$ is a product of the action of CS_2 on alcoholic NH_3 in the cold (Zeise, *B. J.* 4, 98; Hlasiwetz a. Kachler, *A.* 166, 137). It forms colourless prisms, v. sol. water, m. sol. alcohol, sl. sol. ether. The moist salt slowly decomposes into H_2S and ammonium sulphocyanide. The **cupric salt** $CuC_2H_2N_2S_3$ is canary-yellow.

Thiocarbamyl disulphide $C_2H_4N_2S_3$ *i.e.* $(NH_2.CS)_2S_2$. Formed by the action of Cl on a solution of the ammonium salt of the preceding body, and on ammonium di-thio-carbamate (Debus, *A.* 73, 27). Pearly plates, v. sol. hot alcohol, insol. water. Decomposed by boiling water into CS_2, ammonium sulphocyanide, and S.

THIOCARBIMIDES. *Mustard oils.* Compounds RN:CS. Essential oil of mustard is allyl thiocarbimide. They are formed by the action of $CSCl_2$ on primary amines (Rathke, *A.* 167, 218), and by the action of aqueous $HgCl_2$ on the dithiocarbamates $RNH.CS.SNH_3R$ obtained by heating primary amines with CS_2 and alcohol or ether (Hofmann, *B.* 1, 171; 2, 452; 7, 811; 8, 106; Rudneff, *J. R.* 10, 188). Methyl sulphocyanide is partially converted into methyl thiocarbimide by heating at 180°. Allyl sulphocyanide changes to the mustard oil on boiling. Thiocarbimides are also got by distilling alkyl cyanates with P_2S_5 (Michael a. Palmer, *Am.* 6, 258). The thiocarbimides are pungent oils. They are reduced by Zn and HClAq to amines and CH_2S, whereas sulphocyanides yield HCy, mercaptans, and other products. Amines convert thiocarbimides into thio-ureas; thus aniline combines with phenyl thiocarbimide, forming *s*-di-phenyl-thio-urea. Alcoholic potash, or alcohol at 100° forms thio-carbamic ethers NHR.CS.OEt (Hofmann, *B.* 2, 117; Schiff, *B.* 9, 1316). Water at 200°, or HClAq at 100°, forms amine, CO_2, and H_2S, while with sulphocyanides it yields Et_2S, CO_2, and NH_3. Conc. H_2SO_4 forms amine and COS. HNO_3 forms amine and CO_2; whereas with the isomeric sulphocyanides it forms a sulphonic acid. Hydroxylamine unites with thiocarbimides, forming oxy-thio-ureas NHR.CO.NH.OH (Tiemann, *B.* 22, 1939). Chlorine unites with PhN:CS, forming unstable $(PhNCS)_2Cl_2$, whence boiling water forms $(PhNCS)_2O$ [118°], crystallising in yellow needles (Helmers, *B.* 20, 786).

THIOCARBIMIDO-ACETIC ACID $C_3H_3NSO_2$ *i.e.* $CH_2(N:CS).CO_2H$. Formed by boiling thiohydantoïn with HClAq (Volhard, *J. pr.* [2] 9, 6), and by boiling isoamyl sulphocyano-acetate with fuming HClAq (Claësson, *B.* 10, 1352; Heintz, *A.* 136, 232). Trimetric plates, v. e. sol. hot water. Oxidised by HNO_3 to H_2SO_4 and oxalic acid. Weak acid.—BaA'_2 aq. Four-sided prisms, sl. sol. cold water. Benzoic aldehyde and NaOHAq (1 mol.) react, forming the compound $CHPh:C(CO_2Na).S.CO.NH_2$, which crystallises with $1\frac{1}{2}$aq and is converted by HCl into $\begin{smallmatrix}CO.S\\NH.CO\end{smallmatrix}>C:CHPh$ [242°] (Andreasch, *M.* 10, 73).

THIOCARBIMIDO-BENZOIC ACID *v.* *m*-AMIDO-BENZOIC ACID.

THIOCARBONIC ACID.

Thiocarbonates *v.* vol. i. p. 703. The thiocarbonic ethers that have not been treated of in former articles are described below.

Methyl thiocarbonates *v.* vol. iii. p. 399.

Methyl iso-dithiocarbonate $CO(SMe)_2$. (169°). Formed by warming methyl sulphocyanide with H_2SO_4 (Schmitt a. Glutz, *B.* 1, 166).

Ethyl thiocarbonates *v.* vol. ii. p. 520.

Ethylene thiocarbonates *v.* vol. ii. p. 493.

Ethylene di-ethyl di-thio-di-carbonate $C_2H_4(S.CO_2Et)_2$. Formed by heating $C_2H_4Br_2$ with $KS.CO_2Et$ in alcohol (Welde, *J. pr.* [2] 15, 52). Thick oil, converted by alcoholic potash into $C_2H_4(SH)_2$ and $KO.CO_2Et$.

Isobutyl di-thio-carbonic acid $CH_2Pr.O.CS_2H$.

Salts.—NaA'. Formed from C_4H_9ONa and CS_2. Yellowish white needles, v. e. sol. water and alcohol.—KA'. Needles (from alcohol). S.G. $\frac{15}{}$ 1·371 (Clarke, *B.* 11, 1505). Chlorine gas passed into its aqueous solution forms oily $(CH_2PrO.CS)_2S_2$ (Mylius, *B.* 5, 976).

Ethyl ether EtA'. (228°).

Isobutyl ether $CH_2Pr.O.CS.SCH_2Pr$. (249°). S.G. $\frac{12}{}$ 1·009 (Mylius, *B.* 5, 975).

Isoamyl ether $CH_2Pr.O.CS.SC_5H_{11}$. (265°–270°) (Mylius).

Isoamyl di-thio-carbonic acid $C_5H_{11}.O.CS.SH$. Oil, with unpleasant smell.

Salts.—KA'. Formed from fusel oil, KOH, and CS_2 (Balard, *A. Ch.* [3] 12, 307; Erdmann, *J. pr.* 31, 4; Desains, *A. Ch.* [3] 20, 505; Johnson, *C. J.* 5, 142). Gives a lemon-yellow pp. with $CuSO_4$.—PbA'_2. Plates. Iodine forms oily $(C_5H_{11}O.CS)_2S_2$.

Di-isoamyl *s*-di-thio-carbonate $CO(SC_5H_{11})_2$. (281°) (Schmitt a. Glutz).

Cetyl di-thiocarbonate *v.* vol. i. p. 728.

Iso-butyl-tri-thio-carbonic acid $C_4H_9S.CS_2H$. Formed from C_4H_9SNa and CS_2 (Mylius, *B.* 6, 316). The Na salt crystallises in yellow needles, v. sol. alcohol and ether.

Isobutyl ether $(C_4H_9S)_2CS$. (287°). Got by heating aqueous K_2CS_3 with isobutyl iodide. Yellow oil with faint odour.

Di-isoamyl-tri-thiocarbonate $(C_5H_{11}S)_2CS$. (247°). S.G. ·88 (Husemann, *A.* 126, 297). Oil, with unpleasant smell.

Di-allyl tri-thio-carbonate $(C_3H_5S)_2CS$. (170°–175°). S.G. ·94. Formed from allyl iodide and Na_2CS_3 in the cold (Husemann, *A.* 126, 269). Pungent yellow oil, with offensive odour.

THIOCARBONYL - ACETOACETIC ETHER $CS:CAc.CO_2Et$. [156°–162°]. Formed from thiocarbonyl chloride and acetoacetic ether (Bergreen, *B.* 21, 347). Yellow needles, sl. sol. ether and ligroïn.

THIO-CARBONYL-DI-AMIDO-DI-BENZOIC ACID *v.* *m*-AMIDO-BENZOIC ACID.

THIOCARBONYL - BENZOYL - ACETIC ETHER $CS:CBz.CO_2Et$. [164°]. Formed from $CSCl_2$ and benzoylacetic ether (Bergreen, *B.* 21, 351). Yellow needles, sol. alcohol-chloroform.

THIO-CARBONYL CHLORIDE *v.* *Sulphochloride* of CARBON.

Thio-carbonyl tetrachloride *v.* PER-CHLORO-METHYL-MERCAPTAN.

THIO - CARBONYL - ETHYL - *o* - AMIDO-PHENOL $C_6H_4<\begin{smallmatrix}NEt\\O\end{smallmatrix}>CS$. [112°]. (above 300°). Formed from ethyl-*o*-amido-phenol and $CSCl_2$ (Seidel, *J. pr.* [2] 42, 449, 457). Insol. water and dilute NaOHAq, m. sol. cold alcohol. HClAq at 170° forms ethyl-amido-phenol, CO_2, and H_2S. PCl_5 yields $C_6H_4<\begin{smallmatrix}N\\O\end{smallmatrix}\gg CCl$.

THIO - CARBONYL - METHYL - AMIDO-PHENOL $C_6H_4<\begin{smallmatrix}NMe\\O\end{smallmatrix}>CS$. [128°]. (above 300°). Formed by the action of $CSCl_2$ on methyl-*o*-amido-phenol (Seidel, *J. pr.* [2] 42, 452). Needles, insol. water, sl. sol. cold alcohol.

THIO - CARBONYL - DI - (β) - NAPHTHYL - THIO - UREA $C_{10}H_7.N<\begin{smallmatrix}CS\text{———}\\C(NC_{10}H_7)\end{smallmatrix}>S$. [152°]. Formed from di-(β)-naphthyl-thio-urea and $CSCl_2$ in benzene (Freund a. Wolf, *B.* 25, 1466). Stellate groups of needles, m. sol. hot benzene. Melts at 152° with evolution of gas, forming a solid melting at 224°.

THIO-CARBONYL-DI-*p*-TOLYL-THIO-UREA $C_7H_7.N:C<\begin{smallmatrix}N(C_7H_7)\\S\text{———}\end{smallmatrix}>CS$. [109°]. Formed from di-*p*-tolyl-thio-urea [172°] and $CSCl_2$ in ether (Freund a. Wolf, *B.* 25, 1465). Yellowish needles, v. sol. hot alcohol and ether. Converted by HgO into carbonyl-di-tolyl-thio-urea [112°].

THIOCHRONIC ACID $C_6H_6S_5O_{17}$ *i.e.* $C_6(OH)(SO_4H)(SO_3H)_4$. Formed by adding tetrachloro-quinone to a conc. solution of K_2SO_3 (Hesse, *A.* 114, 313; Graebe, *A.* 146, 40). Yellow trimetric prisms, v. sol. hot water, insol. alcohol. Coloured brownish-red by $FeCl_3$. Reduces $AgNO_3$. Converted into hydroquinone disulphonic acid by heating with water at 135°, or by boiling with HClAq.

Euthiochronic acid $C_6H_4S_2O_{10}$ *i.e.* $C_6(OH)_2O_2(SO_3H)_2$. *Di-oxy-quinone disulphonic acid.* Formed by boiling thiochronic acid with KOHAq. Deliquescent yellow needles, v. sol. water and alcohol. Reduced by tin and HClAq to $C_6H_6S_2O_{10}$, which yields Na_2A''2aq and K_2A''2aq, which are re-oxidised in aqueous solution by air to euthiochronates.—Na_4A^{iv}aq (dried at 150°).—K_4A^{iv}2aq. Minute lemon-yellow prisms, v. sol. water.—K_3HA^{iv}aq. Small orange-red four-sided prisms.—Ba_2A^{iv}4aq. Ochre-yellow pp.—Ag_4A^{iv}: amorphous pp.

(α) - **THIO - CINNAMIC ACID** C_9H_8SO *i.e.* $C_6H_5CH:CH.CO.SH$. Formed from cinnamoyl chloride and $Pb(SEt)_2$, the resulting oily ether being boiled with alcoholic KSH (Engelhardt, *Z.* [2] 4, 359).—KA′. Crystalline.

(β)-Thio-cinnamic acid. *Amide* $C_9H_7S.NH_2$. [112°]. Formed by passing H_2S into a solution of cinnamic nitrile in alcoholic NH_3 (Rossum, *Z.* 1866, 362; Krüss, *B.* 17, 1768). Golden plates.

(α)-**THIO-CINNAMIC ALDEHYDE** $(C_9H_8S)_3$. [167°]. Formed by passing H_2S into oil of cinnamon dissolved in alcoholic HCl (Baumann a Fromm, *B.* 24, 1452). Crystalline, v. e. sol. benzene, sl. sol. alcohol.

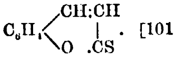
(β)-Thio-cinnamic aldehyde $(C_9H_8S)_3$. [213°]. Formed at the same time as the (α)-isomeride. Prisms, v. sl. sol. cold benzene and alcohol.

Thio-cinnamic orthaldehyde. *Phenyl ether* $C_6H_5CH:CH.CH(SPh)_2$. [81°]. Formed by passing dry HCl into a mixture of cinnamic aldehyde and phenyl mercaptan (Baumann, *B.* 18, 885). Needles (from ligroïn).

p-Bromo-phenyl ether $CHPh:CH.CH(S.C_6H_4Br)_2$. [107°]. Needles (from alcohol or ether).

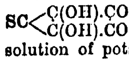
Glycollyl ether $CHPh:CH.CH(S.CH_2.CO_2H)_2$. [143°]. Formed from cinnamic aldehyde and thioglycollic acid (Bongartz, *B.* 21, 481). Plates (from water). Zinc-dust in alkaline solution converts it into $CHPh:CH.CH_2.S.CH_2.CO_2H$ [77°], crystallising from dilute alcohol in plates.

TRI-THIO-CITRIC ETHER $C_3H_5O(CO.SEt)_3$. Formed from tri-phenyl citrate and NaSEt in presence of ether (Seiffert, *J. pr.* [2] 31, 470). Oil, smelling like mercaptan.

THIO-COUMARIN  $C_6H_4\begin{cases}CH:CH\\ \quad\;\; | \\ O\;\;.CS\end{cases}$. [101°].

Formed by heating equal parts of coumarin and P_2S_5 at 120°; the yield is 50 p.c. Also by heating *o*-coumaric acid with P_2S_5. Long yellow needles, v. sol. alcohol, ether, and benzene; insol. water. Sublimable. By heating with aqueous alcoholic KOH it is reconverted into coumarin. Unlike coumarin it readily reacts with hydroxylamine and with phenyl-hydrazine (Tiemann, *B.* 19, 1661).

THIO-CRESOL *v.* Tolyl mercaptan.

THIO-CROCONIC ACID $C_5H_2O_4S$, probably  $SC\begin{cases}C(OH).CO\\ C(OH).CO\end{cases}$. Formed by saturating a warm solution of potassium croconate treated with 2 mols. of HCl, with H_2S.—BaA″ 2aq: brownish-yellow amorphous pp., v. sol. dilute HCl, which after some time changes to reddish-brown crystals with violet reflex, insol. dilute HCl (Nietzki a. Benkiser, *B.* 19, 299).

THIO-CUMINIC ACID. *Amide* $C_{10}H_{13}NS$ *i.e.* $C_3H_7.C_6H_4.CS.NH_2$. Formed by passing H_2S into a solution of cuminic nitrile in alcoholic NH_3 (Czumpelik, *B.* 2, 185). Needles, v. sol. hot alcohol. Converted in alcoholic solution by iodine into $C_{20}H_{22}N_2S$ [45°] crystallising in prisms (Wanstrat, *B.* 6, 322).

THIODICYANDIAMIDINE *v.* Guanyl thiourea.

THIOCYANIC ACID *v.* Sulphocyanic acid.

THIOCYANO- *v.* Sulphocyano-.

DI-THIO-CYANURIC ACID $Cy_3(SH)_2(OH)aq$.

Preparation.—An alcoholic solution of KCyS is mixed with the calculated quantity of HCl, filtered from KCl, and evaporated at 40°. The residue is extracted with strong NH_3Aq and $BaCl_2$ is added to the filtrate. The barium salt gradually separates in globular crystals (Klason, *J. pr.* [2] 33, 121). Yield, very small.

Properties.—White scales (from hot water). Sol. NaOHAq. A solution of the potassium salt gives pps. with $AgNO_3$, $HgCl_2$, and $Pb(OAc)_2$.

Reactions.—1. Conc. HCl at 130° gives cyanuric acid and H_2S.—2. Cold $KMnO_4Aq$ and hot HNO_3Aq form cyanuric acid.—3. *Iodine* forms $(HOCy_3)_2S_4$ as a white crystalline powder.

Salts.—KH_2A'''. Silvery mass of microscopic prisms.—$BaHA'''2aq$.

Tri-thio-cyanuric acid $Cy_3(SH)_3$. Formed by warming powdered $C_3N_3Cl_3$ (1 mol.) with conc. aqueous KSH (4 mols.) (Hofmann, *B.* 18, 2196; Klason, *J. pr.* [2] 33, 116). Minute prisms, when ppd. from dilute solutions; amorphous, from conc. solutions. Nearly insol. hot water, alcohol and ether. Not decomposed at 200°. $FeCl_3$ gives no colour in solutions of the acid, but in conc. solutions of the K salt it gives a white pp. and a yellow solution.

Reactions.—1. HClAq at 130° gives cyanuric acid and H_2S.—2. Alkaline $KMnO_4$ at 20° gives cyanuric acid.—3. Warm HNO_3 forms cyanuric acid.—4. At 360° it gives off CS_2 and some HCyS and leaves melem $C_6H_6N_{10}$.

Salts.—$K_3A'''3aq$.—$K_3H_3A'''_4 6aq$.—NaH_2A'''. Crystals, v. sol. water.—$BaHA'''3aq$. Yellow crystals, ppd. by addition of $BaCl_2$ and NH_3Aq.—$BaH_4A'''_2 2aq$. Prisms, m. sol. water.—$SrHA'''5aq$.—$CaHA'''5aq$. Prisms, m. sol. water.

Methyl ether Me_3A'''. [189°]. Got by heating methyl sulphocyanide with a few drops of HClAq at 100° (Hofmann, *B.* 13, 1351; 18, 2197, 2755, 2774; 19, 2065). Hexagonal crystals. An alcoholic solution of ethylamine at 100° forms $Cy_3(NHEt)(SMe)_2$ [114°] while at 140° it yields $Cy_3(NHEt)_2SMe$ [84°]. Alcoholic NH_3 forms, in like manner, $Cy_3(NH_2)(SMe)_2$ and $Cy_3(NH_2)_2SMe$.

Ethyl ether Et_3A'''. [27°]. (350°). Formed from Cy_3Cl_3 and NaSEt. Colourless tablets (from HOAc) converted by alcoholic NH_3 at 180° into $Cy_3(NH_2)(SEt)_2$ [112°] (crystallising in trimetric forms; $a:b:c = \cdot669:1:\cdot391$, v. sol. ether), accompanied by $Cy_3(NH_2)_2(SEt)$ [165°], which is insol. ether (Klason, *J. pr.* [2] 33, 298).

Amyl ether $(C_5H_{11})_3A'''$. Oil. Yields $Cy_3(NH_2)(SC_5H_{11})_2$ [82°] and $Cy_3(NH_2)_2SC_5H_{11}$ [178°].

Phenyl ether Ph_3A'''. [97°]. Prisms (from HOAc).

p-Tolyl ether $(C_7H_7)_3A'''$. [114°].

THIO-DI-ETHYL-ANILINE *v.* Tetra-ethyl-di-amido-di-phenyl sulphide.

THIO-ETHYL-COUMARIN $C_6H_4\begin{cases}CH:CEt\\ O—CS\end{cases}$. [94°]. Formed by heating (α)-ethyl-coumarin with P_2S_5 at 120° (Aldringen, *B.* 24, 3462). Yellowish-red plates, sol. alcohol. May be sublimed.

THIO-ETHYLENE GLYCOL *v.* Ethylene mercaptan.

THIO-FORMIC ACID H.CO.SH (?) [120°]. Formed by the action of H_2S on lead formate (Wöhler, *A.* 91, 125; Limpricht, *A.* 97, 361), but not from P_2S_5 and formic acid (Hurst, *A.* 126, 68). Small transparent crystals (from alcohol) with alliaceous odour, insol. water. May be sublimed. According to Nicol (*Pr. E.* 10, 425) a solution of thioformic acid, got from

PbA'_2 and H_2S, rapidly decomposes, yielding formic acid.

Salts.—H.CO.SK. Formed from $CHCl_3$ and alcoholic K_2S (Nicol, *T. E.* 29, 531). Needles, sol. water and alcohol, nearly insol. dilute alcohol. $AgNO_3$ added to its aqueous solution forms a white pp., turning black on standing. HNO_3 yields S and formic acid. HgO also gives formic acid.—$(H.CO.S)_2Pb$.

Anilide H.CS.NHPh. *Thioformanilide.* [137°]. Formed from dry phenyl carbamine and H_2S (Hofmann, *B.* 10, 1095, 1238). Formed also by passing dry H_2S over di-phenyl-formamidine NPh:CH.NHPh at 150° (Bernthsen, *A.* 192, 35). Prepared by warming formamidine (5 pts.) with P_2S_5 (3 pts.), the yield being 60 p.c. of the theoretical (Hofmann, *B.* 11, 338). Thin plates (from water), partially decomposed on distillation into H_2S and phenyl carbamine. Its solution tastes bitter. Decomposed by hot KOHAq into aniline, H_2S, and formic acid. Heated in a sealed tube at 180° it yields $C_{14}H_{12}N_2S$ [140°] v. sol. alcohol (Nicol, *B.* 15, 211). NaOEt and EtBr yield oily CH(SEt):NPh (c. 235°) (Wallach a. Wüsten, *B.* 16, 145).

o-Toluide $H.CS.NHC_7H_7$ [96°]. Got by heating formyl-toluide with P_2S_5 (Senier, *C. J.* 47, 762).

p-Toluide. Yellow needles.

Xylide $HCS.NHC_6H_3Me_2$. [105°]. Small needles (from alcohol) (Gudeman, *B.* 21, 2549).

Thio-orthoformic acid. *Ethyl ether* $CH(SEt)_3$. Formed by boiling chloroform with aqueous NaSEt (Gabriel, *B.* 10, 186; Claesson, *J. pr.* [2] 15, 174). Oil, with nasty smell, partly decomposed on boiling. Oxidised by HNO_3 to ethane sulphonic acid. Fuming HClAq yields formic acid and mercaptan

Benzyl ether $CH(SC_7H_7)_3$. [98°]. Formed from $NaSC_7H_7$ and chloroform (Dennstedt, *B.* 11, 2265). White crystals.

Phenyl ether $CH(SPh)_3$. [39·5°]. Trimetric tables. Oxidised by potassium permanganate to $PhS.CH(SO_2Ph)_2$ [176°] (Laves, *B.* 23, 1416; 25, 347).

Reference.—CHLOROFORMIC ACID.

THIO-FORMIC ALDEHYDES

Thio-formic paraldehyde $(CH_2S)_3$. *Methylene sulphide.* Mol. w. 138. [216°]. V.D. 5·08 (obs.).

Formation.—1. By heating Na_2S with methylene iodide (Husemann, *A.* 126, 293).—2. By reducing CS_2 with Zn and HClAq (Girard, *A.* 100, 306).—3. By the action of H_2S on formic aldehyde or trioxymethylene.

Preparation.—By saturating a mixture of formic aldehyde (2 vols.) and conc. HClAq (4 vols.) with H_2S (Baumann, *B.* 23, 67).

Properties.—Prisms, smelling like onions. Insol. cold water, sl. sol. alcohol and ether, m. sol. benzene and CS_2. May be sublimed. Oxidised by $KMnO_4$ to a trisulphone and also $C_3H_6S_3O_5$ crystallising in colourless needles.—Forms: $C_3H_6S_3 2AgNO_3$. — $C_3H_6S_3AgNO_3\,\frac{3}{4}aq.$ — $C_3H_6S_3HgCl_2$. — $(C_3H_6S_3)_2 2PtCl_2$. — $(C_3H_6S_3)_2PtCl_4$ (Hofmann, *B.* 2, 152; 3, 584; Girard, *C. R.* 70, 625).

Thio-formic orthaldehyde.

Ethyl ether $CH_2(SEt)_2$. (184°) (C.); (180°) (F.). S.G. ^{22} ·987. Formed from CH_2I_2 and NaSEt (Claesson, *J. pr.* [2] 15, 176). Liquid with unpleasant smell. Oxidised by HNO_3 to ethane sulphonic acid. $KMnO_4$ and H_2SO_4 yield $CH_2(SO_2C_2H_5)_2$ (Fromm, *A.* 253, 155).

Thio-formic metaldehyde $(CH_2S)_n$. [176°]. Formed, as a white amorphous substance, on warming an aqueous or alcoholic solution of hexamethylene-amine saturated with H_2S (Wohl, *B.* 19, 2344). Insol. most solvents. Decomposed when heated above its melting-point.

Di-thio-formic paraldehyde $(C_3H_6S_2O)_2$ aq. *Dithioglyceric aldehyde.* [82°]. (180°–185°). Formed by passing H_2S into a solution obtained by electrolysis of dilute glycerin (Renard, *A. Ch.* [5] 17, 307). Amorphous waxy mass, sol. warm water, insol. alcohol and ether.

(*a*)-**THIO-FURFURALDEHYDE** $(C_5H_4SO)_2$. [128°]. Formed, together with the (*β*)-isomeride, by passing H_2S into a solution of furfuraldehyde (10 g.) in alcohol (100 c.c.) and HClAq (20 c.c.) at −5° (Baumann a. Fromm, *B.* 24, 3593). Crystals, v. e. sol. alcohol and chloroform, insol. water.

(*β*)-**Thio-furfuraldehyde** $(C_5H_4SO)_3$. [229°]. Needles, v. sl. sol. alcohol, v. sol. chloroform.

Thio-furfuraldehyde $(C_4H_5SO)_n$ [$n = 20$ to 24]. Mol. w. (by Raoult's method) 2182. Formed by mixing an alcoholic solution of furfuraldehyde with alcoholic ammonium sulphide (Cahours, *A.* 69, 85; B. a. F.). White crystalline powder, softens at 80° and is melted at 91°. Thiofurfuraldehyde is decomposed by warm aniline, yielding furfuraldehyde and H_2S (Schiff, *B.* 19, 2153).

THIO-GLYCERIN *v.* GLYCERIN.

THIO-GLYCOL *v.* ETHYLENE MERCAPTAN.

THIO-GLYCOLLIC ACID $CH_2(SH).CO_2H$. *Sulphydro-acetic acid.*

Formation.—1. By reducing the compound $ClSO_2.CHCl.COCl$ with tin and HClAq (Siemens, *B.* 6, 659).—2. By adding $CH_2Cl.CO_2H$ (1 mol.) to conc. KSHAq (2 mols.) (Claesson, *A.* 187, 113).—3. By the action of H_2S on glyoxylic acid in presence of Ag_2O (Böttinger, *A.* 198, 215).—4. By boiling thiohydantoïn with baryta-water (Andreasch, *B.* 12, 1385).—5. Together with HSCy, by the decomposition of rhodanic acid $C_3H_3NS_2O$ with baryta-water (Ginsberg a. Bondzynski, *B.* 19, 113).

Properties.—Oil, miscible with water, alcohol, and ether. Decomposes when quickly heated. Very dilute $FeCl_3$ gives a fugitive indigo-blue colour, changed by a few drops of NH_3Aq to dark red and then to violet. Excess of $FeCl_3$ oxidises it to di-sulphido-di-acetic acid $S_2(CH_2.CO_2H)_2$, which is also readily formed by atmospheric oxidation of the alkaline solution. A solution of the K salt added to $CuSO_4$ gives a bluish-black pp. reduced by further addition of the K salt to the white cuprous salt $Cu_2(S.CH_2.CO_2H)_2$. HCl passed through a mixture of thioglycollic acid and acetoacetic ether gives rise to crystalline $CO_2Et.CH_2.CMe(S.CH_2.CO_2H)_2$ [96°] (Bongartz, *B.* 21, 485). Acetyl-propionic acid forms, in like manner, $CO_2H.CH_2.CH_2.CMe(S.CH_2.CO_2H)_2$ [154°]. Aldehydes react, forming the compound $CRH(S.CH_2.CO_2H)_2$, compounds which are produced either on standing, on warming, or on treatment with $ZnCl_2$ or dry HCl (Bongartz, *B.* 19, 1931; 21, 479). Such compounds obtained by using acetic, benzoic, cinnamic, *o*-oxy-benzoic, and *o*-, *m*-, and *p*-nitro-benzoic aldehydes melt at 108°, 124°, 146°, 148°, 123°, 130°, and 162° respectively. Thioglycollic acid reacts with ketones in presence of $ZnCl_2$ or HCl, forming acids $CRR'(S.CH_2.CO_2H)_2$: such compounds obtained from acetone, acetophenone, and benzophenone melt at 135°, 139°, and 164° respectively.

Salts. — KHA″aq (from water). — KHA″ (from alcohol). Decomposes K_2CO_3, forming $CH_2(SK).CO_2K$.—BaA″ 3aq: crystalline pp.— $BaH_2A''_2$: gummy.—CdA″.—$Hg(S.CH_2.CO_2H)_2$. Needles or flat prisms, v. sol. hot water and alcohol.—$Hg_2(S.CH_2.CO_2)_4BaH_2$. Minute crystals.—$Hg_3(S.CH_2.CO_2)_6AlH_3$. — $Hg_2MnH_2A''_4$. — $HgPbA''_2$.—HgA″.—PbA″.—$Bi(HA'')_3$. [c. 33°]. Yellow pp.—$Cu_2H_2A''_2$. White pp.—$Cu_2BaA''_2$.—Ag_2A''.—$Ag_2(NH_4)A''(NO_3)$.—$Ag_2HgA''_2$.

Ethyl ether EtA′. Formed by boiling thioglycollic acid with alcohol and a little H_2SO_4 (Claesson, *A.* 187, 116). Oil with nasty smell. Slowly decomposed by boiling into H_2S and $S(CH_2.CO_2Et)_2$. Alcoholic $HgCl_2$ ppts. $ClHg.S.CH_2.CO_2Et$, converted by excess of the ether into $Hg(S.CH_2.CO_2Et)_2$ (Wislicenus, *A.* 146, 145).

Ethyl derivative $CH_2(SEt).CO_2H$. Formed by mixing $CH_2Cl.CO_2Et$ with NaSEt and alcohol (Claesson, *B.* 8, 120). Liquid, v. sol. alcohol and ether, m. sol. water. Decomposed by heat, but may be distilled with steam. — KA′.—BaA'_2. — CaA'_2.—MgA'_2 3aq. — ZnA'_2 2aq. —CdA'_2 aq. [85°]. – CoA'_2 2aq. [90°].—NiA'_2 2aq. —CuA'_2 2aq. – AgA′aq. Crystalline pp.

Ethyl ether of the ethyl derivative $CH_2(SEt).CO_2Et$. (188°). S.G. ± 1·0169. Oil. Converted by EtI at 120° into crystalline $CH_2(SEt_2I).CO_2Et$.

Ethyl ether of the isoamyl derivative $CH_2(SC_5H_{11}).CO_2Et$. (230°). S.G. ^{4} ·9797. Oil.

Phenyl derivative v. PHENYL-THIO-GLYCOLLIC ACID.

Benzyl derivative $CH_2Ph.S.CH_2.CO_2H$. [59°]. Formed from $CH_2Cl.CO_2H$ and benzyl mercaptan (Gabriel, *B.* 12, 1641). Flat tables. Yields EtA′ (275°–290°) and the amide $CH_2Ph.S.CH_2.CONH_2$ [97°] crystallising in flat plates.

Phenyl-phenyl derivative $C_6H_4Ph.S.CH_2.CO_2H$. [170°]. Crystals.

Amide $CH_2(SH).CO.NH_2$. A product of the passage of H_2S through an alcoholic solution of chloro-acetamide containing a little NH_3 (Schulze, *Z.* 1865, 73). Groups of small prisms.

Ethyl derivative of the amide $CH_2(SEt).CONH_2$. [44°]. Formed from $CH_2(SEt).CO_2Et$ and ammonia. Thin prisms.

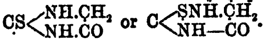
Reference.—NITROSO-THIO-GLYCOLLIC ACID.

THIO-GLYCOLLIC ORTHALDEHYDE. *Ethyl derivative of the ether* $CH_2(SEt).CH(OEt)_2$. (169°). Formed from $CH_2Cl.CH(OEt)_2$ and NaSEt (Autenrieth, *B.* 24, 162). Volatile in steam.

Phenyl derivative of the ethyl ether $CH_2(SPh).CH(OEt)_2$. (273°). Got in like manner.

THIO-HYDANTOÏC ACID $C_3H_6N_2SO_2$ *i.e.* $NH_2.CS.NH.CH_2.CO_2H$ or $NH_2.C(NH).S.CH_2.CO_2H$. Formed by heating sodium chloro-acetate in aqueous solution with thio-urea (Maly, *A.* 189, 380). Crystalline powder, sl. sol. water, v. sol. acids and alkalis. Decomposed by heat. Converted into thio-hydantoïn by warming with Na_2CO_3Aq or HClAq.

THIOHYDANTOÏN $C_3H_4N_2SO$ *i.e.*



$$CS\begin{cases}NH.CH_2\\NH.CO\end{cases} \text{ or } C\begin{cases}S\\NH.CH_2\\NH—CO\end{cases}.$$

Formation.—1. By heating thio-urea with chloro-acetic acid or chloro-acetamide (Volhard, *A.* 166, 383; Mulder, *B.* 8, 1264; Maly, *A.* 168, 133; *B.* 10, 1853; Claesson, *B.* 10, 1352).—2. By heating thioglycollic acid (2 mols.) with cyanamide (1 mol.) in aqueous solution (Andreasch, *B.* 13, 1421; *M.* 1, 442).

Preparation.—Thio-urea (50 g.) dissolved in water (500 c.c.) is mixed with chloro-acetic acid (62 g.) in water (50 c.c.), heated to 90°, cooled, and mixed with the calculated quantity of NaOH (Andreasch, *M.* 8, 414).

Properties.—Long needles (from hot water), insol. alcohol and ether. Decomposes about 200°. Since it cannot be desulphurised by HgO, Liebermann (*A.* 207, 132) suggests that it does not contain the group CS.

Reactions.—1. *Chlorine* passed into its cooled solution in HClAq forms thio-oxy-hydantoïn (Kramps, *B.* 13, 788).—2. Br forms di-bromo-thio-hydantoïn. — 3. $KClO_3$ and HCl yield $C_3H_5KN_2SO_5$, crystallising in monoclinic tables, S. 1·7 at 22°; 23·3 at 100°, converted by nitrous acid into $SO_3H.CH_2.CO_2H$, and by baryta-water into sulpho-acetic acid and urea (Andreasch, *B.* 13, 1423; *M.* 4, 131).—4. Baryta-water forms thioglycollic acid and dicyandiamide. — 5. Boiling HClAq forms thiocarbimido-acetic acid.

Salts.—$Ag_2C_3H_2N_2SO$.—$B'_2H_2SO_4$. Plates. —$B'HNO_3$.– B′HCl.– $B'H_2C_2O_4$ aq. Prisms.— $B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. Minute yellow needles.

References.—DI-BROMO- and NITROSO-THIO-HYDANTOÏN.

DI-THIO-HYDROQUINONE $C_6H_4(SH)_2$. [98°]. Formed by reducing benzene *p*-disulphonic chloride with tin and HClAq (Körner a. Monselise, *G.* 6, 142). Formed also from $(C_6H_4(NH_2))_2S_2$ by diazotisation, treatment with potassium xanthate, and saponification of the product with alcoholic potash (Leuckart, *J. pr.* [2] 41, 205). Six-sided plates, slowly oxidised by air.

THIO-ISATYDE *v.* ISATYDE.

THIO-LACTIC ACID $CH_3.CH(SH).CO_2H$. *α-Sulphydro-propionic acid.*

Formation.—1. From α-chloro-propionic acid and KHS (Schacht, *A.* 129, 1; Lovén, *J. pr.* [2] 29, 368).—2. By the action of H_2S on silver α-chloro-propionate or silver pyruvate (Böttinger, *A.* 188, 320; *B.* 9, 404, 804, 1061; 11, 1561; 18, 486).

Preparation.—By saturating a solution of pyruvic acid with H_2S, and adding conc. HClAq and zinc (Lovén).

Properties.—Syrup, miscible with water, alcohol, and ether. May be distilled *in vacuo*. Its odour is unpleasant. $FeCl_3$ gives a transient indigo colour, and then oxidises it to sulphido-dipropionic acid. $CuSO_4$ gives a violet solution; a smaller quantity of $CuSO_4$ ppts. the cuprous salt. Cobalt acetate and air gives a brown colour.

Salts.—BaA'_2 (at 130°). Gummy mass.— $Hg(S.CHMe.CO_2H)_2$. — $Hg(S.CHMe.CO_2K)_2$ 2aq. $Hg(S.CHMe.CO_2)_2Ba$ 2½aq. — $AgS.CHMe.CO_2H$.

—$Bi(S.CHMe.CO_2H)_3$. — $Pt(S.CHMe.CO_2H)_2$. — $CuS.CHMe.CO_2H$. Yellow pp.—$PbC_3H_4O_2S$.

Ethyl ether EtA′. Oil. Yields $CuS.CHMe.CO_2Et$ as a yellowish powder.

THIO-DILACTYLIC ACID *v.* SULPHIDO-DI-PROPIONIC ACID.

THIO-MALIC ACID $C_4H_6SO_4$. Formed from bromo-succinic acid and aqueous KSH at 110° (Carius, *A.* 129, 6). Deliquescent mass, oxidised by dilute HNO_3 to sulpho-succinic acid.—BaA″.—Ag_2A''. Bulky pp., readily blackening.

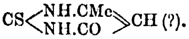
THIO-MESITOL *v.* TRI-METHYL-PHENYL MERCAPTAN.

THIO-DI-METHYL-ANILINE *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL SULPHIDE.

THIO-METHYL-COUMARILIC ETHER $C_{12}H_{12}SO_2$ *i.e.* $C_6H_4<\!\begin{matrix}CMe\\O\end{matrix}\!>C.CO.SEt$. [91°]. Formed from methyl-coumarilic ether and P_2S_5 (Hantzsch, *B.* 19, 2400). Yellow needles (from alcohol), v. sol. ether.

THIO-(a)-METHYL-COUMARIN $C_{10}H_8SO$ *i.e.* $C_6H_4<\!\begin{matrix}CH:CMe\\O-CS\end{matrix}$. [122°]. Formed by heating (a)-methyl-coumarin with P_2S_5 at 120° (Aldringen, *B.* 24, 3460). Yellow needles, insol. water, v. sol. alcohol. Converted by alcoholic potash into (a)-methyl-coumarin.

THIO-METHYL-DI-PHENYL-AMINE *v.* METHYL-IMIDO-DI-PHENYL SULPHIDE.

THIO-METHYL-URACIL $C_5H_6N_2SO$ *i.e.*  $CS<\!\begin{matrix}NH.CMe\\NH.CO\end{matrix}\!>CH$ (?). S. ·054 at 21°. Formed by the action of alcoholic potash on the needles which separate after some days from a solution of thio-urea (1 mol.) and acetoacetic ether (1 mol.) in alcohol to which a little HCl has been added (Nencki a. Sieber, *J. pr.* [2] 25, 72; List, *A.* 236, 1; Behrend, *B.* 19, 219). Plates, v. sl. sol. ether. Decomposed at 280°.

Reactions.—1. The K salt reacts with EtI forming $C_5H_5N_2SOEt$ [145°], and with MeI forming $C_5H_5N_2SOMe$ [220°], which yields $C_6H_7AgN_2SO$. — 2. *Chloro-acetic ether* forms $C_5H_5N_2SO(CH_2.CO_2Et)$ [143°], which yields $C_5H_5N_2SO(CH_2.CO_2H)$ [204°]. — 2. Br forms methyl-uracil, and finally di-oxy-methyl-uracil. Cl acts in like manner, forming $C_5H_6Cl_2N_2O_3$. —3. On warming with lead hydrate in strongly alkaline solution it is converted into methyl-uracil. Conc. HClAq at 150°, conc. NH_3Aq at 150°, and Ac_2O at 185° also form methyl-uracil.

Salts. — $C_5H_4Ag_2N_2SO$. — $C_5H_4CuN_2SO$. — $(C_5H_5N_2SO)_2Hg$. — $C_5H_5N_2NaSO$ 2aq. — $C_5H_5N_2KSO$ ½aq.

THIONAMIC ACID. H. Rose (*P.* 33, 235; 42, 415) found that SO_2 and NH_3 combined in equal volumes, when dry NH_3 was mixed with excess of dry SO_2, to form a yellowish white solid, which quickly decomposed in solution, or moist air, giving $(NH_4)_2SO_4$ and ammonium salts of other sulphur oxyacids. Rose concluded that the substance was $SO_2.NH_3$ from the fact that it was formed by combining equal volumes of the two gases; if this empirical formula is accepted the compound may be $SO_2.NH_2.H$ or $SO.OH.NH_2$. When dry SO_2 was mixed with excess of dry NH_3, Rose found that 1 vol. SO_2 combined with 2 vols. NH_3; the product—an amorphous, white solid—may be $SO_2.NH_2.NH_4$ or $SO.ONH_4.NH_2$.

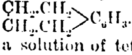
M. M. P. M.

THIONAMIDE. By passing NH_3 into cooled S_2Cl_2 Schiff (*A.* 102, 111) obtained a white solid which was decomposed by warm water to $(NH_4)_2SO_3Aq$. The solid contained NH_4Cl; Schiff regarded it as a mixture of this salt with $SO(NH_2)_2$; he did not attempt to separate the supposed thionamide from NH_4Cl.

M. M. P. M.

(a)-THIO-NAPHTHOIC ACID.

Amide $C_{10}H_7CS.NH_2$. [126°]. Formed from (a)-naphthoic nitrile and alcoholic ammonium sulphide at 30°-35° (Hofmann, *B.* 1, 40; Bamberger, *B.* 21, 54). Crystals. v. sol. alcohol.

Tetrahydride of the amide  $\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!>C_6H_3.CS.NH_2$. Formed by digesting a solution of tetrahydride of (a)-naphthonitrile in alcoholic ammonia saturated with H_2S for some days at 30°-40° (Bamberger a. Bordt, *B.* 22, 629). Dark-yellow oil.

(β)-**Thio-naphthoic acid.** *Amide* $C_{10}H_7.CSNH_2$. [149°]. Formed from (β)-naphthonitrile and ammonium sulphide at 35°-40° (Bamberger a. Bockmann, *B.* 20, 1115). Needles, v. sol. alcohol. Dissolves in hot water, being slowly converted into the nitrile.

THIO-NAPHTHOL *v.* NAPHTHYL MERCAPTAN.

THIO-DI-NAPHTHYL-AMINE *v.* IMIDO-DI-NAPHTHYL SULPHIDE.

THIONATES. Salts of the *thionic acids* (*q. v.*, p. 698). Four series of thionates are known; a fifth probably exists: $M_2S_2O_6$ = dithionates; $M_2S_3O_6$ = trithionates; $M_2S_4O_6$ = tetrathionates; $M_2S_5O_6$ = pentathionates; and probably $M_2S_6O_6$ = hexathionates. The thionates are formed by the action of alkalis on the liquid obtained by passing H_2S into saturated SO_2Aq; also by the oxidation of sulphites, thiosulphates, and mixtures of these, and in other reactions (*cf.* THIONIC ACIDS, p. 698). For general qualitative reactions of thionates and thiosulphates *v.* Debus (*C. J.* 53, 298).

DITHIONATES, $M^I_2S_2O_6$, $M^{II}S_2O_6$, and $M^{III}_2(S_2O_6)_3$. (*Hyposulphates.*) The alkali salts are formed by the interaction of a dilute solution of I in KIAq and dilute $NaHSO_3Aq$ (Spring a. Bourgeois, *Bl.* [2] 46, 151; Sokoloff a. Mattscheffski, *B.* 14, 2058); also by the reaction of $KMnO_4Aq$ on thiosulphates in acetic acid solution, or on sulphites or trithionates (Hönig a. Zatzek, *M.* 4, 738; Fordos a. Gélis, *J. Ph.* [3] 36, 113). The Ba salt is formed by passing SO_2 into water holding MnO_2 in suspension, filtering, and adding BaOAq (for more details *v.* DITHIONIC ACID, p. 698); most of the other dithionates are obtained by the interaction of BaS_2O_6Aq and sulphates; several have been prepared by digesting $H_2S_2O_6Aq$ with metallic hydroxides. The dithionates are sol. water; the salts of the alkali and alkaline earth metals are not readily decomposed either in solution or as solids; solutions of most of the other salts are decomposed by heat, giving off SO_2 (*v.* Klüss, *A.* 246, 179, 284; Geuther, *A.* 226, 232).

Dithionates give off SO_2 when heated to redness, leaving normal sulphates; thus $M_2S_2O_6 = SO_2 + M_2SO_4$; this reaction is characteristic; so also is the reaction of H_2SO_4Aq or HClAq with boiling solutions of dithionates, whereby H_2SO_4Aq is formed and SO_2 is given off, without separation of S.

Ammonium dithionate $(NH_4)_2S_2O_6$. Obtained by decomposing the Ba salt in solution by $(NH_4)_2SO_4$Aq, filtering and crystallising. S.G. 1·704 (Topsoë, *C. C.* 4, 76). Klüss (*A.* 246, 179, 284) gives formula $2Am_2S_2O_6$.aq, and says the salt crystallises in monoclinic needles. Very sol. water; insol. alcohol. Aqueous solution may be boiled without change. Forms *double salts* with AmCl (Fock a. Klüss, *B.* 24, 3017); also with the dithionates of Al, Cd, Co, Cu, Fe, Mn, Ni, and Zn (K., *l.c.*).

Barium dithionate BaS_2O_6. 2aq. Formed by passing SO_2 into water at c. 0° holding coarsely-powdered MnO_2 in suspension, till the MnO_2 is dissolved ($MnO_2 + SO_2 + Aq = MnSO_4Aq$; and also $MnO_2 + 2SO_2 + Aq = MnS_2O_6Aq$), filtering if necessary, adding BaOAq to alkaline reaction ($MnS_2O_6Aq + BaO_2H_2Aq = BaS_2O_6Aq + MnO_2H_2$), filtering from MnO_2H_2, evaporating, and recrystallising from water (*cf.* Stas, *Chem. Proport.* 117). White prisms; S. 24·75 at 18°, 90·9 at 100°, 100·6 at 102° = b.p. of saturated solution; insol. alcohol. The crystals effloresce in air, losing $2H_2O$; a hydrate with $4H_2O$ is obtained by slow evaporation (*v.* Heeren, *P.* 7, 55; Gay-Lussac, *A. Ch.* [2] 10, 312; Baker, *C. N.* 36, 203; *cf.* Spring a. Bourgeois, *Bl.* [2] 46, 151. For crystalline form *v.* Senarmont, *J.* 1857. 142; Rammelsberg, *P.* 58, 295; von Lang, *W. A. B.* 45 [2] 27). Schiff (*A.* 105, 239) described *double salts* with MgS_2O_6 and $Na_2S_2O_6$ (*cf.* Kraut, *A.* 118, 95); Bodländer (*Chem. Zeit.* 14, 1140) described a double salt with $Rb_2S_2O_6$; and Klüss (*A.* 246, 179, 284) double salts with $Ag_2S_2O_6$ and $Tl_2S_2O_6$.

Many of the other dithionates are prepared from the Ba salt.

Potassium dithionate $K_2S_2O_6$. Prepared from a solution of the Ba salt by adding an equivalent quantity of K_2SO_4 in solution, warming, filtering, and evaporating; also by boiling K_2SO_3Aq with MnO_2 filtering, and separating from K_2SO_4 by fractional crystallisation (K_2SO_4 is much less sol. water than $K_2S_2O_6$). White, hexagonal crystals; unchanged in air; decrepitates when heated and then gives off SO_2 and leaves K_2SO_4; S.G. 2·277 (Topsoë, *Bl.* [2] 19, 246). The crystals rotate the plane of polarisation of light; an aqueous solution is optically inactive (Pape, *P.* 139, 224). S. c. 6 at ordinary temperature, c. 66 at 100°; insol. alcohol (Heeren, *P.* 7, 55).

Sodium dithionate $Na_2S_2O_6$. 2aq. Prepared similarly to the K salt. Also formed, according to Bunte (*B.* 7, 646), by heating $Na.Et.S_2O_3$ for some time at 100° (Et_2S_2 distils off). Large, lustrous, rhombic prisms; unchanged in air, S.G. 2·175 at 11° (Baker, *C. N.* 36, 203). S. 47·6 at 16°; 90·9 at 100°; insol. alcohol. Solution is slowly reduced by sodium-amalgam to Na_2SO_3Aq (Spring, *B.* 7, 1161). Kraut (*A.* 117, 97) described a hydrate with $6H_2O$.

Dithionates of the following metals have also been described (the figures indicate the references): Al (1) (3); Be (3); Bi (3); Cd (1) (2) (4); Ca (1) (4) (5); Cr (3); Co (1) (2) (3) (4); Cu (3); Fe (1) (3) (4); Pb (1) (4) (5); Li (2) (4); Mg (1) (4) (5); Mn (4); Hg (1) (2) (3); Ni (2) (4) (5); Rb (6); Ag (1) (2) (4) (5); Sr (2) (4); Tl (3); Sn (3); U (3); Zn (1) (2) (4).

(1) Heeren, *P.* 7, 72, 171; (2) Rammelsberg, *P.* 58, 298; (3) Klüss, *A.* 246, 179, 284; (4) Topsoë, *C. C.* 4, 76; (5) Baker, *C. N.* 36, 203; (6) Piccard, *J. pr.* 86, 456.

TRITHIONATES $M^I_2S_3O_6$ and $M^{II}S_3O_6$. The alkali salts are formed by digesting conc. $MHSO_3$Aq with S at 50°–60° ($6MHSO_3Aq + 2S = 2M_2S_3O_6Aq + M_2S_2O_3Aq + 3H_2O$)(Pelouze, *A. Ch.* [3] 79, 85); also by heating dilute $MHSO_3$Aq, or keeping the solution for a long time in a closed tube (Saint-Pierre, *C. R.* 62, 632); by passing SO_2 into $M_2S_2O_3$Aq ($2M_2S_2O_3Aq + 3SO_2 = 2M_2S_3O_6Aq + S$); by passing SO_2 into M_2SAq (Chancel a. Diacon, *J. pr.* 90, 35; Rathke, *J. pr.* 95, 11); by the interaction of I and a mixture of M_2SO_3 and $M_2S_2O_3$ in solution ($M_2SO_3Aq + M_2S_2O_3Aq + I_2 = M_2S_3O_6Aq + 2MIAq$) (Spring, *B.* 7, 1157); by the interaction of boiling water on $AgKS_2O_3$ or $HgNa_2(S_2O_3)_2$, whereby $K_2S_3O_6$Aq or $Na_2S_3O_6$Aq is formed, along with Ag_2S or HgS (Spring, *l.c.*); by reacting on M_2SO_3Aq with S_2Cl_2 (Spring, *B.* 6, 1108); by decomposing $M_2S_2O_3$Aq by a non-oxidising acid, *e.g.* by H_2SO_4 (Spring a. Levy, *Bull. de l'Acad. roy. de Belge*, 42, 108); by heating $(NH_4)_2SO_4$ with P_2S_5, Spring (*B.* 7, 1158) obtained a little $(NH_4)_2S_3O_6$, along with much $(NH_4)_2S_2O_3$, some NH_4 polysulphides, and P compounds; $K_2S_3O_6$ is also obtained from Wackenroder's solution.

The trithionates are soluble in water; they very readily decompose; heated with water they give off SO_2, deposit S, and form sulphates in solution. Addition of excess of $CuSO_4$Aq to solution of a trithionate causes ppn. of CuS and evolution of SO_2 (Spring, *B.* 6, 1108).

SELENOTRITHIONATES $M_2SeS_2O_6$ are described as *dithio-triselenates* under SELENATES (p. 434).

Potassium trithionate $K_2S_3O_6$. A conc. solution of $K_2S_2O_3$ is formed by dissolving the salt in 8 pts. water and 1 pt. alcohol till the alcohol separates from the aqueous solution; SO_2 is passed into this solution at 25°–30°, solid $K_2S_2O_3$ being added from time to time, till the liquid is yellow and smells of SO_2; the crystals that separate are dissolved in water at 60°–70°, the solution is filtered from S, mixed with eight times its volume of 84 p.c. alcohol, warmed gently, and allowed to crystallise (Plessy, *A. Ch.* [3] 20, 162; for other methods of preparation *v.* Langlois, *A. Ch.* [2] 79, 77; Rathke, *J.* 1864. 164; Chancel a. Diacon, *C. R.* 56, 710). White rhombic needles (Baker, *C. N.* 36, 203). Very sol. water, insol. alcohol. Aqueous solution gives K_2SO_4Aq, SO_2, and S when heated. Debus (*C. J.* 53, 313) found that $K_2S_3O_6$Aq slowly changes at the ordinary temperature, giving K_2SO_4Aq, $K_2S_4O_6$Aq, and $K_2S_5O_6$Aq without separation of S. According to C. a. D. (*l.c.*), $K_2S_3O_6$Aq interacts with K_2S_2Aq to give only $K_2S_2O_3$Aq; with H_2S the products are K_2SO_4Aq, $K_2S_2O_3$Aq, and S (Debus, *C. J.* 53, 329). Sodium-amalgam reacts readily, producing $KNaS_2O_3$ and $KNaSO_3$ (Spring, *B.* 7, 1161).

The other trithionates that have been isolated are those of Ba (Kessler, *P.* 74, 253); Pb (K., *l.c.*; Chancel a. Diacon, *C. R.* 56, 710); Na (K., *l.c.*; Rathke, *J. pr.* 95, 13; Villiers, *C. R.* 106, 1356); and Zn (Fordos a. Gélis, *A. Ch.* [3] 22, 66).

TETRATHIONATES $M^I_2S_4O_6$ and $M^{II}S_4O_6$. The alkali salts are formed by triturating $M_2S_2O_3$ with I, adding a little water and pouring into alcohol (von Klobukoff, *B.* 18, 1869; Eliasberg, *B.* 19, 322; Fock a. Klüss, *B.* 23, 2429); the Pb salt is formed by the prolonged interaction of I and PbS_2O_3, also by the interaction of H_2SO_4Aq and a mixture of PbS_2O_3 with PbO_2 (Chancel a. Diacon, *J. pr.* 90, 55); tetrathionates are also formed, according to Spring a. Levy (*Bull. de l'Acad. roy. de Belge*, 42, 108), by the interaction of thiosulphates and ferrous or cuprous salts, $KMnO_4Aq$, hypochlorites, or $KClO_3$ dissolved in H_2SO_4Aq. $K_2S_4O_6$ is obtained by neutralising Wackenroder's solution by $KC_2H_3O_2$ (*v.* Debus, *C. J.* 53, 278; *cf.* Curtius a. Henkel, *J. pr.* [2] 37, 137). The tetrathionates are e. sol. water, but insol. alcohol; aqueous solutions are generally decomposed on evaporation.

Potassium tetrathionate $K_2S_4O_6$. Formed by adding I, little by little, to conc. $K_2S_2O_3Aq$ till a permanent reddish-brown colour is produced, dissolving the crystals that separate in warm water, filtering from S, adding alcohol till the pp. that forms is re-dissolved, and allowing to crystallise (Kessler, *P.* 74, 253). Spontaneous decomposition of conc. $K_2S_5O_6Aq$ gives $K_2S_4O_6$ and S (Debus, *C. J.* 53, 311). Perfectly dry $K_2S_4O_6$ can be kept unchanged in a dry atmosphere; but in ordinary air, after a time, SO_2 is formed; an aqueous solution of $K_2S_4O_6$ slowly changes to $K_2S_3O_6Aq$, $K_2S_5O_6Aq$, K_2SO_4Aq, and SO_2 (D., *l.c.*). BrAq reacts to form H_2SO_4Aq, S, and KBr; but if the BrAq is added very gradually the S that is formed combines with residual $K_2S_4O_6$ to form $K_2S_5O_6$; similarly, if a little K_2SO_4 is added to $K_2S_4O_6Aq$, and H_2S is then passed in, K_2SO_4 and S are formed, and the S combines with unchanged $K_2S_4O_6$ to form $K_2S_5O_6$ (D., *l.c.* p. 315). Sodium-amalgam forms $KNaS_2O_3Aq$ (Spring, *B.* 7, 1161).

The other tetrathionates that have been isolated are those of Ba (Lewes, *C. J.* 39, 69; Fordos a. Gélis, *A. Ch.* [3] 22, 66; Curtius a. Henkel, *J. pr.* [2] 37, 137); Cd (Kessler, *P.* 74, 253); Cu (Chancel a. Diacon, *C. R.* 56, 510); Fe (F. a. G.); Pb (K.; C. a. D.); Na (K.; von Klobukoff, *B.* 18, 1869); Sr (K.); and Zn (F. a. G.).

PENTATHIONATES $M^I_2S_5O_6$ and $M^{II}S_5O_6$. Wackenroder, in 1845 (*A.* 60, 189), asserted that the liquid formed by passing H_2S into SO_2Aq contained pentathionic acid $H_2S_5O_6$; other chemists confirmed his results, and prepared a few salts of the acid (*v.* Lenoir, *A.* 62, 253; Fordos a. Gélis, *A. Ch.* [3] 22, 66; Kessler, *P.* 74, 257; Ludwig, *Ar. Ph.* [2] 85, 9; Chancel a. Diacon, *C. R.* 56, 710). At a later time the existence of pentathionates was denied, chiefly by Spring (*B.* 12, 2254; 13, 924; 15, 2618), but upheld by Kessler (*B.* 13, 424; *v.* also Takatmatsu a. Smith, *B.* 13, 1976). In 1881 Lewes (*C. J.* 39, 68) seemed to have isolated BaS_5O_6 and $K_2S_5O_6$, but Spring failed to confirm his results. Shaw, however (*C. J.* 43, 357), repeated Lewes's experiments, and obtained $K_2S_5O_6$. In 1888 Debus (*C. J.* 53, 278) made an elaborate investigation of Wackenroder's solution, and prepared $K_2S_5O_6$ therefrom. Curtius a. Henkel (*J. pr.* [2] 37, 137) assert that Wackenroder's solution contains acid tetrathionates, in which the ratio of S to Ba is greater than 4S:Ba, and that these have been mistaken for pentathionates. But Debus's experiments seem to have settled the dispute in favour of the existence of pentathionates. Ammoniacal $AgNO_3Aq$ gives very distinct brown colouration, followed by a black pp. with pentathionates; this reaction distinguishes them from salts of other S oxyacids (*v.* Debus, *l.c.*, p. 297).

Potassium pentathionate $2K_2S_5O_6.3aq$. Debus (*C. J.* 53, 294) prepared this salt from *Wackenroder's solution* (*v.* p. 698) by adding 16·66 g. $KC_2H_3O_2$ (previously fused) to 43 c.c. of the solution of S.G. 1·343; the $KC_2H_3O_2$ was dissolved in as little water as possible acidulated with a few drops of acetic acid; the solution was placed in a large flat dish in a current of air until the liquid had evaporated; the crystalline residue (weighing 26 g.) was repeatedly pressed between filter-paper, and then dissolved in 50 c.c. water + 1 c.c. H_2SO_4, at 40°; the minute quantity of S that separated (c. ·005 g.) was filtered off, and the filtrate was allowed to crystallise in a flat dish. The crystals that separated (18·75 g.) were a mixture of $K_2S_4O_6$ and $K_2S_5O_6$; they were dried by placing them on blotting paper, and the crystals of pentathionate were picked out (5·75 g. were obtained), crystallised twice from water acidulated with a little H_2SO_4Aq, and dried over H_2SO_4. The crystals of pentathionate form four-sided rhombic plates, or six-sided star-like plates; those of tetrathionate form six-sided prisms, with pyramids only on one end, and with the side on which they rest much developed. Lewes (*C. J.* 39, 75) described three salts: $K_2S_5O_6$, $K_2S_5O_6.H_2O$, and $K_2S_5O_6.2H_2O$; Debus's salt was $2K_2S_5O_6.3H_2O$. According to Fock a. Klüss (*B.* 23, 2428), this is the only salt that exists (*cf.* D., *l.c.*, p. 297). The salt can also be obtained by passing H_2S into $K_2S_4O_6Aq$ acidulated with H_2SO_4Aq (D., *l.c.*, p. 315).

Crystals of $2K_2S_5O_6.3H_2O$ begin to decompose, when kept in a stoppered bottle, after a month or so, giving eventually a yellow, pulpy mass of $K_2S_4O_6$, S, and water; the decomposition is caused by water in the interstices of the crystals. By powdering finely, washing with dilute alcohol, and placing over H_2SO_4, Debus (*l.c.* p. 295) kept the salt unchanged for two or three years. $2K_2S_5O_6.3H_3O$ dissolves in c. 2 parts water, forming a clear, neutral solution, which soon decomposes with separation of S and formation of $K_2S_4O_6Aq$ (D., *l.c.*, p. 311); addition of a drop of dilute KOHAq to the solution causes separation of S (p. 291); H_2S ppts. much S, and $K_2S_3O_6$ and $K_2S_2O_3$ are formed in the solution (p. 328); SO_2 produces $K_2S_3O_6Aq$ and $K_2S_2O_3Aq$ (p. 332); the salt is insoluble in alcohol.

Barium pentathionate $BaS_5O_6.3aq$; obtained by Lewes (*C. J.* 39, 68) by partially neutralising Wackenroder's solution by BaOAq, crystallising over H_2SO_4, pouring off from BaS_4O_6, and again crystallising.

Copper pentathionate $CuS_5O_6.4aq$; obtained by Debus (*l.c.*, p. 300) in blue, prismatic crystals, by adding $Cu(C_2H_3O_2)_2Aq$ to Wackenroder's solution and allowing to evaporate. Debus probably obtained *zinc pentathionate*, but not in a pure state (*l.c.*, p. 299).

HEXATHIONATES. By adding $KC_2H_3O_2Aq$ to the mother-liquor from $K_2S_4O_6$ and $K_2S_5O_6$ (*v. supra*), evaporating in a current of air, dis-

solving in water with a little H_2SO_4Aq, allowing to evaporate in portions, and collecting the crystals separately, Debus (*C. J.* 53, 301) obtained a salt in which the ratio of S to O was almost 6S:6O, as required by *potassium hexathionate*.

M. M. P. M.

THIONESSAL *v.* Tetra-phenyl-thiophene.

THIONIC ACIDS. The acids $H_2S_xO_6$, where $x = 2, 3, 4, 5$, and probably 6, are generally called thionic acids, and are distinguished as *di-*, *tri-*, &c., thionic acid. The acids are known only in aqueous solutions; most of these solutions readily oxidise to H_2SO_4Aq. Dithionic acid is produced by the action of certain oxidisers on H_2SO_3Aq; dithionates are formed by oxidising sulphites and thiosulphates; trithionates are formed when mixtures of sulphites and thiosulphates are oxidised, also when SO_2Aq interacts with alkali thiosulphates; tetrathionates result by the action of certain oxidisers on thiosulphates. These processes may be represented diagrammatically as follows (the actual reactions are much more complex):

(1) $2H_2SO_3Aq + O = H_2S_2O_6Aq + H_2O$;

(2) $2M_2SO_3Aq + O = M_2S_2O_6Aq + M_2O$;
$M_2S_2O_3Aq + 3O = M_2S_2O_6Aq$;

(3) $M_2SO_3Aq + M_2S_2O_3Aq + O = M_2S_3O_6Aq + M_2O$;
$2M_2S_2O_3Aq + 3SO_2Aq = 2M_2S_3O_6Aq + S$;

(4) $2M_2S_2O_3Aq + O = M_2S_4O_6Aq + M_2O$.

After passing H_2S for a long time into nearly saturated H_2SO_3Aq, the solution contains $H_2S_3O_6$, much $H_2S_4O_6$, $H_2S_5O_6$, and probably $H_2S_6O_6$, along with H_2SO_4, dissolved colloidal S, and a little S in suspension. This solution is known as *Wackenroder's solution* (Wackenroder, *A.* 60, 189 [1845]). It has been examined by many chemists; a very thorough investigation was made by Debus in 1888 (*C. J.* 53, 278; where references will be found to other memoirs). The solution examined by Debus was prepared by passing a slow current of H_2S into 480 c.c. nearly saturated SO_2Aq at a little above 0° for two hours, keeping in a stoppered bottle for forty-eight hours at the ordinary temperature, passing in H_2S for two hours, after forty-eight hours again passing in H_2S, and repeating these treatments until the liquid no longer smelled of SO_2 after standing for a couple of hours at the ordinary temperature (about two weeks were required before the action was completed). The liquid thus obtained contains a large quantity of S, partly as a hard brittle solid, partly as a soft and gummy mass, and partly in suspension in minute particles which pass through filter paper; the liquid remains milky after filtration, and does not become clear on standing for two or three weeks (regarding the variety of S in solution, *v.* Sulphur, *Allotropic forms of*, p. 608). Debus (*l.c.*, p. 348) thinks that the product of the direct interaction of SO_2Aq and H_2SAq is $H_2S_4O_6$ ($3SO_2Aq + H_2SAq = H_2S_4O_6Aq$); that part of this $H_2S_4O_6$ reacts with excess of SO_2Aq to form $H_2S_3O_6Aq$ and $H_2S_2O_3Aq$ (? $H_2S_4O_6Aq + H_2SO_3Aq = H_2S_3O_6Aq + H_2S_2O_3Aq$), and that part of the $H_2S_4O_6Aq$ reacting with $H_2S_2O_3Aq$ forms $H_2S_5O_6Aq$ (? $H_2S_4O_6Aq + H_2S_2O_3Aq = H_2S_5O_6Aq + H_2SO_3Aq$) (D., *l.c.*, p. 333); that the H_2S reacts with $H_2S_4O_6Aq$ to form H_2O and S, part of the S combining, as it is formed, with $H_2S_3O_6Aq$ to form $H_2S_4O_6Aq$, $H_2S_5O_6Aq$ and $H_2S_6O_6Aq$, and part remaining in solution as colloidal S. If H_2S is passed into Wackenroder's solution, more $H_2S_5O_6$ is formed; and if the passage of H_2S is continued until all reaction ceases the thionic acids are decomposed, and the final products are S and H_2O, so that the equation $SO_2Aq + 2H_2SAq = 3S + 2H_2OAq$ correctly represents the interaction of SO_2Aq with H_2SAq so far as the final products are concerned (*v.* D., *l.c.*, p. 351).

Solutions of the thionic acids more or less rapidly decompose, the final products being H_2SO_4Aq, SO_2Aq, and S; oxidisers such as Cl or HNO_3Aq—in some cases air is sufficient—convert them into H_2SO_4Aq; reducers, such as Na amalgam, produce $H_2S_2O_3Aq$, sometimes also H_2SO_3Aq, and in some cases H_2SAq. None of the acids has been isolated apart from water; salts of all are known (*v.* Thionates, p. 695). The acids are all dibasic.

Regarding the constitution of the thionic acids *v.* Mendeléeff, *B.* 3, 870; Michaelis, *A.* 170, 31; Spring, *B.* 6, 1108; Debus, *C. J.* 53, 351.

Dithionic acid $H_2S_2O_6Aq$. (*Hyposulphuric acid.*) A solution of this acid is formed by suspending coarsely-powdered MnO_2 in water, and passing in SO_2 while the liquid is kept at c. 0°; filtering, adding BaOAq to alkaline reaction, and filtering from $BaSO_4$ and MnO_2H_2; evaporating, crystallising out $BaS_2O_6.2aq$, and decomposing this salt in solution by the equivalent quantity of H_2SO_4Aq; filtering from $BaSO_4$, and evaporating *in vacuo* till a liquid of S.G. 1·347 is obtained ($MnO_2 + 2SO_2Aq = MnS_2O_6Aq$; $MnO_2 + SO_2Aq = MnSO_4Aq$) (Spring a. Bourgeois, *Bl.* [2] 46, 151). If evaporation is continued beyond this concentration, H_2SO_4Aq and SO_2 are formed; the same decomposition occurs when $H_2S_2O_6Aq$ is evaporated by heat. $H_2S_2O_6Aq$ is reduced by Zn and HClAq to H_2SO_3Aq at 0° (Otto, *A.* 147, 187); it is oxidised to H_2SO_4Aq by Cl, HNO_3, $KClO_3$ and HCl &c.; it slowly oxidises in air (*cf.* Dithionates, p. 695). Thomsen (*Th.* 2, 259) gives the following heats of formation of $H_2S_2O_6Aq$:—$[S^2,O^5,Aq] = 211,080$; $[2SO^2,O,Aq] = 68,920$; $[2SO^2Aq,O] = 53,520$; for the heat of oxidation of $H_2S_2O_6Aq$ to H_2SO_4Aq he gives ($S_2O_5Aq + O = 2SO_3Aq$) $[S^2O^5Aq,O] = 73,740$.

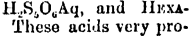
Trithionic acid $H_2S_3O_6Aq$. A dilute solution of this acid is formed by decomposing $K_2S_3O_6Aq$ by the equivalent quantity of $HClO_4Aq$ or H_2SiF_6Aq, and filtering from $KClO_4$ or K_2SiF_6 (Langlois, *C. R.* 10, 461; 62, 842; Kessler, *P.* 74, 250). The dilute solution cannot be evaporated, even *in vacuo*, without partial decomposition, with formation of SO_2 and S; when heated it rapidly changes to H_2SO_4Aq, SO_2 and S. The dilute solution is colourless and odourless, and has a sour and bitter taste (*cf.* Trithionates, p. 696). The K salt, from which the acid solution is obtained, may be prepared by dissolving $K_2S_2O_3$ in water containing one-eighth part of alcohol, adding the salt till the alcohol separates from the aqueous solution, passing in SO_2, with addition from time to time of a little $K_2S_2O_3$, temperature being kept at 25°-30°, till the liquid is yellow and smells of SO_2, setting aside till crystals separate, and re-crystallising from warm water (filtering from separated S) (Plessy, *A. Ch.* [3] 11, 182).

Tetrathionic acid $H_2S_4O_6Aq$. PbS_4O_6Aq is decomposed by the equivalent quantity of H_2SO_4Aq (not by H_2S, which reacts with $H_2S_4O_6$), and the filtrate from $PbSO_4$ is concentrated on the water-bath, and then *in vacuo* over H_2SO_4 (Fordos a. Gélis, *C. R.* 115, 920). PbS_4O_6 may be prepared by pouring a solution of 2 pts. $Na_2S_2O_3.5H_2O$ in much warm water into a dilute warm solution of 3 pts. lead acetate, and thoroughly washing the ppd. PbS_2O_3 with warm water, adding water enough to partially dissolve the PbS_2O_3, then adding 1 pt. I, and letting stand for some days, with frequent shaking, filtering from PbI_2, evaporating and crystallising ($2PbS_2O_3 + 2I + Aq = PbS_4O_6Aq + PbI_2$).

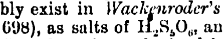
$H_2S_4O_6Aq$ is colourless and odourless; it has a sour taste. Dilute $H_2S_4O_6Aq$ may be boiled without change, but the conc. solution decomposes to H_2SO_4Aq, SO_2, and S. Dilute HClAq or H_2SO_4Aq does not interact with cold $H_2S_4O_6Aq$; on warming H_2S is given off; HNO_3Aq or Cl rapidly oxidises $H_2S_4O_6Aq$ to H_2SO_4Aq (*cf.* Tetrathionates, p. 696). Thomsen (*Th.* 2 262) gives the following data for H.F.:— $[S^4,O^5,Aq] = 192,430$; $[2SO^2,S^2,O,Aq] = 50,270$; $[2SO^2Aq,S^2,O] = 34,870$; $[2S^2O^2Aq,O] = 53,490$.

Pentathionic acid $H_2S_5O_6Aq$, and Hexathionic acid $H_2S_6O_6Aq$. These acids very probably exist in *Wackenroder's solution* (*v. supra*, p. 698), as salts of $H_2S_5O_6$, and probably also of $H_2S_6O_6$, have been obtained from that solution; solutions of the acids have not been isolated (*v.* Pentathionates, p. 697, and Hexathionates, p. 697).

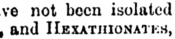
M. M. P. M.

THIONINE. The group 

$\begin{array}{l} S\text{————}C_6H_3 \\ C_6H_3(NH_2).N\text{——} \end{array}\!\!>NH$

i.e. 

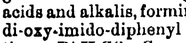
$C_6H_3(NH_2)\!<\!\begin{array}{c}S\\N\end{array}\!\!>\!C_6H_3{:}NH$ (Bernthsen a. Goske, *B.* 20, 931).

THIONOL $C_{12}H_7NSO_2$ *i.e.* 

$\begin{array}{l} S\text{————}C_6H_3 \\ C_6H_3(OH).N\text{——} \end{array}\!\!>O.$

Formed by heating imido-di-phenyl sulphide with dilute H_2SO_4 at 150°-160° (Bernthsen, *A.* 230, 188). Brownish-red powder, which acquires green lustre on rubbing. Insol. cold water, sol. acids and alkalis, forming a violet solution. Yields di-oxy-imido-diphenyl sulphide (*q. v.*) on reduction.—$B'_2H_2SO_4$. Green needles.—$B'BaO$ (dried at 100°). Plates with green lustre.—$B'Ag_2O$ (dried at 100°). Brown amorphous pp.

THIONOLINE *v.* Oxy-amido-imido-diphenyl sulphide.

THIONURIC ACID $C_4H_5N_3SO_6$ *i.e.* 

$CO\!<\!\begin{array}{l}NH.CO\\NH.CO\end{array}\!\!>\!CH.NH.SO_3H$. Formed by the simultaneous action of NH_3 and SO_2 on alloxan in aqueous solution (Liebig a. Wöhler, *A.* 26, 268, 314, 331). Formed also by warming nitroso-barbituric acid with ammonium sulphite (Baeyer, *A.* 127, 210). Crystalline mass of needles, v. sol. water. Decomposed by boiling water into uranil and H_2SO_4. Reduces ammoniacal $AgNO_3$ to a mirror.—$(NH_4)_2A''aq$. Four-sided tables, sl. sol. cold water. At 200° it yields $(NH_4)_2SO_4$ and xanthinine (Finck, *A.* 132, 298).—$(NH_4)HA''$. White needles.—CaA''. Prisms.—$PbA''aq$.

THIONYL-*m*-AMIDO-BENZOIC ACID $SO{:}N.C_6H_4.CO_2H$.

Methyl ether MeA'. [57°]. (212° at 100 mm.). Formed from methyl *m*-amido-benzoate and $SOCl_2$ (Michaelis, *A.* 274, 250). Yellow crystalline mass, v. sol. ether and benzene.

Ethyl ether EtA'. Oil.

THIONYL-DIAMIDO-DI-PHENYL-ETHYLENE $C_2H_4(C_6H_4.N{:}SO)_2$. [202°]. Formed from di-amido-stilbene and $SOCl_2$ (Michaelis, *A.* 274, 265). Red needles, m. sol. benzene and $CHCl_3$.

THIONYL-AMIDO-PHENOL. *Ethyl derivative* $C_6H_4(OEt).N{:}SO$. [32°]. (220° at 200 mm.). Formed from *p*-amido-phenetol and $SOCl_2$ (Michaelis, *A.* 274, 246). Light-yellow needles, v. sol. ether. Slowly decomposed by water.

THIONYL-AMYLAMINE $SO{:}NC_5H_{11}$. (87° at 60 mm.). Formed from amylamine (103°) in ether and $SOCl_2$ (Michaelis, *A.* 274, 191). Oil, decomposed by water.

THIONYL-ANILINE $C_6H_5N{:}SO$. (200°). S.G. ^{15} 1·236. Formed from aniline in benzene solution and $SOCl_2$ (Michaelis, *B.* 23, 3480; 24, 745). Liquid with peculiar odour, sol. alcohol. Converted by alkalis into aniline and sulphite. Chlorine forms tri-chloro-aniline [78°]. Conc. HClAq also forms aniline and SO_2. The compound $C_6H_2Br_3N{:}SO$ [75°] is formed from tri-bromo-aniline in benzene and $SOCl_2$. The compounds [1:2]$C_6H_4Cl.N{:}SO$ [−8°], [1:3] $C_6H_4Cl.N{:}SO$ (233°) and [1:4] $C_6H_4Cl.N{:}SO$ [36°] (237°) are formed in like manner. *o*-, *m*-, and *p*- Thionyl-bromo-anilines melt at 4°, 32°, and 61° respectively (Michaelis, *A.* 274, 221). Thionyl-tetra-bromo-aniline melts at 78°. Thionyl-*p*-iodo-aniline [54°] and [4:2:1] $C_6H_3I_2N{:}SO$ [74°] are also crystalline.

Reference.—Nitro-thionyl-aniline.

THIONYL BROMIDE $SOBr_2$ *v.* Sulphur oxybromides, p. 617.

THIONYL-ISOBUTYLAMINE C_4H_9NSO *i.e.* $CHMe_2.CH_2.N{:}SO$. (116°). Formed from $SOCl_2$ and isobutylamine in ether (Michaelis, *A.* 274, 191). Liquid, with pleasant smell.

THIONYL CHLORIDE $SOCl_2$ *v.* Sulphur oxychlorides, p. 617.

THIONYL-CUMIDINE $C_6H_4Pr.N{:}SO$. (158°). Got from $SOCl_2$ and the cumidine obtained from isopropyl-benzene by nitration and reduction (Michaelis, *A.* 274, 239). Oil, not decomposed by boiling water.

Thionyl-ψ-cumidine $C_6H_2Me_3.N{:}SO$. [−10°]. (246°). Oil, v. sol. alcohol and ether.

THIONYL-ETHYLAMINE $EtN{:}SO$. (73°). Formed by adding $SOCl_2$ to an ethereal solution of ethylamine cooled below 0° (Michaelis, *B.* 24, 756).

THIONYL-MESIDINE $C_6H_2Me_3.N{:}SO$. [−11°]. (241°). S.G. ^{14} 1·121. Volatile with steam (Michaelis, *A.* 274, 240).

THIONYL-METHYLAMINE $MeN{:}SO$. (59°). Liquid (Michaelis, *A.* 274, 187).

THIONYL-METHYL-ANILINE $SO(C_6H_4.NHMe)_2$. [154°]. Formed from $SOCl_2$ and methyl-aniline in ethereal solution in presence of $AlCl_3$ (Michaelis a. Godchaux, *B.* 23, 3019). Colourless needles, v. sol. alcohol. Yields a nitrosamine $SO(C_6H_4.NMe.NO)_2$. [171°].

THIONYL-(α)-NAPHTHYLAMINE $C_{10}H_7.N{:}SO$. [33°]. (226° at 100 mm.). Formed from (α)-naphthylamine in benzene and $SOCl_2$ (Michaelis, *A.* 274, 253). Reddish yellow needles, slowly converted by water into naphthylamine sulphite.

Thionyl-(β)-naphthylamine [53°]. Needles. The thionyl derivative of bromo-(β)-naphthylamine [63°] melts at 118°.

THIONYL-*o*-NITRO-ANILINE $C_6H_4N_2SO_3$ *i.e.* $C_6H_4(NO_2)$.N:SO. [62°], the *m-* compound melts at 63°, while the *p*-isomeride melts at 70° (Michaelis, *A.* 274, 225).

THIONYL-NITRO-MESIDINE $C_9H_{10}N_2SO_3$ *i.e.* $C_6HMe_2(NO_2)$.N:SO. [77°]. Got from nitro-mesidine [74°] (Michaelis, *A.* 274, 241). Light yellow needles, v. e. sol. benzene.

Thionyl-di-nitro-mesidine. [127°]. Formed from di-nitro-mesidine [193°].

THIONYL-NITRO-NAPHTHYLAMINE $C_{10}H_6(NO_2)$.N:SO. Nitro-naphthylamines [191°] and [119°] yield thionyl derivatives melting at 89° and 135° respectively (Michaelis, *A.* 274, 258).

THIONYL-NITRO-TOLUIDINE $C_7H_6N_2SO_3$ *i.e.* $C_6H_3Me(NO_2)$.N:SO. The compounds from (2,1,4)-nitro-toluidine [75°] and (3,1,4)-nitro-toluidine [114°] melt at 44° and 39° respectively (Michaelis, *A.* 274, 232).

DI-THIONYL-PHENYLENE-DIAMINE $C_6H_4(N:SO)_2$. The *m-* and *p-* compounds melt at 44° and 116° respectively (Michaelis, *A.* 274, 261).

THIONYL-PHENYLETHYL-AMINE $PhCH_2.CH_2.N:SO$. (172° at 25 mm.). Liquid, decomposed by water into SO_2 and base. SO_2 passed into its ethereal solution forms amorphous $PhCH_2.CH_2.NH.SO_2H$, whence benzoic aldehyde yields $PhCH_2.CH_2.N(SO_2H).CHPh.OH$ [114°] (Michaelis, *B.* 26, 2167).

THIONYL-PHENYL-HYDRAZINE *v.* Action of $SOCl_2$ on PHENYL-HYDRAZINE.

THIONYL-PHENYL-PROPYLAMINE $CH_2Ph.CH_2.CH_2.N:SO$. Formed from phenyl-propylamine hydrochloride and $SOCl_2$ (Michaelis a. Jacobi, *B.* 26, 2161). SO_2 passed into its ethereal solution forms the amorphous compound $NH(SO_2H).C_3H_6Ph$, which reacts with benzoic aldehyde forming $SO_2H.N(CHPh.OH).C_3H_6Ph$ [106°].

THIONYL-PROPYLAMINE PrN:SO. (104°). Smells like bleaching-powder (Michaelis, *A.* 274, 190).

THIONYL-TOLUIDINE $C_6H_4Me.N.SO$. Formed from toluidine and $SOCl_2$. The *o-* compound is liquid (184° at 100 mm.). The *m-* compound is liquid (220°). The *p-* isomeride [7°] (c. 224°) may be crystallised by cooling (Michaelis a. Herz, *B.* 23, 3482; 24, 753; *A.* 274, 231). The thionyl derivatives of (3,1,4)- and (5,1,2)-bromo-toluidines melt at 47° and 50° respectively.

THIO-ORCIN $C_6H_3Me(SH)_2$. [35°]. Formed by reducing $C_6H_3Me(SO_2Cl)_2$ with tin and HClAq (Gabriel, *B.* 12, 1640).—$PbC_7H_6S_2$.

THIONYL-XYLIDINE $C_6H_3Me_2N:SO$. The (1,2,4)- compound [−9°] (131° at 20 mm.), (1,3,4)- compound (238°), and (1,4,2)- isomeride [−8°] (119° *in vacuo*) are all oily (Michaelis, *A.* 274, 237). Thionyl-fluoro-xylidine (144° at 45 mm.) is also an oil.

THIO-OXALIC ACID. *Ethyl ether* $C_6H_{10}SO_3$ *i.e.* $CO_2Et.CO.SEt$. (217° cor.). S.G. $\frac{0}{0}$ 1·145. Formed by the action of $Cl.CO.CO_2Et$ on mercaptan (Morley a. Saint, *C. J.* 43, 400). Colourless liquid with faint odour like garlic. Decomposed by KOHAq into mercaptan, alcohol, and oxalate. Alcoholic KOH (1 mol.) forms EtSH and $CO_2Et.CO_2K$. Water slowly decomposes it, forming oxalic acid, alcohol, and mercaptan. Dry NH_3 forms mercaptan and $CO_2Et.CONH_2$.

(β)-Thio-oxalic acid $NH_2.CS.CO_2H$. The salt $C_2H_2KNSO_2$ is formed by the action of cold conc. KOHAq on the ethers. It crystallises in needles, v. sol. water and decomposed by evaporating. The free acid is unstable.

Amide of the methyl ether. $NH_2.CS.CO_2Me$. [86°]. Formed by passing dry H_2S into $Cy.CO_2Me$ (Weddige, *J. pr.* [2] 7, 79; 9, 133; 10, 193). Light-yellow crystals, sol. water, alcohol, and ether.

Amide of the ethyl ether $NH_2.CS.CO_2Et$. Mol. w. 133. [64°]. Formed in like manner. Lemon-yellow crystals. Re-converted by boiling with alcohol and $Pb(OH)_2$ into cyanoformic ether. Methylamine and ethylamine form the crystalline compounds $CO(NHMe).CS.NH_2$ and $CO(NHEt).CS.NH_2$ respectively.

Amide of the isobutyl ether $NH_2.CS.CO_2C_4H_9$. [58°]. Lemon-yellow crystals, sl. sol. water.

Di-amide $CO(NH_2).CS.NH_2$. Formed from $CO_2Et.CS.NH_2$ and alcoholic ammonia (Weddige, *J. pr.* [2] 9, 137). Lemon-yellow needles (from alcohol), sl. sol. water.

Di-thio-oxalic acid. *Amide* $CS(NH_2).CS(NH_2)$. *Hydrogen rubeanide.* Mol. w. 120. Formed, together with yellow $Cy.CS.NH_2$, by combination of cyanogen with H_2S (Wöhler, *P.* 3, 177; Völckel, *A.* 38, 315). Formed also by passing cyanogen into an alcoholic solution of NaSH and ppg. by HCl (Wollner, *J. pr.* [2] 29, 129; Ephraim, *B.* 22, 2305). Prepared by passing H_2S into an ammoniacal solution of $CuSO_4$ which has been decolourised by KCy (Formánek, *B.* 22, 2655). Small yellowish-red crystals, sl. sol. water, sol. alcohol and ether. Dilute KOHAq forms oxalic acid, conc. KOHAq forms KCy and KCyS. Boiling HClAq forms oxalic acid. MeI and MeOH at 150° form SMe_3I. Alcoholic hydroxylamine hydrochloride (2 mols.) forms $C_2(NH_2)_2(NOH)_2$ and H_2S. Benzoic aldehyde, acting on a boiling solution, forms a compound [209°] which is apparently $\mathrm{CHPh}{<}\genfrac{}{}{0pt}{}{\mathrm{S}}{\mathrm{N}}{\geqslant}\mathrm{C.C}{\leqslant}\genfrac{}{}{0pt}{}{\mathrm{S}}{\mathrm{N}}{>}\mathrm{CHPh}$ (Ephraim, *B.* 24, 1027).—$PbC_2H_2N_2S_2$: orange pp. (Wallach, *B.* 13, 528). Yields PbS on boiling with water.

Anilide CS(NHPh).CS(NHPh). [133°]. Formed from oxanilide by successive treatment with PCl_5 and H_2S (Wallach, *B.* 13, 527). Golden plates.

Di-methyl-di-amide CS(NHMe).CS(NHMe). [140°]. Formed from thiocyanic acid, alcohol, and methylamine (Wallach, *A.* 262, 360). Yellow crystals, sl. sol. alcohol. Converted by NaOEt and propyl chloride into $C(NMe)(SC_3H_7).C(NMe)(SC_3H_7)$ (170°–175°).

Di-ethyl-di-amide CS(NHEt).CS(NHEt). [58°]. Formed in like manner. Yellowish-red crystals, insol. water. Converted by NaOEt and EtI into C(NEt)(SEt).C(NEt)(SEt) (126°–129°).

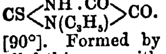
Di-amyl-di-amide $CS(NHC_5H_{10}).CS(NHC_5H_{10})$. [60°]. Formed from thiocyanic acid, alcohol, and amylamine (Wallach, *A.* 262, 362). Red prisms.

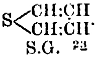
Di-benzyl-diamide $CS(NHCH_2Ph).CS(NHCH_2Ph)$. [115°]. Formed from thiocyanic acid, alcohol, and benzylamine. Yellowish-red crystals, sl. sol. warm alcohol.

Hexa-thio-ortho-oxalic acid. *Ethyl ether* $C_2(SEt)_6$. Formed from C_2Cl_6 and NaSEt (Claesson, *J. pr.* [2] 15, 212). Heavy oil.

THIO-OXY- *v.* SULPHYDRO-.

THIO-PARABANIC ACID. *Methyl derivative v.* METHYL-THIO-PARABANIC ACID.

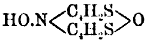
Allyl derivative $C_6H_6N_2SO_2$ *i.e.*  $CS{<}{\genfrac{}{}{0pt}{}{NH.CO}{N(C_3H_5)}}{>}CO$. *Oxalyl-thio-sinamine.* [90°]. Formed by warming the dicyanide of allyl-thio-urea with dilute H_2SO_4 (Maly, *Z.* 1869, 260). Lemon-yellow needles, m. sol. cold water.

THIOPHENE C_4H_4S *i.e.*  $S{<}{\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}}$ (84° cor.). V.D. 3·0 (calc. 2·9). S.G. ^{23} 1·062; $\frac{4}{0}$ 1·0884; $\frac{15}{4}$ 1·0705 (R. Schiff, *B.* 18, 1601). S.V. 84·9. R_∞ 41·4 (Nasini a. Scala, *G.* 17, 70). H.C.p. 670,900 (Berthelot a. Matignon, *C. R.* 111, 10; *Bl.* [3] 4, 252). H.F. –14900. *Critical temperature* 317° (Pawlewski, *B.* 21, 2141). *Critical pressure* 47·7 atmospheres. Occurs in coal-tar benzene to the extent of about ·5 p.c. (V. Meyer, *B.* 16, 1471).

Formation.—1. In small quantity by passing acetylene through boiling sulphur (V. Meyer a. Sandmeyer, *B.* 16, 2176).—2. By heating succinic anhydride with P_2S_5.—3. By heating sodium succinate with P_2S_3, the yield being 50 p.c. of the theoretical amount (Volhard a. Erdmann, *B.* 18, 454). It is not formed by heating *s*-di-bromo-succinic acid with P_2S_3 or P_2S_5 (Ossipoff, *J. R.* 20, 245).—4. By heating erythrite with P_2S_5 (Paal a. Tafel, *B.* 18, 688).—5. From its (*α*)-carboxylic acid, which is obtained by heating mucic acid with BaS (Paal a. Tafel, *B.* 18, 456).—6. In small quantities by passing Et_2S through a red-hot tube (Meyer, *B.* 18, 217).—7. In small quantities by passing ethylene, coal-gas, or ligroïn-vapour over heated iron pyrites.—8. In small quantities by heating P_2S_5 with crotonic acid, with *n*-butyric acid, with paraldehyde, or with ether (Meyer).

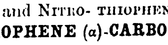
Isolation.—20 pts. commercial 'pure' benzene is shaken for four hours with 1 pt. of H_2SO_4. The acid is diluted with two or three times its weight of water and treated at once with steam. Nearly pure thiophene passes over. Yield, about 3½ p.c. by volume of the H_2SO_4 used (Schulze, *B.* 18, 497).

Properties.—Liquid with faint odour, not decomposed below 335°. Not solid at –20°. Greatly resembles benzene. Oxidised by HNO_3 with great violence. On shaking with isatin and H_2SO_4 it yields a blue colouring matter (indophenine). Not affected by boiling with sodium. Benzene that contains thiophene gives a bright-blue colour to H_2SO_4 containing nitrous acid. Thiophene (10 g.) shaken with alcohol (100 g.), cold saturated $HgCl_2$ solution (1,000 g.), and NaOAc (70 g.) dissolved in water (130 g.) forms a white pp. containing $C_4H_3(HgCl)S$, which crystallises from alcohol in white plates [183°], and $C_4H_2(HgCl)_2S$, a white powder, insol. alcohol (Volhard, *A.* 267, 172). The compound $C_4H_3(HgCl)S$ is converted by AcCl into *α*-thienyl methyl ketone and by I into di-iodo-thiophene. Thiophene combines with $CHPh_3$ and with di-bromo-di-(*β*)-naphthyl oxide (Liebermann, *B.* 26, 853).

Reactions.—1. *Chloral* and H_2SO_4 yield $CCl_3.CH(C_4H_3S)_2$.—2. BzCl and $AlCl_3$ form thienyl phenyl ketone.—3. *Phenyl-glyoxylic acid* and H_2SO_4 form $C_{12}H_8NSO_2$, which dissolves in chloroform with crimson, and in H_2SO_4 with purple colour.—4. Cl and Br yield chloro- and bromo- derivatives.—5. H_2SO_4 forms a brown solution containing a sulphonic acid, and slowly decomposes the thiophene, forming H_2S, SO_2 and an amorphous pp.—6. H_2SO_4 and KNO_2 form a compound called 'nitroso-dithiophene'  $HO.N{<}{\genfrac{}{}{0pt}{}{C_4H_2S}{C_4H_2S}}{>}O$ (?), ppd. by water as a dark insoluble powder (Liebermann, *B.* 20, 3231).—7. Passed with PCl_3 through a red-hot tube it forms $C_4H_3S.PCl_2$ (218°) which is decomposed by water into $C_4H_3S.P(OH)_2$ [70°] and is converted by Cl into $C_4H_3S.PCl_4$, which is converted by SO_2 into $C_4H_3S.POCl_2$ (259°) and by water into $C_4H_3S.PO(OH)_2$ [159°] (Sachs, *B.* 25, 1514).—8. *Diazobenzene chloride* and $AlCl_3$ forms (*β*)-phenyl-thiophene [57°] (Möhlau a. Berger, *B.* 26, 2001).

References.—AMIDO-, BROMO-, DI-BROMO-DI-NITRO-CHLORO-, TRI-CHLORO-NITRO-, IODO-, IODO-NITRO-, and NITRO- THIOPHENE.

THIOPHENE (*α*)-CARBOXYLIC ACID

$C_5H_4SO_2$ *i.e.*  $S{<}{\genfrac{}{}{0pt}{}{CH\!-\!\!-\!\!-\!CH}{C(CO_2H):CH}}$ *Thiophene 'β'-carboxylic acid.* [126·5°]. (260° cor.). H.F. 85,400. H.C.p. 591,900 (Stohmann, *J. pr.* [2] 43, 12). Formed by adding sodium-amalgam to a mixture of $Cl.CO_2Et$ with (*α*)-iodothiophene, with di-iodo-thiophene, or with di-bromo-thiophene (Nahnsen, *B.* 17, 2192; 18, 2304; Bonz, *B.* 18, 2306). Formed also by heating mucic acid with BaS for 6 hours at 205°, the yield being 12 p.c. of the theoretical (Paal a. Tafel, *B.* 18, 456). Obtained by oxidation of (*α*)-ethyl-thiophene (Schleicher, *B.* 18, 3017), of (*α*)-propyl-thiophene (Ruffi, *B.* 20, 1740), of thienyl methyl ketone (Peter, *B.* 17, 2645; 18, 542), and of thienyl ethyl ketone (Ernst, *B.* 20, 518) with alkaline $KMnO_4$.

Properties.—Slender white needles (from water) or long flat needles (by sublimation), v. sol. hot water, sl. sol. cold, v. e. sol. alcohol and ether, m. sol. chloroform, sl. sol. ligroin. Gives a blue colour on warming with isatin and H_2SO_4 (indophenine reaction). Yields thiophene on distilling with lime. Yields a di-bromo- derivative [211°].

Salts.—BaA'_2 2aq. Small crystals. S. 22·19 at 14·5°.—CaA'_2 3aq. S. 18·5 at 18·5°.—ZnA'_2 (dried). S. 14 at 15°.—PbA'_2 (dried) ·5 at 18·5°.—AgA': plates or needles. S. ·195 at 11°.

Ethyl ether EtA'. (218° cor.). S.G. ^{22} 1·1155. Liquid, smelling like benzoic ether.

Chloride $C_4H_3S.COCl$. (190° uncor.). Liquid, smelling like benzoyl chloride.

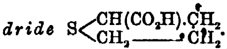
Amide $C_4H_3S.CONH_2$. [174°] (Meyer, *A.* 236, 210). Prisms, m. sol. ether. Phenyl thiocarbimide forms $C_4H_3S.CO.NH.CO.NHPh$. [206°]

Anilide $C_4H_3S.CONHPh$. [140°]. Formed by the action of phenyl cyanate on thiophene in presence of $AlCl_3$ (Leuchart a. Schmidt, *B.* 18, 2340). Iridescent plates.

Amidoxim $C_4H_3S.C(NOH).NH_2$. [92°]. Formed by the action of hydroxylamine on the nitrile (Meyer, *A.* 236, 213). Long prisms (from benzene).

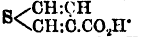
Nitrile (192°) (D.); (200° cor.) (Peter, *B.* 18, 543). Formed by distilling thienyl-glyoxylic acid with aqueous hydroxylamine (Douglas, *B.* 25, 1311).

Tetrahydride



$S\left\langle\begin{matrix}\mathrm{CH(CO_2H).CH_2}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}\right.$ [51°]. H.F. 114,900. H.C.p. 700,400. Formed by reducing the acid, in alkaline solution, with sodium-amalgam (Ernst, *B.* 19, 3278; 20, 518). Plates or needles (from ligroin), v. e. sol. water and alcohol, v. sol. ether. Volatile with steam. Much decomposed on distillation. Reduces ammoniacal $AgNO_3$. Salts.—CaA'_2 3aq. Crystalline, sol. water. — AgA'. M. sol. water. *Methyl ether* MeA'. (c. 206°). *Ethyl ether* EtA'. Liquid.

Thiophene (β)-carboxylic acid

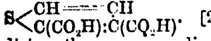


$S\left\langle\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}C.CO_2H}\end{matrix}\right.$ (γ)-*Thiophenic acid.* [136°]. S. ·44 at 17°. Formed by the action of alkaline $KMnO_4$ on (β)-methyl-thiophene (Muhlert, *B.* 18, 3008) or (β)-ethyl-thiophene, the yield being about 8 p.c. (Damsky, *B.* 19, 3284). Needles (from water), sol. ether, votatile with steam. Gives the indophenine reaction.—CaA'_2 ½aq. S. (of CaA'_2) 7·92 at 14·5°.—BaA'_2 (dried). S. 11·54 at 17°.—AgA'. Needles or plates, v. sl. sol. Aq.

Amide $C_4H_3S.CONH_2$. [178°]. Converted by phenyl cyanate into $C_4H_3S.CO.NH.CO.NHPh$. [206°].

Thiophene 'α'-carboxylic acid. [118°]. (258° cor.). This is a mixture of the (α)- and (β)- acids. It is got by saponifying the mixed nitrile which is formed by distilling a mixture of potassium thiophene (α) and (β) sulphonates with KCy (V. Meyer, *B.* 16, 2174; 18, 2315; Bonz, *B.* 18, 2308). Formed also by oxidising a mixture of (α)-methyl-thiophene (2 pts.) and (β) methyl-thiophene (3 pts.) and by slow evaporation of an aqueous solution of the mixed thiophene carboxylic acids in the cold (Egli, *B.* 18, 548; V. Meyer, *B.* 19, 2891; *A.* 236, 221). Volatile with steam. Can be separated into the (α)- and (β)- acids by crystallisation.

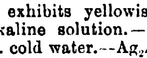
Thiophene dicarboxylic acid



$S\left\langle\begin{matrix}\mathrm{CH{=\!=\!=}CH}\\ \mathrm{C(CO_2H){:}C(CO_2H)}\end{matrix}\right.$ [270°]. Formed by oxidising the corresponding di-methyl-thiophene with alkaline $KMnO_4$ (Grünewald, *B.* 20, 2586). Formed also by oxidising (β)-methyl-thienyl methyl ketone (Gerlach, *A.* 267, 153). Long needles (from water), v. e. sol. ether. Not volatile with steam. Resorcin at 200° forms a fluorescein which exhibits yellowish-green fluorescence in alkaline solution.—PbA''.—BaA''. Crystals, sl. sol. cold water.—Ag_2A''. White pp.

Methyl ether Me_2A''. [59·5°]. Plates.

Thiophene dicarboxylic acid



$S\left\langle\begin{matrix}\mathrm{C(CO_2H){:}CH}\\ \mathrm{C(CO_2H){:}CH}\end{matrix}\right.$

Formation.—1. By oxidation by alkaline $KMnO_4$ of di-methyl-thiophene from coal tar (Messinger, *B.* 18, 567), from (α)-ethyl-thienyl methyl ketone, from (α)-ethyl-thiophene (α)-carboxylic acid (Schleicher, *B.* 18, 3020), from methyl-thienyl methyl ketone (Demuth, *B.* 18, 3025), and from (α)-methyl-thiophene carboxylic acid (Levi, *B.* 19, 656).—2. By saponifying its nitrile, which may be got by fusing potassium thiophene disulphonate with KCy (Jaekel, *B.* 19, 191).—3. By saponifying its ether which is got by the action of sodium-amalgam on a mixture of di-bromo-thiophene and $ClCO_2Et$ (Bonz, *B.* 18, 2306).

Properties.—Crystalline powder, v. sl. sol. cold water, sol. ether. Not melted at 300°. Does not give the fluoresceïn reaction.

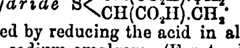
Salts. — BaA'' aq. Crystalline, v. sl. sol. cold water.—CaA'' 3aq.—Ag_2A'': white pp.

Methyl ether Me_2A''. [145°] (J.); [147°] (S.); [151°] (D.). White needles from alcohol.

Ethyl ether Et_2A''. [47°] (J.); [52°] (S.). Long needles (from alcohol).

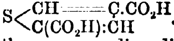
Nitrile $C_4H_2SCy_2$. [92°]. Crystals.

Tetrahydride



$S\left\langle\begin{matrix}\mathrm{CH(CO_2H).CH_2}\\ \mathrm{CH(CO_2H).CH_2}\end{matrix}\right.$ [162° cor.]. Formed by reducing the acid in alkaline solution by sodium-amalgam (Ernst, *B.* 19, 3275). Plates, v. sol. water, sol. ether. Reduces hot ammoniacal $AgNO_3$. Hot conc. H_2SO_4 evolves CO (1 mol.).—BaA'': scales.—Ag_2A'': white powder.—Me_2A''. Oil.

Thiophene dicarboxylic acid



$S\left\langle\begin{matrix}\mathrm{CH{=\!=\!=}C.CO_2H}\\ \mathrm{C(CO_2H){:}CH}\end{matrix}\right.$. Formed by oxidation of the corresponding di-methyl-thiophene by alkaline $KMnO_4$ (Zelinsky, *B.* 20, 2022). Needles, sl. sol. cold water. Decomposes and partially sublimes at 280°, v. sol. hot water.—Ag_2A''.

Methyl ether Me_2A''. [121°]. Plates.

Ethyl ether Et_2A''. [36°].

Thiophene tri-carboxylic acid $C_4SH(CO_2H)_3$. Formed by oxidation of di-methyl-thienyl methyl ketone with $KMnO_4$ (Messinger, *B.* 18, 2302).

Methyl ether Me_3A'''. [118°] Plates, v. sol. alcohol and ether.

References.—Bromo- and Iodo- THIOPHENE CARBOXYLIC ACID and Nitro-THIOPHENIC ACID.

THIOPHENE GREEN $C_{21}H_{22}N_2S$. The leuco-base $C_4SH_3.CH(OH)(C_6H_4NMe_2)_2$ is got by heating thiophenic aldehyde with di-methyl aniline, $ZnCl_2$, and a little alcohol at 100° (Levi, *B.* 20, 513). It crystallises in needles [93°], and is readily oxidised to thiophene green $C_4SH_3.C(OH)(C_6H_4NMe_2)_2$, which is an oil and forms the salts $(C_{21}H_{22}N_2S)_3ZnCl_2$ 2aq, $B'H_2SO_4$, $B'_2 3H_2C_2O_4$ 2aq, and $B'2C_6H_3N_3O_7$, crystallising in scales with coppery lustre.

Leuco-thiophene green *v.* TETRA-METHYL-DI-AMIDO-DI-PHENYL-THIENYL-METHANE.

THIOPHENE (α)-SULPHINIC ACID $C_4H_3S.SO_2H$. [67°]. Formed by the action of zinc-dust on an alcoholic solution of thiophene sulphonic chloride (Weitz, *B.* 17, 800). Needles, v. sol. water, alcohol, and ether. Gives the indophenine reaction.—BaA'_2 2aq. White plates, v. sol. water.—ZnA'_2 3aq.—AgA'. Crystalline pp.

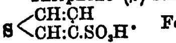
THIOPHENE 'α'-SULPHONIC ACID $C_4H_3S.SO_3H$. Formed by shaking thiophene (20 g.) dissolved in ligroïn (2,000 c.c.) with H_2SO_4 (300 c.c.) for 2 hours (V. Meyer a. Kreis, *B.* 16, 2172; Biedermann, *B.* 19, 1615). Deliquescent mass. Yields thiophene on distillation. It is doubtless a mixture of the (α) and (β) acids. —NaA'aq.—BaA'_2 3aq.—CaA'_2.—PbA'_2 aq. Very soluble powder.—AgA' 3aq. Plates (Weitz, *B.* 17, 796).

Ethyl ether EtA'. Oil.

Chloride $C_4H_3S.SO_2Cl$. [28°]. (above 200°). Oil or colourless crystals.

Amide $C_4H_3S.CONH_2$. [142°] (Langer, *B.* 17, 1568). Needles (from water).—$C_4H_3S.CO.NHAg$. Pearly scales.

Anilide $C_4H_3S.CONHPh$. [96°].

Thiophene (β)-sulphonic acid  $S<\begin{matrix}CH:CH\\CH:C.SO_3H\end{matrix}$. Formed by the action of sodium-amalgam on di-bromo-thiophene (β)-sulphonic acid, which is got by sulphonation of di-bromo-thiophene (Langer, *B.* 17, 1567; 18, 553). Obtained in like manner from iodo-thiophene sulphonic acid, and from tri-bromo-thiophene sulphonic acid (Rosenberg, *B.* 18, 1776). Crystalline solid, v. sol. water. Gives a blue colour with isatin and H_2SO_4.—BaA'_2.

Chloride $C_4H_3S.SO_2Cl$. [43°]. Plates, v. sol. ether, insol. ligroïn.

Amide $C_4H_3S.SO_2NH_2$. [148°]. Tables.

Thiophene disulphonic acid $C_4H_2S(SO_3H)_2$. Formed by reduction of di-bromo-thiophene 'β'-di-sulphonic acid by sodium-amalgam (Langer, *B.* 18, 554, 1114; Rosenberg, *B.* 18, 3030). Crystalline, v. sol. water.—$BaA''2\frac{1}{2}aq$.

Chloride $C_4H_2S(SO_2Cl)_2$. [149°]. Scales.

Amide $C_4H_2S(SO_2NH_2)_2$. [c. 280°]. Needles.

Thiophene disulphonic acid $C_4H_2S(SO_3H)_2$. Formed by reducing iodo-thiophene (αβ)-di-sulphonic acid with sodium-amalgam (Langer, *B.* 18, 560).

Amide $C_4H_2S(SO_2NH_2)_2$. [142°]. Plates. Gives the indophenine reaction.

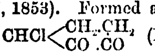
Thiophene disulphonic acid $C_4H_2S(SO_3H)_2$. Formed from lead thiophene sulphonate and fuming H_2SO_4 (Jaekel, *B.* 19, 185, 1066). Crystalline, v. sol. water and alcohol.—$K_2A''aq$: prisms, v. sol. water.—$Na_2A''3aq$. Needles, v. sol. water.—$BaA''3aq$. Flat prisms, sl. sol. water.—$CuA''4aq$. Blue needles.—Ag_2A''.

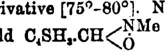
Chloride $C_4H_2S(SO_2Cl)_2$. [77·5°]. Needles (from ether).

Amide $C_4H_2S(SO_2NH_2)_2$. [211·5].

References.—Di-bromo-, Iodo- and Nitro-thiophene sulphonic acid.

THIOPHENIC ACID *v.* Thiophene carboxylic acid.

THIOPHENIC ALDEHYDE $C_4H_3S.CHO$. (198° cor.). S.G. ²¹ 1·215. Formed by distilling (α)-thienyl-glyoxylic acid (Biedermann, *B.* 19, 637, 1853). Formed also by the action of H_2S on  $CHCl<\begin{matrix}CH_2.CH_2\\CO\ .CO\end{matrix}$ (Hantzsch, *B.* 22, 2838). Oil, smelling like benzoic aldehyde. Oxidised by air to thiophene (α)-carboxylic acid.

Oxim $C_4H_3S.CH(NOH)$. *Thiophene synaldoxim.* [128°]. Needles (from ether). Converted by NaOHAq into thiophene carboxylic nitrile (Hantzsch, *B.* 24, 47). Yields an acetyl-derivative [75°-80°]. NaOMe and MeI in MeOH yield  $C_4SH_3.CH<\begin{matrix}NMe\\O\end{matrix}$ [120°], crystallising in tables; converted by dilute H_2SO_4 into the aldehyde and (β)-methyl-hydroxylamine (Goldschmidt a. Zanoli, *B.* 25, 2588). Phenyl cyanate in ether forms $C_4SH_3.CH:NO.CO.NHPh$ [70°], crystallising in needles.

Oxim $C_4H_3S.CH:NOH$. *Thiophene anti-aldoxim.* Formed by the action of hydroxylamine hydrochloride, NaOHAq and Na_2CO_3 on the aldehyde (Goldschmidt a. Zanoli, *B.* 25, 2590). Converted by phenyl cyanate into $C_4SH_3.CH:NO.CO.NHPh$ [144°], whence NaOH forms $C_4SH_3.CH:N.NHPh$ [46°]. *o*-Tolyl cyanate forms $C_4H_3S.CH:NO.CO.NH.C_7H_7$ [66°].

Phenyl hydrazide $C_4SH_3.CH:N_2HPh$. [134·5°]. Needles (from alcohol).

THIOPHENIC IMIDO-ETHYL ETHER $C_4H_3S.C(OEt):NH$. The salt B'HCl is formed by the action of dry HCl on the nitrile of thiophene carboxylic acid (Douglas, *B.* 25, 1312). It is crystalline, and is converted by hydroxylamine into $C_4H_3S.C(OEt):NOH$ [67°].

THIOPHENINE is Amido-thiophene.

THIOPHENOL *v.* Phenyl mercaptan.

THIOPHENURIC ACID $C_7H_7NSO_3$. [172°]. Excreted in the urine of rabbits after injection of sodium thiophene (α)-carboxylic acid (Jaffé a. Levi, *B.* 21, 3458). Prisms, resembling hippuric acid (from water), v. sl. sol. ether, v. sol. alcohol. Split up by boiling baryta-water into glycocoll and thiophene (α)-carboxylic acid.—$BaA'_2 2aq$. Needles, v. sol. water.—$CaA'_2 xaq$.—AgA'.

THIO-PHENYL-ACETIC ACID. *Amide* $C_6H_5.CH_2.CS.NH_2$. [98°]. Formed by heating phenyl-acetamide (3 pts.) with P_2S_5 (2 pts.), and also by allowing a solution of phenyl-acetonitrile in alcoholic ammonium sulphide to stand for some days (Bernthsen, *B.* 11, 503; *A.* 184, 292). Trimetric crystals (from alcohol), decomposed on distillation into H_2S and $C_6H_5.CH_2.CN$.

Reactions.—1. Boiling NH_3Aq forms phenyl-acetamide.—2. HgO forms phenyl-acetonitrile.—3. Zn and HClAq form phenyl-ethyl-amine (Colombo a. Spica, *B.* 8, 821).—4. *Benzoic aldehyde* forms oily $C_{23}H_{20}N_2S_2$ (?)—5. *Sodium-amalgam* forms $Ph.CH_2.CH_2NH_2$ and a compound $C_{24}H_{27}NS_2$ [108°].—6. *Iodine* added to a hot alcoholic solution forms $C_{16}H_{14}N_2S$ [42°].—7. MeI forms $(CH_2Ph.C(NH).SMe)HI$ [139°], which gives rise to $(C_9H_{11}NS)_2H_2PtCl_6$.—8. EtI forms $(C_{10}H_{13}NS)HI$ [116°], which is v. e. sol. water, and yields, on treatment with NaOHAq, the free base $CH_2Ph.C(NH).SEt$, which is an oil that quickly decomposes into mercaptan and phenyl-acetonitrile. The salts $(C_{10}H_{13}NS)HCl$ [c. 120°], $B'_2H_2PtCl_6$ [below 130°], and B'HBr are crystalline.—9. *Aniline* forms the compound $CH_2Ph.C(NH_2):NPh$.

THIO-PHENYL-ALLOPHANIC ACID *v.* Phenyl-thio-allophanic acid.

THIO-DI-PHENYL-AMINE *v.* Imido-di-phenyl sulphide.

THIO-PHENYL-CARBAMIC ACID *v.* Phenyl-thio-carbamic acid.

THIO-DI-PHENYL KETONE *v.* Thio-benzophenone.

THIO-DI-PHENYL-METHYL-AMINE *v.* Methyl-imido-di-phenyl sulphide.

DI-THIO-PHTHALIC ACID $C_6H_4(CO.SH)_2$. The salt K_2A'' is formed by dissolving KSH (2 mols.) in an alcoholic solution of phenyl phthalate (1 mol.). The free acid splits up at once into H_2S and thiophthalic anhydride (Schreder, *B.* 7, 706).

(α)-Di-thio-isophthalic acid. The K salt, formed by the action of KSH on phenyl isophthalate, crystallises in yellow needles.

Ethyl ether Et_2A''. Formed by adding water to the hydrochloride of $C_6H_4(C(NH).SEt)_2$ (Luckenbach, *B.* 17, 1435). Small needles.

(β)-Di-thio-isophthalic acid. *Amide* $C_6H_4(CSNH_2)_2$. [200°]. Formed by heating isophthalic nitrile with alcoholic ammonium

sulphide (L.). Needles, sol. hot alcohol. Reconverted into the nitrile by lead acetate. Boiling KOHAq forms isophthalic acid.

THIO-PHTHALIC ANHYDRIDE $C_8H_4SO_2$ *i.e.* $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>S$. [114°]. (284°). Formed by the action of KSH on phthalyl chloride, or on phenyl phthalate (Graebe a. Zschokke, *B.* 17, 1175). Formed also by the action of As_2S_3 on phthalyl chloride (Rayman, *Bl.* [2] 47, 898). Plates, v. sol. hot alcohol, ether, and chloroform, sl. sol. water. Volatile with steam. Sol. alkalis and converted by long boiling with alkalis into phthalic acid. Ammonia forms phthalimide. Resorcin and H_2SO_4 give a thiofluoresceïn, the alkaline solution of which is deep red with green fluorescence.

THIO-PHTHALIDE $C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>S$. [57°]. Formed by heating $C_6H_4Cy.CH_2.SCy$ with conc. HClAq for 5 hours at 180° (Day a. Gabriel, *B.* 23, 2480). Thin needles (from dilute alcohol).

THIO-PHTHALIMIDINE C_8H_7NS *i.e.* $C_6H_4<\begin{smallmatrix}C(NH)\\CH_2\end{smallmatrix}>S$ or $C_6H_4Cy.CH_2SH$. [62°]. Formed by warming *o*-cyano-benzyl sulphocyanide with H_2SO_4 at 65° (Day a. Gabriel, *B.* 23, 2481). Formed also by adding KSHAq to *o*-cyano-benzyl chloride in alcohol. Needles, which darken in air, v. sol. alcohol and ether. Boiling NaOHAq forms thiophthalide. KSH added to its alcoholic solution forms $C_{16}H_{10}S_3$, crystallising from nitrobenzene in needles with green lustre.—B'HCl. Needles.—$B'_2H_2PtCl_6$. Orange-yellow prisms.—B'HI. Needles.—**Picrate**: slender needles.

THIOPHTHENE $C_6H_4S_2$ *i.e.* $\begin{smallmatrix}CH{-}C{-}CH.\\CH.S.C.S.CH\end{smallmatrix}$ (225° cor.). Formed by distilling citric acid (1 pt.) with P_2S_3 (2 pts.), adding NaOHAq, and distilling with steam (Biedermann a. Jacobson, *B.* 19, 2444). Oil, not solid at −10°. Gives the indophenine reaction.—$B'C_6H_3N_3O_7$. [133°]. Yellow needles, v. sol. alcohol and benzene.

Reference.—TETRA-BROMO-THIOPHTHENE.

THIOPHYLLINE $C_7H_8N_4O_2$. [264°]. Occurs, in small quantity, in extract of tea (Kossel, *B.* 21, 2164). Crystals (containing aq), more sol. water and alcohol than theobromine, v. sol. NH_3Aq. Forms salts with acids. On evaporation with chlorine-water it leaves a scarlet residue, turned violet by NH_3Aq.—$C_7H_7AgN_4O_2$. Amorphous, converted by MeI into caffeïne $C_7H_7MeN_4O_2$ [229°].

(*a*)-**THIO-PROPIONIC ACID** C_3H_6OS. *Methyl ether* $CH_3.CH_2.CO.SMe$. (120°). V.D. 51·23. Formed from propionyl chloride and lead mercaptide in the cold (Obermeyer, *B.* 20, 2922).

(β)-Thio-propionic acid Et.CS.OH. The salt NaA'aq formed by boiling propionitrile with alcoholic ammonium sulphide is crystalline (Dupré, *Bl.* [2] 29, 304).

Amide EtC(NH).SH. [42°]. Formed by heating propionamide (5 mols.) with P_2S_5 (1 mol.) in benzene for a short time (Hubacher, *A.* 259, 229). Yellowish plates, v. e. sol. benzene.

THIO-ISOPROPYL-COUMARIN $C_{12}H_{12}SO$ *i.e.* $C_6H_4<\begin{smallmatrix}CH:C(C_3H_7)\\O{-}CS\end{smallmatrix}$. [81°]. Formed by heating isopropyl-coumarin with P_2S_5 at 120° (Aldringen, *B.* 24, 3463). Reddish-yellow needles, sol. hot alcohol, sl. sol. ether.

THIO-PRUSSIAMIC ACIDS. By heating ammonium sulphocyanide there is formed, besides thio-urea, dithiodiprussiamic acid $C_6H_7N_9S_2$, a yellowish-white powder, sl. sol. hot water; thiodiprussiamic acid $C_6H_8N_{10}S$, amorphous, m. sol. hot water; and ammonium dithiotriprussiamate $C_9H_{13}N_{15}S_2$, which crystallises from water. The first acid gives no colour with $FeCl_3$, the two other bodies give a red colour. The lead salts of these acids dissolve in hot water.

THIOTETRAPYRIDINE, so called, $C_{20}H_{18}N_4S$ (?). [155°]. Formed by heating nicotine (1 pt.) with sulphur (6 pts.) at 150° till the mass is chrome-green (Cahours a. Etard, *Bl.* [2] 34, 452). Yellow prisms (from alcohol).—B'2HCl.—$B'HHgCl_3$.—$B'H_2PtCl_6$: yellow amorphous pp.

THIO-PYROCATECHIN *v.* OXY-PHENYL MERCAPTAN.

THIO-PYROMUCIC ACID. *Amide* $C_4H_3O.CS.NH_2$. [127°]. Formed by passing H_2S into a solution of furfuronitrile in alcohol-ether (Douglas, *B.* 25, 1314). Yellowish crystals, sl. sol. cold water, v. sol. alcohol.

THIO-PYRUVIC ACID. The compound $(C_3H_4O_2S)C_3H_4O_3$ [87°] separates as a powder when H_2S is passed into pyruvic acid (Böttinger, *A.* 188, 325). It is v. e. sol. water and is converted by boiling HIAq into $CH_3.CH(SH).CO_2H$. Boiling water forms H_2S and thiopyruvic acid.

DI-THIO-RESORCIN $C_6H_4(SH)_2$. Mol. w. 142. [27°]. (243°). Formed by reducing the sulphochloride $C_6H_4(SO_2Cl)_2$ with tin and HClAq (Patschke, *J. pr.* [2] 2, 418, Körner, *G.* 6, 140). Crystals, smelling like some geraniums. $Pb(OAc)_2$ added to its alcoholic solution ppts. orange $C_6H_4S_2Pb$, whence MeI forms $C_6H_4(SMe)_2$ (278°) (Obermeyer, *B.* 20, 2927).

THIO-RUFIC ACID $C_{10}H_{11}S_3O_4$. Formed by the action of CS_2 on a mixture of NaOEt and acetoacetic ether (Norton a. Oppenheim, *B.* 10, 701). Pearly orange scales, nearly insol. water.—NaA': brick-red needles.—CaA'_2: red needles.

THIO SALICYLIC ACID *v.* OXY-THIO-BENZOIC ACID.

THIOSINAMINE *v.* ALLYL-THIO-UREA.

THIO-SUCCINIC ACID. *Anhydride* $C_2H_4<\begin{smallmatrix}CO\\CS\end{smallmatrix}>O$. '*Sulphosuccinyl.*' [31°]. (225°). Formed by adding succinyl chloride dissolved in benzene or CS_2 to an aqueous solution of Na_2S. Got also by distilling succinic acid (100 g.) with P_2S_5 (100 g.) (Auger, *A. Ch.* [6] 22, 333). White crystals. Its aqueous solution gives off H_2S on heating. Phenyl-hydrazine forms $CO_2H.C_2H_4.C(SH){:}N.NHPh$ [120°] and $C_2H_4<\begin{smallmatrix}CO\\C(N_2HPh)\end{smallmatrix}>O$ [216°], which on distillation changes to succinyl-phenyl-hydrazine [155°]. Phenyl-hydrazine also produces $C_2H_4(CO.N_2H_2Ph)_2$ [219°] (Zanetti, *C. C.* 1889, 668). Sodium-amalgam forms $C_4H_5NaSO_2$, converted by phenyl-hydrazine acetate into $CO_2H.C_2H_4.CH{:}N_2HPh$ [c. 175°].

Di-thio-succinic acid $C_2H_4(CO.SH)_2$. The salt K_2A'', got by boiling succinyl-phenol with KSH in alcohol, crystallises in minute needles, v. sol. water, alcohol, and ether (Weselsky, *B.* 2, 518). Its aqueous solution is decomposed by spontaneous evaporation. Acids split it up into H_2S and thiosuccinic anhydride (*v. supra*).

Ethyl ether $C_2H_4(CO.SEt)_2$. (271°). Formed from di-phenyl succinate (42 g.) and sodium mercaptide (30 g.) in dry ether in the cold (Seiffert, *J. pr.* [2] 31, 469). Oil, smelling of garlic.

THIO-SUCCINURIC ACID $C_5H_8N_2SO_3$. [211°]. Formed by heating succinic anhydride with thio-urea at 140° (Pike, *B.* 6, 1105). Yellowish powder, insol. alcohol and ether, sl. sol. water and HOAc. Decomposed by alkalis into thio-urea and succinic acid.

(α) - DI - THIO - TEREPHTHALIC ACID $C_8H_6S_2O_2$ *i.e.* $C_6H_4(CO.SH)_2$. Formed by the action of alcoholic KSH on di-phenyl terephthalate (Schreder, *B.* 7, 708). Amorphous, v. sl. sol. alcohol.

(β) - Di - thio - terephthalic acid. *Amide* $C_6H_4(CS.NH_2)_2$. [263°]. Formed by heating terephthalic nitrile with alcoholic ammonium sulphide (Luckenbach, *B.* 17, 1430). Yellow amorphous powder, insol. alcohol. Boiling with lead acetate reproduces the nitrile.

THIOSULPHATES. Salts of the hypothetical *thiosulphuric acid* $H_2S_2O_3$. These salts were called *hyposulphites* before the isolation of the true hyposulphites ($M_2S_2O_4$, p. 592). $Na_2S_2O_3.5aq$ is still, however, commonly known as sodium hyposulphite. Thiosulphates are formed by boiling normal alkali sulphites in solution with S; ($M_2SO_3Aq + S = M_2S_2O_3Aq$); caustic alkali solutions and milk of lime also give thiosulphates by boiling with S. Thiosulphates are produced by the action of air, SO_2, or $K_2Cr_2O_7Aq$ on the alkali and alkaline earth polysulphides in solution ($M_2S_5Aq + 3O = M_2S_2O_3Aq + 3S$; $2M_2S_5Aq + 3SO_2Aq = 2M_2S_2O_3Aq + 9S$; $2M_2S_4Aq + 4M_2Cr_2O_7Aq + H_2O$ $= 5M_2S_2O_3Aq + 4Cr_2O_3 + 2MOHAq$ (Döpping, *A.* 46, 172). Spring (*B.* 7, 1157) by heating $(NH_4)_2SO_4$ with P_2S_5 got a large quantity of $(NH_4)_2S_2O_3$, along with $(NH_4)_2S_x$, and also some $(NH_4)_2S_3O_6$, and P compounds; and by the interaction of H_2S and $SO_2.NH_2.ONH_4$ he obtained $(NH_4)_2S_2O_3$. A little $H_2S_2O_3Aq$ is said to be formed by the interaction of steam and molten S (Myers, *A.* 129, 351).

The alkali salts, also the Ca and Sr salts, are readily soluble in water; many of the others are insoluble or only slightly soluble; the insoluble salts are often obtained from solutions of the alkali salts by double decomposition. Thiosulphates are decomposed by heating strongly; alkali salts leave a mixture of sulphate and sulphide; other salts also give off H_2S and S. Aqueous solutions of thiosulphates evolve H_2S when boiled, forming sulphates, or sulphides if the metal of the thiosulphate is ppd. by H_2S.

Aqueous solutions of thiosulphates are decomposed by dilute mineral acids, with separation of S and evolution of SO_2. Salts of the acid used are formed, and $H_2S_2O_3Aq$, which then decomposes to H_2SO_3Aq and S. This reaction has been studied by several chemists (*v.* Berthelot, *C. R.* 108, 971; Vaubel, *B.* 22, 1686, 2703; Vortmann, *B.* 22, 2307; Foussereau, *C.R.* 104, 1842). Colefax (*C. J.* 61, 176) in 1892 examined the interaction of $Na_2S_2O_3Aq$ and acids; he found that when the products of the change are not removed the interaction stops before all the $H_2S_2O_3Aq$ is decomposed. C. determined the effects on the velocity and the limit of the reaction of concentration, increasing the relative mass of the acid used, the nature of the acid, temperature, and the presence of SO_2 in the solution before acidification (reference to older memoirs are given by C.).

Thiosulphates are converted into tetrathionates by the action of I; oxidisers such as HNO_3, $KClO_3$ and HClAq, and $KMnO_4Aq$ produce sulphates. According to Hönig a. Zatzek (*M.* 4, 738), $KMnO_4$ in solution in acetic acid produces dithionates.

For the general qualitative reactions of thiosulphates compared with those of thionates *v.* Debus (*C. J.* 53, 298).

SELENOTHIOSULPHATES M_2SeSO_3 are described as *Thioselenates*, under SELENATES (p. 434).

Constitution of thiosulphates. The formula $SO_2.OM.SM$ is generally adopted for the normal thiosulphates of monovalent metals (Odling, *C. N.* 29, 153; *cf.* Schorlemmer, *C. J.* [2] 7, 254; Williamson, *C. J.* [2] 7, 259). Some chemists, considering the resemblances between thiosulphates and sulphites, have suggested the formula $SO\begin{smallmatrix}\diagup OM\\ \diagdown O.SM\end{smallmatrix}$ (*v.* Blomstrand, *Die Chemie der Jetztzeit* [Heidelberg, 1869], 258; Buchanan, *B.* 3, 485; Michaelis, *G. O.* [5th ed.] 1, 745). The formation of thiosulphates by boiling sulphites with S is readily represented by either formula, according as sulphites are regarded as $SO_2.OM.M$ or $SO.OM.OM$. As the balance of evidence is in favour of the formula $SO_2.OM.M$, it is likely that the salts formed by adding S to the sulphites are $SO_2.OM.SM$. The production of $(NH_4)_2S_2O_3$ by the interaction of $(NH_4)_2SO_4$ and P_2S_5 (Spring, *B.* 7, 1158) also confirms the formula $SO_2.OM.SM$, inasmuch as a thiosulphate is produced in this reaction from a sulphate ($SO_2.ONH_4.ONH_4$ giving $SO_2.ONH_4.SNH_4$). Spring's synthesis of $H_2S_2O_3$ from SO_3 and H_2S—for the actual reaction carried out, viz. formation of $(NH_4)_2S_2O_3$ by first combining SO_3 and NH_3, and then interacting with H_2S, is equivalent to the synthesis of $H_2S_2O_3$ (*v.* S., *l.c.*)—is also in keeping with the formula $SO_2.OM.SM$. By warming EtBr with $Na_2S_2O_3Aq$, Bunte (*B.* 7, 646) obtained the salt $EtNaS_2O_3$. This salt is decomposed by dilute acids giving EtSH and $SO_2.OH.ONa$; when heated it gives off Et_2S_2 and SO_2, leaving Na_2SO_4. These reactions indicate that $EtNaS_2O_3$ is $SO_3Na.EtS$; hence the formula of $Na_2S_2O_3$ is probably $SO_3Na.NaS$. One of the Na atoms in $Na_2S_2O_3$ is then probably in direct union with an atom of S; and as $EtNaS_2O_3$ easily gives $SO_2.OH.ONa$, along with EtSH, it is likely that the formula of this salt is $SO_2.ONa.SEt$, and hence that the formula for $Na_2S_2O_3$ is $SO_2.ONa.SNa$. The formula $SO_2.OH.SH$ makes possible the existence of two isomeric salts $MM'S_2O_3$, viz. $SO_2.OM.SM'$ and $SO_2.OM'.SM$; two such salts are known where M = Na and M' = K. (*v.* POTASSIUM THIOSULPHATE, p. 706).

Ammonium thiosulphate $(NH_4)_2S_2O_3$. Obtained by the interaction of $(NH_4)_2CO_3$ and CaS_2O_3Aq, filtering and evaporating (Rammelsberg, *P.* 56, 298); white, rhombic, deliquescent leaflets, crystallising with xH_2O. Fock a. Klüss (*B.* 22, 3099; 23, 534) obtained the anhydrous salt by reacting on SO_2Aq with $(NH_4)_2S_x$, evaporating at a low temperature and finally over H_2SO_4, and thoroughly drying between filter paper (*cf.* Arppe, *A.* 96, 118). The anhydrous salt is not deliquescent (F. a. K.). *Double salts* are described by F. a. K. (*l.c.*; also *B.* 23, 1753): (1) with CdS_2O_3; (2) with MgS_2O_3; (3) with $K_2S_2O_3$, the salt obtained was $SO_2.OK.SNH_4$. F. a. K. could not obtain $SO_2.ONH_4.SK$; (4) with $Cu_2S_2O_3$ and Cu_2I_2, also with Cu_2I_2 and NH_4I (Brun, *C. R.* 114, 667); (5) with PbS_2O_3 (Rammelsberg, *P.* 56, 308); (6) with HgS_2O_3 (R., *l.c.*).

Barium thiosulphate $BaS_2O_3.aq$. A white pp. obtained by mixing $Ba(C_2H_3O_2)_2Aq$ and $Na_2S_2O_3Aq$, and completing ppn. by alcohol; loses all water at 170°, at red heat gives $BaS, BaSO_3, BaSO_4$, and S (H. Rose, *P.* 21, 437; Rammelsberg, *P.* 56, 295).

Double salts. (1) With CdS_2O_3 (Fock a. Klüss, *B.* 23, 1753); (2) with $Cu_2S_2O_3$ (Cohen, *C. J.* 51, 38); (3) with PbS_2O_3 (Rammelsberg, *P.* 56, 308).

Cadmium thiosulphate $CdS_2O_3.2aq$ (F. a. K., *B.* 23, 534); *double salts* with (1) $Na_2S_2O_3$, (2) $K_2S_2O_3$, (3) SrS_2O_3 (F. a. K., *B.* 23, 1753; Vortmann a. Padberg, *B.* 22, 2637).

Calcium thiosulphate $CaS_2O_3.6aq$. Formed by mixing hot conc. solutions of $CaCl_2$ and $Na_2S_2O_3$, evaporating under 60°, separating NaCl, which crystallises first, and allowing to cool (Kessler, *P.* 74, 282). Also obtained by heating $CaSO_3$ and S with water, or by boiling milk of lime with S, passing in SO_2, and crystallising below 60° (Herschel, *N. Ed. P. J.* 1, 8, 296; 2, 154). Forms large, clear, six-sided, triclinic prisms, that effloresce in air at 40°; S. 100 at 3° (H., *l.c.*). Conc. solution gives $CaSO_3$ and S by heating above 60°. Rammelsberg (*P.* 56, 308) describes a *double salt* with PbS_2O_3.

Cobalt thiosulphate $CoS_2O_3.6aq$ (Rammelsberg, *P.* 56, 398; Fock a. Klüss, *B.* 22, 3310). A *double salt* with $Na_2S_2O_3$ is described by Vortmann a. Padberg (*B.* 22, 2637).

Copper thiosulphates. According to von Hauer (*W. A. B.* 13, 443) an *acid cuprous salt* $Cu_2H_4(S_2O_3)_3$, is obtained, in microscopic, golden-yellow needles, by adding conc. $CuSO_4Aq$ to $Na_2S_2O_3Aq$ till the liquid is deep yellow, and gently warming, washing the pp. with water and alcohol, and drying over H_2SO_4. *Double salts* of $Cu_2S_2O_3$: (1) with BaS_2O_3 (Cohen, *C. J.* 51, 38); (2) with $K_2S_2O_3$ (C., *l.c.*; Rammelsberg, *P.* 56, 321); (3) with $Ag_2S_2O_3$ (C., *l.c.*); (4) with $Na_2S_2O_3$ (Lenz, *A.* 40, 99; Siewert, *J.* 1866, 257; Kessel, *B.* 10, 1677, 2000; Schütte, *J. pr.* 70, 249; Vortmann, *M.* 9, 165).

Iron thiosulphate. The *ferrous salt* $FeS_2O_3.5aq$ was obtained by Vortmann a. Padberg (*B.* 22, 2637) by rubbing BaS_2O_3 with conc. $FeSO_4Aq$ (the salts being present in the ratio of equal numbers of molecules), filtering from $BaSO_4$, adding a mixture of alcohol and ether, and allowing the green, oily liquid that separated to stand for some days. Small green crystals; very sol. water; solution is decomposed by boiling, with separation of FeS. A *double salt* with $Na_2S_2O_3$ is described by V. a. P. (*l.c.*). For accounts of former attempts to prepare pure ferrous thiosulphate *v.* Fordos a. Gélis (*J. Ph.* [3] 4, 333); Berthelot (*A. Ch.* [5] 2, 58); Vogel (*J. pr.* 8, 102); Koene (*P.* 63, 245, 431); Rammelsberg (*P.* 56, 306).

No *ferric thiosulphate* has been isolated.

Lead thiosulphate PbS_2O_3. Obtained by adding $Na_2S_2O_3Aq$ to $Pb(NO_3)_2Aq$, or $Pb(C_2H_3O_2)_2Aq$, and washing the pp. with cold water. A white solid; very sl. sol. water; sol. solutions of alkali thiosulphates (*v.* Pape, *J.* 1864. 57; Letts, *C. J.* [2] 8, 424). For reaction with PCl_5—giving $PbCl_2$, HCl, SO_2, $SOCl_2$, $POCl_3$ and probably $PSCl_3$—*v.* Buchanan (*B.* 8, 485). Rammelsberg (*P.* 56, 308) has described *double salts* with the thiosulphates of NH_4, Ba, Ca, K (*v.* also Spring, *B.* 7, 1157), and Na (*v.* also Vortmann a. Padberg, *B.* 22, 2637).

Lithium thiosulphate $Li_2S_2O_3.3aq$ (*v.* Fock a. Klüss, *B.* 22, 3096).

Magnesium thiosulphate $MgS_2O_3.6aq$. By passing SO_2 into MgSAq till colourless, boiling $MgSO_3$ in SO_2Aq with S, or adding BaS_2O_6Aq to $MgSO_4Aq$ and filtering, a solution is obtained which on evaporation at a low temperature gives small, white, prismatic crystals of this salt. Loses $3H_2O$ at 170°, and gives off SO_2 and S at red heat, leaving $MgSO_4$ and MgO (Herschel, *N. Ed. P. J.* 1, 8, 296; 2, 154; Rammelsberg, *P.* 56, 303; Fock a. Klüss, *B.* 22, 3310). *Double salts* (1) with $(NH_4)_2S_2O_3$, (2) with $K_2S_2O_3$ are described by R. (*l.c.*; *v.* also Kessler, *P.* 74, 256; also F. a. K., *B.* 23, 534).

Manganese thiosulphate $MnS_2O_3.5aq$. Formed similarly to $FeS_2O_3.5aq$ (Vortmann a. Padberg, *B.* 22, 2637). A *double salt* with $Na_2S_2O_3$ is described by V. a. P. (*l.c.*).

Mercury thiosulphates. Neither the mercurous nor the mercuric salt has been isolated. Addition of a thiosulphate to solution of a mercurous salt ppts. Hg_2S; with a mercuric salt, a compound of HgS with the mercuric salt employed is said to be formed (Rammelsberg, *P.* 56, 314). *Double salts* of *mercurous thiosulphate* with (1) $(NH_4)_2S_2O_3$, (2) $Cu_2S_2O_3$, (3) $Na_2S_2O_3$ are described by Rammelsberg (*l.c.*); and a double salt of *mercuric thiosulphate* with $K_2S_2O_3$ by Vortmann a. Padberg (*B.* 24, 1351).

Nickel thiosulphate $NiS_2O_3.6aq$ (Rammelsberg, *P.* 56, 309; Fock a. Klüss, *B.* 22, 3310). For a *double salt* with $Na_2S_2O_3$ *v.* Vortmann a. Padberg (*B.* 22, 2637).

Platinum thiosulphate. Not isolated; but Schottländer (*A.* 140, 200) describes a *double salt* $PtS_2O_3.3Na_2S_2O_3.10aq$.

Potassium thiosulphate $K_2S_2O_3$. Obtained by boiling conc. K_2SO_3 with excess of S; or by adding hot $K_2Cr_2O_7Aq$ to hot K_2S_5Aq, little by little, waiting after each addition till the separated Cr_2O_3 is pure green in colour

$$(2K_2S_5Aq + 4K_2Cr_2O_7Aq + H_2O = 5K_2S_2O_3Aq + 2KOHAq + 4Cr_2O_3);$$

(Döpping, *A.* 46, 172; Kessler, *P.* 74, 274). In either case the filtered solution is evaporated to the crystallising point, and the crystals of $K_2S_2O_3.xH_2O$ are heated to c. 180°. By evaporating at 30°, thin, four-sided, deliquescent prisms are obtained of the *hydrated salt* $3K_2S_2O_3.H_2O$ (Rammelsberg, *P.* 56, 296; Kessler, *l.c.*; Fock a. Klüss, *B.* 22, 3096). This hydrate is very sol. water, but insol. alcohol; it loses all water at c. 180°; heated more strongly it decomposes to K_2S_5 and K_2SO_4 (R., *l.c.*). Other hydrates are described by D. a. P., *l.c.* (*v.* also Plessy, *A. Ch.*

[3] 11, 182; F. a. K., *l.c.*). The final products of the action of SO_2 on $K_2S_2O_3Aq$ are $K_2S_3O_6Aq$, $K_2S_4O_6Aq$, and $K_2S_5O_6Aq$ (Debus, *C. J.* 53, 343).

Double salts.—(1) with $(NH_4)_2S_2O_3$ (Fock a. Klüss, *B.* 23, 534); the salt obtained was $SO_2.OK.SNH_4$, the isomeric salt $SO_2.ONH_4.SK$ could not be isolated; (2) with $Bi_2(S_2O_3)_3$ (Carnot, *C. R.* 83, 338); (3) with CdS_2O_3 (F. a. K., *B.* 23, 534); (4) with $Cu_2S_2O_3$ (Cohen, *C. J.* 51, 38); (5) with $HgCy_2$ (F. a. K., *B.* 24, 1351); (6) with HgS_2O_3 (F. a. K., *l.c.*); (7) with PbS_2O_3 (Rammelsberg, *P.* 56, 308; Spring, *B.* 7, 1157); (8) with $Ag_2S_2O_3$ (Cohen, *C. J.* 51, 38; Schwicker, *B.* 22, 1728, describes $KAgS_2O_3.NH_3$). (9) With $Na_2S_2O_3$ two salts are obtained: (i.) $SO_2.OK.NaS.2aq$, by the interaction of Am_2S_5Aq and $NaKSO_3.2aq$; (ii.) $SO_2.SK.ONa.2aq$, by the interaction of Am_2S_5Aq and $KNaSO_3$ (*v.* SULPHITES, p. 587); the first salt melts at c. 57° and has S. = 213·7 at 15°, heated with EtBr it gives $SO_2.OK.SEt$; the second salt melts at c. 62° and has S. = 105·3 at 15°, heated with EtBr it gives $SO_2.ONa.SEt$ (Schwicker, *B.* 22, 1728).

Silver thiosulphate $Ag_2S_2O_3$. This salt has probably not been isolated pure. On adding dilute $AgNO_3Aq$ to $K_2S_2O_3Aq$ a white pp. is formed, and is dissolved on shaking; addition of more $AgNO_3Aq$ produces a greyish, flocculent pp., which is a mixture of $Ag_2S_2O_3$ and Ag_2S. By treating this pp. with NH_3Aq, filtering from Ag_2S, exactly neutralising the filtrate by HNO_3Aq, and quickly drying the white flocculent pp. that formed between filter paper, Herschel (*N. Ed. P. J.* 1, 26, 398; 2, 154) obtained fairly pure $Ag_2S_2O_3$. A white powder; slightly soluble water; solution has a sweet taste; decomposes readily to Ag_2S and H_2SO_4Aq.

Double salts. Ag_2O and Ag salts generally dissolve readily in solutions of alkali thiosulphates, forming double salts, either of the form $2AgMS_2O_3.aq$, or of the form $Ag_2M_4(S_2O_3)_3.2aq$ (Herschel, *l.c.*). (1) With $(NH_4)_2S_2O_3$; by adding excess of AgCl to $(NH_4)_2S_2O_3Aq$, and washing the white crystalline pp., $2Ag(NH_4)S_2O_3.aq$ is obtained. Using less AgCl and ppg. the solution by alcohol produces $Ag_2(NH_4)_4(S_2O_3)_3.2aq$ (H., *l.c.*). (2) With $Na_2S_2O_3$; addition of $AgNO_3Aq$, drop by drop, with constant shaking, to $Na_2S_2O_3Aq$, till a permanent pp. begins to form, followed by addition of alcohol, ppts. $Ag_2Na_4(S_2O_3)_3.2aq$; the salt is washed with alcohol, and dried *in vacuo* (Lenz, *A.* 40, 94); when the mother-liquor from this salt is allowed to evaporate $2AgNaS_2O_3.aq$ is deposited (Herschel, *l.c.*; *cf.* Lenz, *l.c.*). The second of these salts is much less soluble in water than the first; it dissolves in $Na_2S_2O_3Aq$, with formation of $Ag_2Na_4(S_2O_3)_3.2aq$. Both salts are decomposed by boiling their aqueous solutions, with formation of Ag_2S. (3) With $K_2S_2O_3$; two salts are known similar to the sodium salts. Schwicker (*B.* 22, 1738) describes the compound $AgKS_2O_3.NH_3$. Herschel (*l.c.*) obtained double salts with CaS_2O_3 and with SrS_2O_3.

Sodium thiosulphate $Na_2S_2O_3.5aq$.

Formation.—1. By boiling Na_2SO_3Aq with S.—2. By passing SO_2 into solution of sodium polysulphides.—3. By the action of SO_2 on *soda waste* suspended in water, whereby CaS_2O_3Aq is formed; followed by addition of Na_2SO_4, filtration from $CaSO_4$, and evaporation.

Preparation.—$Na_2SO_3.xaq$ is dissolved in a little water, the solution is boiled with flowers of sulphur for a considerable time, and filtered; the clear, colourless liquid is evaporated to the crystallising point, and the crystals that separate are purified by recrystallisation from water.

Properties.—Large, white, monoclinic prisms; S.G. 1·736 at 10° (Kopp, *J.* 8, 45; *cf.* Schiff, *J.* 12, 41; Smith, *Am. J. Pharm.* 53, 148). Melts at 45° in the water of crystallisation (Kopp, *J.* 8, 45); at 48·5° (Tilden, *C. J.* 45, 268). The crystals are dehydrated by keeping *in vacuo* over H_2SO_4, or by heating to 100°. S. 49·75 at 0°, 69·44 at 20°, 104·16 at 40°, 192·3 at 60° (Kremers, *P.* 99, 50). An aqueous solution of the salt is easily supersaturated; thus Schiff (*A.* 113, 350) dissolved 171 parts $Na_2S_2O_3.5aq$ (= 108·9 parts $Na_2S_2O_3$) in 100 parts water at 19·1°, and Kremers obtained a solution of 217·4 parts $Na_2S_2O_3$ in 100 parts water at the ordinary temperature. According to Baumhauer (*J. pr.* 104, 148), a supersaturated solution may be cooled to −10° without crystallising; addition of a crystal of the salt causes rapid crystallisation, with the evolution of much heat (*cf.* Parmentier a. Amat, *C. R.* 98, 735) Solution of $Na_2S_2O_3.5aq$ in water is accompanied by the disappearance of much heat; Rüdorff (*B.* 2, 68) says that 110 parts $Na_2S_2O_3.5aq$ dissolving in 100 parts water lower the temperature from 10·7° to −8°, *i.e.* through 18·7°. Schiff (*A.* 113, 350) gives the following data for S.G. and composition of aqueous solutions of $Na_2S_2O_3.5aq$:—

S.G. of sol.	P.c. $Na_2S_2O_3.5aq$	P.c. $Na_2S_2O_3$	S.G. of sol.	P.c. $Na_2S_2O_3.5aq$	P.c. $Na_2S_2O_3$
1·0052	1	0·637	1·1440	26	16·564
1·0105	2	1·274	1·1499	27	17·201
1·0158	3	1·911	1·1558	28	17·838
1·0211	4	2·584	1·1617	29	18·475
1·0264	5	3·185	1·1676	30	19·113
1·0317	6	3·822	1·1738	31	19·750
1·0370	7	4·459	1·1800	32	20·387
1·0423	8	5·096	1·1862	33	21·024
1·0476	9	5·733	1·1924	34	21·661
1·0529	10	6·371	1·1986	35	22·298
1·0639	11	7·008	1·2048	36	22·935
1·0584	12	7·645	1·2110	37	23·572
1·0695	13	8·282	1·2172	38	24·209
1·0751	14	8·919	1·2234	39	24·846
1·0807	15	9·556	1·2297	40	25·484
1·0863	16	10·193	1·2362	41	26·121
1·0919	17	10·830	1·2427	42	26·758
1·0975	18	11·476	1·2492	43	27·395
1·1031	19	12·105	1·2558	44	28·032
1·1087	20	12·742	1·2624	45	28·669
1·1145	21	13·379	1·2690	46	29·306
1·1204	22	14·016	1·2756	47	29·943
1·1263	23	14·653	1·2822	48	30·580
1·1322	24	15·290	1·2888	49	31·218
1·1381	25	15·927	1·2954	50	31·855

$Na_2S_2O_3.5aq$ is insol. alcohol.

According to Jochum (*C. C.* 1885. 642), a *trihydrated salt* $Na_2S_2O_3.3aq$ is obtained by adding alcohol to a saturated solution of the ordinary salt, removing the oily liquid that separates, and adding to it 98 p.c. alcohol. According to Parmentier a. Amat (*C. R.* 98, 735), $Na_2S_2O_3.5aq$ is obtained crystallised in needles, melting at c. 32°, by placing a supersaturated solution of the ordinary salt in a freezing mixture in a closed vessel.

Reactions.—1. *Heat* decomposes $Na_2S_2O_3$; the change begins at c. 220° with separation of S, at c. 400° Na_2SO_4 and Na_2S_5 are formed, and at a higher temperature more S is given off, and Na_2SO_4 and Na_2S remain.—2. $Na_2S_2O_3Aq$ interacts with *iodine* in KIAq to form NaIAq and $Na_2S_4O_6Aq$; according to Villiers (*C. R.* 108, 402) some $Na_2S_3O_6$ is also formed. With a mixture of Na_2SO_3 and $Na_2S_2O_3$ in solution I produces NaIAq, Na_2SO_4Aq and $Na_2S_4O_6Aq$ (Colefax, *C. J.* 61, 198, 1083).—3. $Na_2S_2O_3$ is oxidised by *potassium permanganate* solution; in alkaline solutions the oxidation is complete to Na_2SO_4Aq according to Hönig a. Zatzek (*M.* 4, 738); Glaser (*M.* 6, 329) says that the oxidation is also complete in neutral solutions; Luckow (*Fr.* 32, 53) represents the oxidation, on boiling, either in neutral, acid, or alkaline solution as producing Na_2SO_4 and $Na_2S_2O_6$.—4. *Acids* interact with $Na_2S_2O_3Aq$, forming Na salts of the acids, and $H_2S_2O_3Aq$, which then decomposes to H_2SO_3Aq and S; when the products are not removed from the solution the reaction stops before all the $H_2S_2O_3$ is decomposed (Colefax, *C. J.* 61, 176; and *v.* beginning of article THIOSULPHATES, p. 705).

Combinations.—1. With *water* (*v. supra, Properties*).—2. With various *thiosulphates* to form *double salts.* Double salts with CdS_2O_3, CoS_2O_3, FeS_2O_3, PbS_2O_3, MnS_2O_3, NiS_2O_3, $Tl_2S_2O_3$, and ZnS_2O_3 are described by Vortmann a. Padberg (*B.* 22, 2637); Fock a. Klüss (*B.* 23, 1753) also describe that with CdS_2O_3. Rammelsberg (*P.* 56, 308) prepared salts with PbS_2O_3 and $Hg_2S_2O_3$. For a double salt with HgS_2O_3 *v.* Schwicker (*B.* 22, 1728). For the double salts with $K_2S_2O_3$ *v.* POTASSIUM THIOSULPHATE, *double salts*, No. (9) (p. 707), and for those with $Ag_2S_2O_3$ *v.* SILVER THIOSULPHATE, *double salts*, No. (2) (p. 707). Schottländer (*A.* 140, 200) describes a double salt $3Na_2S_2O_3.PtS_2O_3.10aq$.

Strontium thiosulphate $SrS_2O_3.5aq$. Prepared like the Ba salt (Herschel, *N. Ed. P. J.* 1, 26, 398; 2, 154; Kessler, *P.* 74, 274). Fock a. Klüss (*B.* 22, 3310) describe a salt $SrS_2O_3.aq$.

Thallium thiosulphate $Tl_2S_2O_3$. A white, crystalline pp., formed by adding $Na_2S_2O_3Aq$ to fairly conc. TlOHAq (Crookes, *C. J.* 17, 136; Hebberling, *A.* 184, 11). For a *double salt* with $Na_2S_2O_3$ *v.* Werther (*J. pr.* 92, 130); Vortmann a. Padberg (*B.* 22, 2637); also Jochum (*C. C.* 1885. 642).

Zinc thiosulphate ZnS_2O_3. Prepared by double decomposition from $ZnSO_4Aq$ and BaS_2O_3Aq (*v.* Rammelsberg, *P.* 56, 295; Fordos a. Gélis, *J. pr.* 29, 291). For a compound with NH_3 *v.* R. (*l.c.*). For a *double salt* with $Na_2S_2O_3$ *v.* Vortmann a. Padberg (*B.* 22, 2637).

M. M. P. M.

THIOSULPHURIC ACID $H_2S_2O_3Aq$. This acid almost certainly exists in the liquid obtained by adding a dilute weak acid to dilute $Na_2S_2O_3Aq$, the acid and salt being mixed in equivalent quantities; the $H_2S_2O_3Aq$ soon begins to decompose to H_2SO_3Aq and S. Landolt (*B.* 16, 2958) has made an extensive investigation into the conditions and time of existence of $H_2S_2O_3$ in solution. Thomsen (*Th.* 2, 256) gives the thermal data; $[SO^2Aq,S] = -9310$; $[SO^2,S,Aq] = -1610$.

For the salts of $H_2S_2O_3$ *v.* THIOSULPHATES.

M. M. P. M.

THIOTOLENE *v. Methyl-thiophene.*

THIO-*o*-TOLUIC ACID. *Amide* $C_6H_4Me.CS.NH_2$. [88°]. Formed from *o*-toluic nitrile (Gabriel a. Heymann, *B.* 24, 786).

Thio-*p*-toluic acid. *Amide.* [168°]. Formed by passing H_2S into an alcoholic solution of *p*-toluic nitrile (Paterno a. Spica, *B.* 8, 441). Yellowish needles. Zinc and HClAq yield $C_6H_4Me.CH_2NH_2$.

THIO-TOLUIDINE *v.* DI-AMIDO-DI-TOLYL SULPHIDE.

THIO-*p*-TOLYL-DI-PHENYL-DI-GUANIDINES *v.* DI-PHENYL-DI-GUANIDO-DI-TOLYL SULPHIDE and DI-PHENYL-DI-CARBIMIDO-TETRA-AMIDO-TETRA-TOLYL DISULPHIDE.

THIO-TOLYL-DI-PHENYL-THIO-UREA *v.* DI-PHENYL-DI-THIOURAMIDO-DI-TOLYL SULPHIDE.

THIO-URAMIDO-BARBITURIC ACID $C_5H_6N_4SO_3$ *i.e.* $NH_2.C(NH).S.CH\left<\begin{matrix}CO.NH\\CO.NH\end{matrix}\right>CO$. Formed by the action of thio-urea on an aqueous solution of chloro-, bromo-, or di-bromo-barbituric acid (Mulder, *B.* 12, 2309; Trzcinski, *B.* 16, 1057). Formed also by heating alloxan with thio-urea and alcoholic SO_2 at 100° (Nencki, *B.* 4, 722; 5, 451). Slender needles, insol. water, sol. hot HClAq. Converted by boiling KOHAq into thio-dialuric acid $C_4H_4N_2SO_3$ $1\frac{1}{2}aq$ (?) which yields KA′aq. H_2SO_4 ($\frac{1}{2}$ pt.) at 150°–160° forms uro-sulphinic acid $C_5H_4N_4SO_2$.

THIO-URAMIDO-BENZENE *p*-SULPHONIC ACID. The salt $NH_2.CS.NH.C_6H_4.SO_3K$, formed by heating potassium sulphocyanide with amido-benzene *p*-sulphonic acid at 140°, crystallises from dilute alcohol in aggregates of thin needles (Pellizzari, *A.* 248, 156).

***m*-THIO-URAMIDO-BENZOIC ACID** $NH_2.CS.NH.C_6H_4.CO_2H$. [187°]. Formed from *m*-amido-benzoic acid and potassium sulphocyanide (Arzruni, *B.* 4, 406). Formed also by allowing a solution of *m*-cyanamido-benzoic acid in colourless ammonium sulphide to stand for 24 hours (Traube, *B.* 15, 2118). Needles. Converted by ammoniacal $AgNO_3$ into *m*-uramido-benzoic acid. Not coloured by $FeCl_3$.

***p*-THIO-URAMIDO-BENZYL-THIO-UREA** $NH_2.CS.NH.C_6H_4.CH_2.NH.CS.NH_2$. *p-ω-di-thi-uramido-toluene.* [176°]. Formed by heating *p*-amido-benzyl-amine hydrochloride (1 mol.) with potassium sulphocyanide (2 mols.) in aqueous solution (Amsel a. Hofmann, *B.* 19, 1289). White needles.

THIO-URAMIDO-BUTYRIC ACID. *Anhydride* $NH:C\left<\begin{matrix}S-CHEt\\NH.CO\end{matrix}\right.$. [200°]. Formed from *α*-bromo-*n*-butyric acid and thio-urea (Andreasch, *M.* 8, 419). Needles, v. sol. hot water.

Thio-uramido-iso-butyric acid. *Anhydride* $C_5H_8N_2SO$ *i.e.* $NH:C\left<\begin{matrix}S-CMe_2\\NH.CO\end{matrix}\right.$. [242°]. Formed from bromo-isobutyric acid and thio-urea (Andreasch, *M.* 8, 410). Plates, sl. sol. water. Oxidised by HCl and $KClO_3$ to urea and *α*-sulpho-iso-butyric acid.

***o*-THIO-URAMIDO-CINNAMIC ACID** $NH_2.CS.NH.C_6H_4.CH:CH.CO_2H$. [236°–239°]. Got by heating the sulphocyanide of *o*-amido-cinnamic acid $C_6H_4(NH_2.HSCy)CH:CH.CO_2H$

[152°] at 115° (Rothschild, *B.* 23, 3342). V. sol. hot HOAc and NH_3Aq.

α-Thio-ψ-uramido-cinnamic acid $C_{10}H_{10}N_2SO_2$ *i.e.* $NH:C(NH_2).S.C(CO_2H):CHPh$. Formed from benzoic aldehyde, thiohydantoïn, and NaOHAq (Andreasch, *M.* 8. 421). Needles (from alcohol), decomposed by alkalis.

β-THIO-ψ-URAMIDO-PROPIONIC ACID $NH:C(NH_2).S.CH_2.CH_2.CO_2H$. Formed by heating *β*-iodo-propionic acid with thio-urea and water and a little NaOH (Andreasch, *M.* 6, 831). Small pyramids (containing 2aq), sl. sol. cold water and cold alcohol. Decomposed by baryta into cyanamide and $CH_2(SH).CH_2.CO_2H$. $KClO_3$ and HCl yield *β*-sulpho-propionic acid.

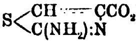
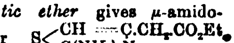
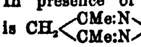
ωp-**DI-THIO-URAMIDO-TOLUENE** *v.* THIO-URAMIDO-BENZYL-THIO-UREA.

DI-*p*-THIO-URAMIDO-DI-TOLYL-*o*-SULPHIDE [2:1:4] $S(C_6H_3Me.NH.CS.NH_2)_2$. *Thio-p-tolyl-di-thiurea.* [121°]. Formed by evaporating to dryness an aqueous solution of di-*p*-amido-di-tolyl sulphide, hydrochloride and ammonium sulphocyanide (Truhlar, *B.* 20, 669). White amorphous powder. Sol. alcohol and benzene, sl. sol. ether.

THIO-UREA CSN_2H_4 *i.e.* $CS(NH_2)_2$ or $HS.C(NH_2):NH$. Mol. w. 76. [170°]. S. 9 in the cold (Volhard, *J. pr.* [2] 9, 13).

Formation.—1. By heating dry ammonium sulphocyanide for two hours at 170°, cooling to 100°, adding an equal weight of water at 80°, filtering, and allowing to crystallise (Emerson Reynolds, *C. J.* 22, 1; Claus, *A.* 179, 113; Smolka a. Friedreich, *M.* 10, 90).—2. By the action of tin and HCl, or of HI, on persulphocyanic acid $C_2H_2N_2S_3$ (Glutz, *A.* 154, 39).—3. By passing dry H_2S into an ethereal solution of cyanamide (Baumann, *B.* 6, 1375).—4. By allowing a solution of cyanamide, mixed with yellow ammonium sulphide, to stand for a day (Baumann, *B.* 8, 26).—5. From cyanamide and thioacetic acid.—6. Together with urea by the action of ammonia on COS (Berthelot, *C. R.* 94, 1069).

Properties.—Silky trimetric needles, melting at 170°. After one fusion it melts at 149° (Prätorius, *J. pr.* [2] 21, 141). V. sol. water, nearly insol. alcohol and ether. Tastes bitter, not coloured by $FeCl_3$. According to Armstrong (*C. J. Proc.* 8, 2), the molecule of thio-urea is $C_2S_2N_4H_8$.

Reactions.—1. *Water* at 140° forms ammonium sulphocyanide. *Alcohol* at 100° acts in like manner (Haller, *Bl.* [2] 45, 706).—2. An alcoholic solution of *nitrous ether* quickly converts it into ammonium sulphocyanide.—3. Prolonged *heating* at 170° also converts it into ammonium sulphocyanide. At 180° it slowly forms guanidine sulphocyanide and ammonium tri-thio-carbonate. Nitrous acid gives off nitrogen.—4. KOH at 100° slowly forms NH_3, KSH, K_2CO_3, and a little KCyS. Alcoholic potash acts in like manner (Haller, *C. R.* 102, 974). H_2SO_4 and HCl act in the same way.—5. Aqueous $KMnO_4$ forms urea and other products (Maly, *M.* 11, 277).—6. *Oxidising agents* (*e.g.* H_2O_2, $K_2Cr_2O_7$, KNO_2, $KMnO_4$, and iodine) form $S_2(C(NH_2):NH)_2$, which has an insoluble nitrate (Storch, *M.* 11, 452).—7. Ammoniacal $AgNO_3$ forms urea and Ag_2S.—8. HgO, added to a cold aqueous solution, produces cyanamide. PbO acts in like manner. At 100° the product is dicyandiamide (Hofmann, *B.* 2, 605).—9. *Acetoacetic ether* reacts forming an ether $C_5H_7N_2SO(OEt)$, which on saponification yields $CS\left\langle\begin{matrix}NH.CMe\\NH.CO\end{matrix}\right\rangle CH$, v. sl. sol. water (Behrend, *B.* 19, 219).—10. $CCl_3.COCl$ forms $C_4H_5Cl_3N_2S_2O_2$, crystallising in slender needles, m. sol. alcohol, sl. sol. water, v. sl. sol. ether; converted by Br into $CCl_3.SO_2Br$ (McGowan, *C. J.* 49, 191; 51, 669; *J. pr.* [2] 36, 220). $CCl_3.SO_2Cl$ added to an alcoholic solution of thio-urea forms the chloride $Cl_2CSN_2H_4$, which is ppd. on adding ether, while the filtrate contains the compound $(CSN_2H_4)_2(CCl_3.SO_2)_2$ [125°], which is more sol. alcohol than water, and gives with Br a pp. of $CCl_3.SO_2Br$.—11. $CCl_3.SO_2NH_4$ in alcohol forms flat prisms of $(CSN_2H_4)CCl_3SO_2H$ [139°], m. sol. water and ether, v. sol. alcohol, converted by Br into $CCl_3.SO_2Br$ (M'Gowan, *C. J.* 51, 667; *J. pr.* [2] 36, 219).—12. *Chloro-acetone* forms $(NH_2.CS.NH.CH_2.CO.CH_3)HCl$ [126°] (Pawlewski, *B.* 21, 402).—13. $ClCO_2Et$ forms $(NH_2.CS.NH.CO_2Et)HCl$ [117°].—14. $CH_2Cl.OH$ gives $C_2H_4N_2S$, a white amorphous powder, insol. water, nearly insol. all usual menstrua, reconverted into thio-urea by HClAq (von Hemmelmayr, *M.* 12, 89).—15. *Di-bromo-succinic acid* forms fumaric acid on heating (Nencki a. Sieber, *J. pr.* [2] 25, 74).—16. A hot conc. solution of *di-bromo-pyruvic acid* forms 'sulphuvinuric acid' $C_4H_4N_2SO_2$, which crystallises with 2aq, reduces Fehling solution to Cu_2O in the cold, and to a copper mirror on warming, and yields the salts CaA'_2, MgA'_2, ZnA', HA'HCl, HA'HBr, and $HA'HNO_3$aq (N. a. S.).—17. *Bromo-pyruvic ether* forms amido-thiazole carboxylic ether  $S\left\langle\begin{matrix}CH=CCO_2Et\\C(NH_2):N\end{matrix}\right.$ [173°] (Steude, *A.* 261, 30).—18. *Bromo-acetoacetic ether* gives *μ*-amido-thiazyl-acetic ether  $S\left\langle\begin{matrix}CH=C.CH_2.CO_2Et\\C(NH_2):N.\end{matrix}\right.$ [94°], which yields an acid [c. 130°], split up on fusion into CO_2 and amido-methyl-thiazole (Steude). *α-Chloro-acetoacetic ether* forms $C_3NSMe(NH_2).CO_2Et$ [175°] (Zürcher, *A.* 250, 281).—19. Thio-urea heated with an alcoholic solution of *chloro-acetic acid* and *phenyl-hydrazine* forms $C_9H_9N_3SO$ [175°] (Probst, *J. pr.* [2] 45, 416).—20. Fusion with (*β*)-*iodopropionic acid* and a little water forms $C_4H_8N_2SO_2$ [176°], which crystallises from water in needles (containing 2aq), sl. sol. alcohol, insol. ether (Andreasch, *M.* 6, 832).—21. *Di-chloro-acetic acid* forms thiohydantoïn. *α-Bromo-propionic acid* forms methyl-thiohydantoïn (206° uncor.) (Dixon, *C. J.* 63, 815).—22. *Aldehyde* heated in a sealed tube with thio-urea forms $CSN_2H_4(CHMe)$, which is sl. sol. ether and cold alcohol, and is decomposed by hot water (Reynolds, *C. N.* 24, 87).—23. *Succinic anhydride* at 140° forms $C_8H_8N_2SO_3$ [211°].—24. *Citraconic anhydride* at 130° forms $C_6H_8N_2SO_2$ [223°] (Pike, *B.* 6, 1104).—25. *Acetyl-acetone* and a small quantity of HClAq form $CH_2(CMe:N.CS.NH_2)_2HCl$ [219°]. In presence of excess of HCl the product is  $CH_2\left\langle\begin{matrix}CMe:N\\CMe:N\end{matrix}\right\rangle CS$ [210°] (Evans, *J. pr.* [2] 48, 503).

Salts.—$B'HNO_3$. Crystalline.—B'HCl. Formed from the stannous double chloride and

H_2S. Crystalline.—$B'HI$. Tables.—B'_4NH_4Cl. [154°]. Felted crystalline mass (Reynolds, *C. J.* 59, 385).—B'_4NH_4I. [186°].—$B'_2H_2PtCl_6$. Yellow prisms, v. sol. water and alcohol. Can be dried at 100°.—B'_2HPtCl_3. Got when saturated solutions of thio-urea and $PtCl_4$ are mixed. Dark-red prisms, insol. water, alcohol and ether.—B'_2AuCl. Yellow monoclinic crystals, got by adding $AuCl_3$ to a saturated solution of thio-urea.—$B''TlSO_4$.—B'_2CuSO_4. White silky needles. Got by mixing conc. solutions of thio-urea and $CuSO_4$.—$B'_5Cu_2(SO_4)$ 2aq.—B'_3CuCl. Colourless dimetric crystals, sol. water, but ppd. by HCl and KCl. Alkaline in reaction. Attacked by H_2S with difficulty. Does not absorb CO (Rathke, *B.* 17, 301).—$B'_2Cu_2Cl_2$ aq. Ppd. by adding $CuCl_2Aq$ to aqueous thio-urea (Rathke, *B.* 14, 1779; 17, 301). Minute needles, insol. water.—B'_2CuCl. Flat needles. Formed by mixing the two preceding salts into which it is decomposed by water.—$B'4HgO$.—$B'_2(HgO)_3$ 3aq. Ppd. by adding neutral $Hg(NO_3)_2$ to a dilute solution of thio-urea (Emerson Reynolds, *A.* 150, 235; Kurnakoff, *B.* 24, 3956). Crystalline. Loses thio-urea on washing with water.—B'_4HgCl_2: large crystals, v. sol. water.—B'_2HgCl_2: minute needles, nearly insol. water (Claus, *B.* 9, 227).—$B'HgI_2$ (Maly, *B.* 9, 173).—$B'HgCyS$. Needles, decomposed by heat into dicyandiamide, HCy, and HgS (Nencki, *B.* 6, 598).—B'_2PbCl_2: needles (Claus, *A.* 179, 135).—$B'Pb(CyS)_2$.—B'_2SnCl_2.—B'_2ZnCl_2: spherical groups of prisms (from water).—B'_2CdSO_4.—B'_8SiBr_4 (Emerson Reynolds, *C. J.* 51, 202).—B'_2Ag_2O 4aq. Crystalline.—$B'AgNO_3$ (K.).—B'_2AgNO_3. [141°]. Silky crystals, sol. hot alcohol (Emerson Reynolds, *C. J.* 61, 249).—B'_2AgCl. [171°]. Needles, m. sol. hot alcohol.—B'_2AgBr. [121°].—B'_2AgI.—B'_2AgCy. [126°].—$B'_8Ag_2C_2O_4$: needles.

Chloride $(CSN_2H_4)_2Cl_2$. Formed by passing Cl into a conc. alcoholic solution of thio-urea (Claus, *A.* 179, 139). Formed also by the action of $CCl_3.SO_2Cl$, and of ICl, ICl_3, or $POCl_3$ on thio-urea (M'Gowan, *C. J.* 49, 191; *J. pr.* [2] 33, 188). Small needles, v. sol. water, m. sol. alcohol, insol. ether. Decomposed by alkalis, yielding cyanamide. Alcoholic KI removes chlorine, setting thio-urea free. Dilute HNO_3 forms crystals of $(CSN_2H_4)_2(NO_3)_2$, which is sl. sol. water, insol. alcohol and ether.

Bromide $(CSN_2H_4)_2Br_2$. Formed by adding Br to an alcoholic or cold aqueous solution of thio-urea; in aqueous solution excess of Br produces urea (Claus, *A.* 179, 138; M'Gowan, *C. J.* 51, 378; *J. pr.* [2] 36, 216). Crystals. Its aqueous solution deposits S when heated. Sodium-amalgam reproduces thio-urea.

Iodide $(CSN_2H_4)_2I_2$. Formed from thio-urea, I, and alcohol (M'Gowan, *J. pr.* [2] 33, 192). Prisms.

Methylo-iodide $(CSN_2H_4)MeI$. [117°]. Formed slowly by combination of thio-urea with MeI in the cold (Bernthsen a. Klinger, *B.* 11, 493). Prisms, v. sol. water and alcohol. AgCl gives the chloride, which forms the platinochloride $(B'MeCl)_2PtCl_4$ aq.

Ethylo-chloride $B'EtCl$. Crystals.

Ethylo-bromide $(CSN_2H_4)EtBr$. Hexagonal plates (Claus a. Siegfried, *A.* 179, 145). Decomposes at 100°.

Ethylo-iodides $(CSN_2H_4)EtI$. Crystalline. Gives with moist Ag_2O a base. Boiling aqueous alkalis liberate mercaptan.—$B'_2Et_2PtCl_6$ (dried at 100°). Tables.—B'_2EtI. Needles (from alcohol) (Claus, *B.* 8, 41).

Benzylo-chloride $(CSN_2H_4)C_7H_7Cl$. [168°]. Formed from benzyl chloride and thio-urea. Yields unstable benzyl-thio-urea $CSN_2H_3C_7H_7$ [72°], which decomposes at 100° into dicyandiamide and benzyl mercaptan (Bernthsen a. Klinger, *B.* 12, 574).—$(CSN_2H_4C_7H_7Cl)_2PtCl_4$.

Compound with oxalic ether $(CSN_2H_4)_2Et_2C_2O_4$. [150°]. Monoclinic crystals (Nencki, *B.* 7, 780). Decomposed by hot water.

Compounds with amines $(CSN_2H_4)_4NMeH_3Br$. [138°]. Formed from methylamine hydrobromide and thio-urea in alcohol (Reynolds, *C. J.* 59, 392). Felted crystals.—$(CSN_2H_4)_3NEt_2H_2Br$. [134°]. Formed by boiling thio-urea together with diethylamine hydro-bromide and absolute alcohol.—$(CSN_2H_4)_3NEt_3HBr$.—$(CSN_2H_4)_2NEt_4I$ [135°]. Prisms.—$(CSN_2H_4)_2NEt_4Br$ [160°]. Rectangular prisms (Reynolds, *C. J.* 59, 388).

Acetyl derivative CSN_2H_3Ac. Mol. w. 118. [165°]. Formed by heating thio-urea with Ac_2O (Nencki, *B.* 6, 598). Formed also from thio-acetic acid and cyanamide (Prätorius, *J. pr.* [2] 21, 147). Prisms (from hot water), v. sol. alcohol, m. sol. ether.—$B'H_2PtCl_6$. Crystalline.

Propionyl derivative (Freytag, *J. pr.* [2] 20, 381).

Benzoyl derivative CSN_2H_3Bz. [170°]. Formed by warming thio-urea (2 mols.) with BzCl (1 mol.) (Pike, *B.* 6, 755). Got also from benzoyl sulphocyanide and NH_3Aq (Miguel, *Bl.* [2] 25, 252). Needles (from alcohol); sl. sol. cold water. Tastes bitter.

o-Oxy-benzoyl derivative $NH_2.CS.NH.CO.C_6H_4.OH$. [182°]. S. (boiling alcohol) 7. Formed from salicyl thiocarbimide and aqueous NH_3 (Miguel, *A. Ch.* [5] 11, 304).

THIO-ψ-URIC ACID *v.* THIO-URAMIDO-BARBITURIC ACID.

THIO-VALERIC ALDEHYDE $C_5H_{10}S$. (115°). Formed, together with $C_5H_8S_3$ [95°], by heating isovaleric aldehyde (23 pts.) with S (9 pts.) in sealed tubes at 250° for eight hours (Barbaglia, *G.* 11, 95; *B.* 17, 2654). Oil with penetrating odour like onions, sol. alcohol and ether. Does not combine with $NaHSO_3$.

Isomeride $C_5H_{10}S$. [69°]. V.D. $(H=1)$ 50·76. Formed by passing H_2S into a dilute aqueous solution of isovaleric aldehyde. Fibrous crystals (from ether), insol. water.

THIOXENE *v.* DI-METHYL-THIOPHENE.

THIOXYLENOL *v.* XYLYL MERCAPTAN.

THIOXYL METHYL KETONE *v.* DI-METHYL-THIENYL METHYL KETONE.

THORIUM Th. (*Thorinum.*) At. w. 232. Mol. w. unknown. The m.p. of Th has not been determined; it is certainly very high (Nilson, *B.* 15, 2541). S.G. 11·1 at 17° (N., *l.c.*, p. 2543). S.H. ·02787 (N., *B.* 16, 161). Crystallises in regular octahedral and hexagonal forms, isomorphous with Si (Brögger, *Z. K.* 7, 442; *cf.* Nilson, *B.* 15, 2546; 16, 162 *note*). S.V.S. 20·9.

Historical.—In 1818 Berzelius announced the discovery of the oxide of a new element in a rare Norwegian mineral; to the metal of this oxide he gave the name thorium (from the Scandinavian god *Thor*). A few years later Berzelius found that the substance he had supposed to be a new earth was really yttrium phosphate. In 1828, however, Berzelius isolated a new earth from another Norwegian mineral; he named the new earth thoria, and the mineral from which it had been prepared he called *thorite* (*P.* 16, 385). In 1851 Bergemann discovered a new metal and called it *donarium*; but this metal was shown to be identical with the thorium of Berzelius by Damour (*C. R.* 34, 685), Berlin (*P.* 87, 608), and Bergemann himself (*P.* 85, 558). In 1862 Bahr supposed he had found a new metal, which he called *wasium*, but soon afterwards he recognised that the metal was identical with thorium (*P.* 119, 572; 132, 227). The metal thorium was isolated by Berzelius in 1828 (*P.* 16, 385); it was also obtained by Chydenius in 1861 (*Bl.* [2] 1, 130); and in a state of greater purity by Nilson in 1882 (*B.* 15, 2537).

Occurrence.—Compounds of Th have been found only in very small quantities in a few localities. *Thorite* from Lövön in Norway contains c. 59 p.c. ThO_2 according to Berzelius; an orange-coloured variety of this mineral, *orangite*, was found by Bergemann to contain 74 p.c. ThO_2; Nilson (*B.* 15, 2519) found from 50 to 59 p.c. ThO_2 in different specimens of *thorite*. Small quantities of ThO_2 have been found in specimens of *pyrochlore*, *monazite*, *samarskite*, *euxenite*, *gadolinite*, and *orthite*. Several minerals containing Th have been discovered by Hidden a. Mackintosh in North Carolina and Colorado; one of these is a silicophosphate of Th, another a silicate of Th and Y, another a silicate of Th and U, and another is a uranate of Th, Pb, and Y (*Am. S.* [3] 36, 461; 38, 474).

Formation. — 1. By reducing $ThCl_4$ or $2ThCl_4.KCl$, by heating with K (Berzelius, *P.* 16, 385). — 2. By reducing fused $ThCl_4$, or $2ThCl_4.KCl$, by means of Na (Chydenius, *Bl.* [2] 1, 130; 6, 433; Nilson, *B.* 15, 2537).

Preparation.—Powdered *thorite* is evaporated with HClAq to dryness; the residue is heated to render silica insoluble, and treated with water; the solution is filtered and ppd. by H_2S; the filtrate from PbS is ppd. by NH_3Aq, and the pp. of crude $ThO_2.xH_2O$ is thoroughly washed and dissolved in HClAq; $Th(C_2O_4)_2$ is ppd. from this solution by $H_2C_2O_4Aq$, and the pp., after being thoroughly washed with boiling water, is decomposed by heating; the crude ThO_2 thus obtained is converted into $Th(SO_4)_2$ by treatment in a Pt basin with conc. H_2SO_4 after being thoroughly moistened with water. The impure $Th(SO_4)_2$ thus obtained is freed from acid and water by heating, and is dissolved in as little ice-cold water as possible (c. 5 parts are required), and the solution is heated to c. 20°, when $Th(SO_4)_2.9H_2O$ ppts. The $Th(SO_4)_2.9H_2O$ is dehydrated by heating; the $Th(SO_4)_2$ is dissolved in the minimum quantity of ice-cold water and the solution is heated to c. 20°; the crystals of $Th(SO_4)_2.9H_2O$ that separate are dehydrated, dissolved in ice-cold water, and the hydrated sulphate is ppd. by heating to 20°. This treatment is repeated a few times, when pure $Th(SO_4)_2.9H_2O$ is obtained. This method of purifying crude sulphate of Th, which is given by Nilson (*B.* 15, 2521), depends on the great differences between the solubilities in water of $Th(SO_4)_2$ and $Th(SO_4)_2.9H_2O$; the former, when pure, is soluble in 20·6 parts water at 0°, the latter requires 88 parts water at 0°, and much more at 20°, for solution. The sulphates of the metals present in the crude $Th(SO_4)_2$ prepared as described are much more soluble in water at 20° than $Th(SO_4)_2.9H_2O$. For other methods of preparing salts of Th from *thorite* *v.* Berzelius (*l.c.*), Chydenius (*l.c.*), Delafontaine (*Ar. Sc.* [2] 18, 343), and Cleve (*Bl.* [2] 21, 115).

To prepare Th from pure $Th(SO_4)_2$, Nilson (*B.* 15, 2538) dissolved the salt in water, ppd. by KOHAq and boiled, washed the $ThO_2.xH_2O$ thoroughly, dissolved in HClAq and reppd. by KOHAq (to remove all traces of H_2SO_4); he thoroughly washed the pp. by decantation, dissolved it in HClAq, added KCl, in the ratio $2ThCl_4:KCl$, evaporated to dryness in a Pt basin, and dried the residue by warming over a flame, stirring constantly, and then powdering and heating again. The dry double salt of $ThCl_4$ and KCl was heated to redness in a stream of dry HCl (prepared from conc. H_2SO_4 and sublimed NH_4Cl), HCl was removed by a stream of H, and some of the salt was transferred to a cylinder of wrought iron (fitted with a lid which screwed on), in which a layer of dry NaCl had been placed; pieces of sodium were arranged over the Th-K salt in the cylinder, on these was placed another layer of the Th-K salt, and the cylinder was thus nearly filled with alternate layers of Na and the double salt; the contents of the cylinder were pressed together by a piston which fitted into the cylinder, sufficient dry NaCl was added to fill the cylinder, the lid was screwed on, and the apparatus was heated to full redness for about fifteen minutes; after cooling, the contents of the apparatus were treated with cold water, whereby chlorides were dissolved and the excess of sodium was converted into NaOH and dissolved (the action is apt to be explosive); the thorium was washed with water, then with alcohol, and finally with ether, and dried at 100°.

The yield of thorium by this method is almost equal to that calculated from the equation. For a detailed description of the iron cylinder used for reduction *v.* Nilson a. Pettersson, *W.* 4, 554 (on the preparation of Be).

Properties.—Prepared as described, Th forms a greyish-white, glistening powder; the powder consists of small, thin, six-sided, crystalline leaflets; the larger crystals are as white and lustrous as silver, the smaller are grey and less lustrous. The crystals are somewhat brittle. S.G. at 17° 11·1 to 11·23; the latter number referring to the well-crystallised metal (Nilson, *B.* 15, 2543; 16, 160). S.H. (0° to 100°) ·02787, hence at. heat = 6·4 (N., *B.* 16, 161). Crystallises in combinations of regular octahedra and hexahedra; isomorphous with Si (N., *l.c.*, and *note*, p. 162). S.V.S. 20·9. The emission-spectrum of Th has been mapped by Thalén (*Détermin. des Longueurs d'Onde des Raies Métalliques* [Upsala, 1868]); the most marked lines are three in the indigo; 4393, 4382, and 4281. Soret (*Ar. Sc.* [2] 63, 59; [3] 4, 94) found that $ThCl_4Aq$ cuts off almost the whole of the ultra-violet part of the spectrum.

Th is unchanged in air up to 100°-120°; when heated to a higher temperature it burns to ThO_2 with production of much white light. Th is readily oxidised by heating in O; on this account some of the metal is oxidised in the process of preparation if the lid of the cylinder does not fit tightly. Nilson's experiments (*B.* 15, 2541) show that Th does not melt at the full heat of a wind-furnace. Th does not react with water; it combines directly with Cl, Br, I and S. The metal is slowly acted on by H_2SO_4 or HNO_3, rapidly by HClAq or *aqua regia*; alkali solutions do not seem to react.

The at. w. of Th has been determined: (1) by analysing $Th(SO_4)_2$ and hydrates of this salt (Berzelius, *P.* 16, 398 [1829]; Chydenius, *P.* 119, 43 [1861]; Delafontaine, *Ar. Sc.* 18, 343 [1863]; Hermann, *J. pr.* 93, 114 [1864]; Cleve, *Bl.* [2] 21, 116 [1874]; Nilson, *B.* 15, 2527 [1882]; Krüss a. Nilson, *B.* 20, 1665 [1887]); (2) by analyses of the double Th-K sulphate (Berzelius, *l.c.*); (3) by analyses of the acetate, oxalate, and formate of Th (Chydenius, *l.c.*); (4) by determining S.H. of Th (Nilson, *B.* 16, 153 [1883]); (5) by finding V.D. of $ThCl_4$ (Krüss a. Nilson, *B.* 20, 1665 [1887]). The mol. w. of Th is not known.

Th is distinctly metallic in its chemical relations; the only oxide that has been isolated with certainty, ThO_2, is basic, forming salts ThX_2 ($X = SO_4$, $2NO_3$, &c.). There are indications of the existence of a higher oxide (? Th_2O_7). Thorium forms the last member of the even-series family of Group IV. in the periodic classification of the elements. The members of this family are C, Ti, Zr, Ce, —, Th. The four elements Ti, Zr, Ce, and Th closely resemble one another in their chemical properties; they are also similar to the odd-series family of Group IV., namely, Si, Ge, Sn, —, Pb. For a general account of Group IV. (and more especially of C and Si) *v.* CARBON GROUP OF ELEMENTS (vol. i. p. 682); for a description of the even-series family (Ti, Zr, Ce, Th) *v.* TITANIUM GROUP OF ELEMENTS (this vol. p. 749); and for the odd-series family (Ge, Sn, Pb; Si being described in vol. i. p. 652) *v.* TIN GROUP OF ELEMENTS (this vol. p. 735).

The atom of thorium is tetravalent in the gaseous molecule $ThCl_4$.

Reactions and Combinations (Nilson, *B.* 15, 2541).—1. Heated in *air*, oxidation begins at c. 120°, and at much below red heat the metal burns brilliantly to ThO_2.—2. Heated in a stream of *oxygen*, the metal burns to ThO_2, with the production of dazzling white light.—3. Th burns to ThX_4 when heated in *chlorine*, in *bromine* vapour, or in vapour of *iodine*.—4. When heated with *sulphur* part of the S volatilises, and when the temperature is above the b.p. of S combination occurs with production of much light, ThS_2 being formed.—5. According to Troost (*C. R.* 116, 1227). Th combines with *carbon*, when ThO_2 is mixed with C and heated in CO_2 in the electric arc (*v. Carbide, infra*).—6. *Water* does not react with Th at any temperature, so far as experiments have been tried. Nilson (*l.c.*) gives no details, but says 'Thorium is not changed by water under any conditions.'—7. *Sulphuric acid* reacts slowly with Th; when dilute, the acid evolves H; when conc. and hot, SO_2 is given off.—8. The action of *nitric acid* is slight; the dilute warm acid acts very gradually; conc. acid is almost without action.—9. *Hydrochloric acid* rapidly dissolves Th, forming $ThCl_4$, and giving off H; the action is most complete with conc. acid.—10. *Aqua regia* dissolves Th easily.—11. *Alkaline solutions* seem not to react with Th.

Detection and Estimation.—Salts of Th are colourless when the acid is colourless. Alkalis, and also $(NH_4)_2SAq$, ppt. gelatinous, white $ThO_2.2H_2O$, insoluble in excess of the precipitant; alkali carbonates form a white pp. soluble in excess; solution in $(NH_4)_2CO_3Aq$ becomes turbid at 60°, but goes clear on cooling; saturation of a solution of a salt of Th with K_2SO_4 forms white $Th(SO_4)_2.K_2SO_4.2H_2O$, insoluble in K_2SO_4Aq, but soluble in water; K_4FeCy_6Aq ppts. white $ThFeCy_6$; oxalic acid and alkali oxalates ppt. white amorphous $Th(C_2O_4)_2$, insoluble in dilute acids, soluble in solutions of alkali oxalates or $NH_4.C_2H_3O_2$, especially on warming.

Th is generally estimated by ppn. as $ThO_2.2H_2O$ or $Th(C_2O_4)_2$, and subsequent conversion into ThO_2 by heating.

Thorium, bromide of. The gummy, white mass obtained by Berzelius (*P.* 16, 385), by evaporating a solution of $ThO_2.2H_2O$ in HBrAq, was probably $ThBr_4$. The *hydrated salt* $ThBr_4.10aq$ seems to have been obtained, from $ThO_2.2aq$, by Jannasch, Locke, a. Lesinsky (*Zeit. f. anorg. Chemie*, 5, 283).

Thorium, carbide of. By heating an intimate mixture of ThO_2 and C in the electric arc, in an atmosphere of CO_2, Troost (*C. R.* 116, 1227) obtained a hard, brittle solid, containing from 8·2 to 9·5 p.c. C, and therefore approximating to the formula ThC_2 (which requires 9·38 p.c. C). S.G. 10·15 at 15°; scratches glass slightly; decomposes cold water, giving off H and strongly smelling hydrocarbons; gradually decomposes in moist air; burns rapidly and brilliantly when heated to redness.

Thorium, chloride of, $ThCl_4$. Mol. w. 373·5. V.D. 172·2 at 1050°–1270° (Krüss a. Nilson, *B.* 20, 1671). This compound is formed by heating a mixture of ThO_2 and C in a stream of dry Cl; the $ThCl_4$ sublimes in white needles. Krüss a. Nilson (*B.* 20, 1675) prepared pure $ThCl_4$ by heating Th to incipient redness in a stream of dry, air-free HCl; then raising the temperature to full redness, in order to sublime a little $FeCl_2$, formed from the iron in the thorium used; and finally subliming the $ThCl_4$ at an incipient white heat. (For details of the apparatus used *v.* Nilson a. Pettersson, *J. pr.* [2] 33, 1 [on preparation of $BeCl_2$]).

$ThCl_4$ crystallises in lustrous, white needles; moderately hygroscopic, but remains some hours in the air before deliquescing (K. a. N., *l.c.*). Does not volatilise at c. 420° (Chydenius, *P.* 119, 43). The V.D. found by K. a. N. at temperatures from 1050° to 1270° shows that the formula $ThCl_4$ is molecular. K. a. N. got the value 142 for V.D. at 1400°, showing that dissociation had begun. Troost (*C. R.* 101, 360) obtained values for V.D. of $ThCl_4$ at c. 950° considerably lower than those of K. a. N. It is likely that his specimen was not pure, or that the apparatus used contained traces of O sufficient to cause decomposition to ThO_2 and Cl (K. a. N., *l.c.*, p. 1674).

Hydrated thorium chloride $ThCl_4.8H_2O$ was obtained by Cleve in thin, white prisms, by concentrating a solution of $ThO_2.2H_2O$ in HClAq, allowing to crystallise, and drying over H_2SO_4 (*Bl.* [2] 21, 116).

Double salts.—$ThCl_4$ combines with *potassium chloride* to form $2ThCl_4$, $KCl.18H_2O$; obtained by mixing very conc. solutions of the constituents. Forms small, white crystals; v. sol. water, also sol. alcohol; dehydrated by heating in HCl (Cleve, *Bl.* [2] 21, 116). By heating a dry mixture of $ThCl_4$ and NH_4Cl in HCl, Chydenius (*Bl.* [2] 1, 130; 6, 433) obtained a compound with *ammonium chloride*, which, when crystallised from water *in vacuo*, had the composition $ThCl_4.8NH_4Cl.8H_2O$; loses $6H_2O$ at 100°. Cleve (*l.c.*) prepared a compound with *platinic chloride* $ThCl_4.PtCl_4.12H_2O$; and Nilson (*l.c.*) a compound with *platinous chloride* $2ThCl_4.3PtCl_2.24H_2O$.

Thorium, ferrocyanide of, $ThFeCy_6.4H_2O$. A white powder; prepared by adding K_4FeCy_6Aq to solution of a salt of Th (Cleve, *Bl.* [2] 21, 116).

Thorium, fluoride of, $ThF_4.4H_2O$. Obtained by adding HFAq to $ThCl_4Aq$; the gelatinous pp. becomes powdery after a time (Chydenius, *Bl.* [2] 1, 130; 6, 433). Loses H_2O at 100°, and $2H_2O$ at 140°–200°; heated to redness gives ThO_2 and HF. Berzelius (*P.* 16, 385) obtained a heavy white powder by heating $ThO_2.2H_2O$ with HFAq. Combines with *potassium fluoride*; Chydenius (*l.c.*) obtained two salts, (1) $ThF_4.KF$ by mixing $ThCl_4Aq$ with KHF_2Aq, (2) $ThF_4.2KF.4H_2O$ by boiling $ThO_2.2H_2O$ with conc. KHF_2Aq and HFAq. The isolation of a third salt, $7ThF_4.8KF.6H_2O$, is doubtful.

Thorium, hydride of. By heating ThO_2 with excess of Mg powder, in a stream of H, Winkler (*B.* 24, 885) obtained a grey powder, which gave off H with dilute HClAq, and burnt when heated in O. Analyses of this powder gave 72·86 p.c. Th, ·50 p.c. H, 17·57 p.c. Mg, and 9·07 p.c. O. Supposing the ThO_2, Mg, and H interacted in accordance with the equation $ThO_2 + 2Mg + 2H = ThH_2 + 2MgO$, then, from the quantities of ThO_2 and Mg used, the product would give on analysis 73·77 p.c. Th, ·63 p.c. H, 15·45 p.c. Mg, and 10·15 p.c. O. From these data Winkler concluded that a hydride, ThH_2, was formed in the reaction.

Thorium, hydroxides of, *v.* OXIDES AND HYDRATED OXIDES (*infra*).

Thorium, iodide of. The white gummy mass, crystallising after a time, obtained by Chydenius (*Bl.* [2] 1, 130; 6, 433) by evaporating a solution of $ThO_2.2H_2O$ in HIAq, was probably ThI_4. The substance goes brown in the light.

Thorium, nitride of. By heating ThO_2 or $ThCl_4$ in NH_3, also by heating $ThCl_4$ and NH_4Cl in HCl, Chydenius (*l.c.*) obtained a small quantity of what he supposed to be either a nitride of Th or a compound of the metal with N and H.

Thorium, oxides and hydrated oxides of. Besides the oxide ThO_2 a peroxide, probably Th_2O_7, is said to exist.

THORIUM DIOXIDE ThO_2. (*Thoria.*) Mol. w. not known. Obtained by ppg. a salt of Th by alkali, $(NH_4)_2SAq$, or KCNAq, drying, and strongly heating; also by decomposing $Th(C_2O_4)_2$ by heat. A fine, white powder. S.G. 10·22 at 17° (Nilson, *B.* 15, 2536). S.V.S. 25·87. S.H. (0° to 100°) ·0548 (N. a. Pettersson, *B.* 13, 1459). By heating ThO_2 with borax in a porcelain oven, Nordenskjöld obtained the oxide in microscopic crystals isomorphous with SnO_2 and ZrO_2 (*P.* 150, 219). ThO_2 has not been fused; it is not reduced by heating with C, but when mixed with C and heated in Cl the chloride $ThCl_4$ is obtained. ThO_2 does not react with molten alkalis. It is scarcely acted on by acids; warm conc. H_2SO_4, however, converts it into $Th(SO_4)_2$.

HYDRATES OF THORIUM DIOXIDE. The *dihydrate* $ThO_2.2H_2O$ (= ThO_4H_4, *thorium hydroxide*) is obtained by ppg. a solution of a salt of Th by an alkali, $(NH_4)_2SAq$, or KCNAq, washing, and drying at 100°. It forms a hard, white solid. $ThO_2.2H_2O$ combines with CO_2 in the air; it dissolves in acids, forming salts ThX_2, where X $= SO_4$, $2NO_3$, &c. Another hydrate, $4ThO_2.H_2O$ ($= Th_4O_7(OH)_2$, *thorium metahydroxide*) is obtained, according to Cleve (*Bl.* [2] 21, 116), by heating ThO_2 (obtained by decomposition of $Th(C_2O_4)_2$) with excess of HNO_3Aq or HClAq at 100° till the acid is driven off, adding water, and then ppg. the opalescent solution so obtained by NH_3Aq, washing, and drying at 100°. This hydrate is said to be insoluble in dilute acids.

THORIUM PEROXIDE Th_2O_7. An oxide with this composition is said to be produced by adding H_2O_2Aq and NH_3Aq to a solution of a salt of Th (Cleve, *Bl.* [2] 43, 53; Lecoq de Boisbaudran, *C. R.* 100, 605).

Thorium, oxysulphide of. By strongly heating ThO_2, obtained from $ThO_2.2H_2O$, in CS_2 vapour, Chydenius (*Bl.* [2] 1, 130; 6, 433) obtained a solid substance to which he gave the formula $2ThO_2.ThS_2 = Th_3O_4S_2$. According to Krüss a. Volk (*Zeit. f. anorg. Chemie*, 5, 75; 6, 49), the compound obtained by heating ThO_2 in CS_2 is ThOS, and the same compound is formed by heating $2ThCl_4.KCl$ in H_2S.

Thorium, phosphide of. By heating Th in vapour of P, Berzelius (*P.* 16, 385) obtained a dark grey, metal-like, lustrous solid, which was changed to Th phosphate by heating in air.

Thorium, platinocyanide of, $Th(PtCy_4)_2.16H_2O$. Yellow-green, orthorhombic prisms (Cleve, *Bl.* [2] 21, 116).

Thorium, salts of. All the normal compounds which have been isolated by replacing H of acids by Th belong to the class ThX_2, where $X = 2NO_3$, $2IO_3$, SO_4, SO_3, $\frac{2}{3}PO_4$, &c.; basic salts also exist. The chief salts of oxyacids are *borate*, *carbonate*, *chlorate*, *chromate*, *iodate* and *periodate*, *molybdate*, *nitrate*, *oxalate*, *phosphates*, *selenate* and *selenites*, *silicates*, *sulphate* and *sulphite*, and *tartrate*.

Thorium, silicofluoride of. By treating $ThO_2.2H_2O$ with H_2SiF_6Aq, Cleve (*Bl.* [2] 21, 116) obtained a semi-transparent, crystalline solid, probably $Th(SiF_6)_2$; insol. in excess of H_2SiF_6; over H_2SO_4 gave off HF and SiF_4.

Thorium, sulphide of, ThS_2. Obtained by heating Th with S; excess of S sublimes, and when the temperature passes the b.p. of S the elements combine with evolution of heat and light (Nilson, *B.* 15, 2542; *cf.* Berzelius, *P.* 16, 385). Also formed by heating ThO_2, obtained from $Th(C_2O_4)_2$, to white heat in vapour of CS_2 (Chydenius, *Bl.* [2] 1, 130; 6, 433); but, according to Krüss a. Volk (*l.c.*), the compound thus formed is ThOS. A black powder. Burns when heated in air, giving off SO_2 and leaving

ThO_2. Not acted on by HClAq or HNO_3Aq; *aqua regia* dissolves the compound, forming $Th(SO_4)_2$. Molten KOH forms K_2S and ThO_2; heating in Cl produces $ThCl_4$.

Thorium, sulphocyanide of. The salt [? $Th(SCy)_4$] is obtained, as a viscid mass, by evaporating a solution of $ThO_2.2H_2O$ in HSCNAq. A solution of the compound gives a pp. with $HgCy_2$, said to be $Th(OH)_2SCy.HgCy_2.H_2O$; and the filtrate is said to give crystals of $Th(OH)(SCy)_3.3HgCy_2.12H_2O$ (Cleve, *Bl.* [2] 21, 116). M. M. P. M.

THUJIGENIN $C_{14}H_{12}O_7$ or $C_{28}H_{24}O_{14}$. Occurs in small quantity in *Frondes Thujæ*, the green parts of *Thuja occidentalis* (Rochleder a. Kawalier, *Sits. W.* 29, 10). Minute needles, v. sl. sol. water, sol. alcohol. NH_3 colours its alcoholic solution green. AcCl forms resinous $C_{14}H_{11}AcO_7$.

THUJIN $C_{20}H_{22}O_{12}$. Occurs in the green branches of *Thuja occidentalis* (Rochleder a. Kawalier, *Sits. W.* 29, 10). Minute lemon-yellow four-sided tables, sol. alcohol. Tastes bitter. Its alcoholic solution is coloured yellow by alkalis, is turned reddish-brown by air, gives a yellow pp. with lead acetate, and gives a dark-green colour with $FeCl_3$. Reduces ammoniacal $AgNO_3$. Boiling dilute H_2SO_4 turns it first green, then yellow, and splits it up into sugar and thujetin. Boiling baryta-water hydrolyses it in like manner.

Thujetin $C_{28}H_{28}O_{16}$. Yellow solid, nearly insol. water, sol. alcohol and ether. Not altered by dilute HCl or H_2SO_4. Its alcoholic solution is turned a splendid bluish-green colour by NH_3Aq. Gives, in alcoholic solution, a red pp. with lead acetate, and a black colour with $FeCl_3$. Boiling baryta-water converts it into thujetic acid $C_{28}H_{22}O_{13}$, which crystallises in minute lemon-yellow needles, sol. alcohol and ppd. by water.

(β)-THUJOL is Tanacetone.

THUJONE $C_{10}H_{16}O$. (212°). S.G. ^{22} ·9265. Occurs, together with the terpene $C_{10}H_{16}$ and lævorotatory fenchone, in the essential oil of thuja obtained by distilling the ends of the branches and the leaves of *Thuja occidentalis* with water (Schweizer, *A.* 51, 398; Jahns, *Ar. Ph.* 221, 748; Wallach, *A.* 272, 109). Yields an oxim.

Reactions.—1. When heated with *ammonium formate* it yields a formyl derivative which on saponification gives rise to 'thujoneamine' $C_{10}H_{17}.NH_2$ (199°), which forms the salts $B'_2H_2PtCl_6$ and B'HCl. Thujone-amine hydrochloride decomposes on distillation into NH_4Cl and thujene $C_{10}H_{16}$ (c. 173°), S.G. ^{20} ·84.—2. $KMnO_4$ forms two 'thujaketonic acids.'—3. Br forms $C_{10}H_{13}Br_3O$ [122°] (Wallach, *A.* 275, 179).

(α)-Thujaketonic acid $C_{10}H_{16}O_3$ *i.e.* $CH_3.CO.C_7H_{12}.CO_2H$. [76°]. S. c. 2·5 at 100°. Transparent plates. Yields an oxim [c. 186°].

(β)-Thujaketonic acid $C_7H_{12}(CO.CH_3).CO_2H$. [79°]. S. 1·43 at 100°. Small matted needles. On distillation it yields methyl heptyl ketone (186°) S.G. ^{20} ·854, which gives ψ-cumene dihydride C_9H_{14} on heating with $ZnCl_2$ at 100° (Wallach, *A.* 275, 166). Forms an oxim [106°] which crystallises in needles.—AgA': v. sl. sol. cold water.

THULIUM. This name was given by Cleve in 1879 to the metal of a new earth which he announced to be present in specimens of *gadolinite* (*C. R.* 89, 478). The name thulium was derived from *Thule*, the old name for Scandinavia. The presence of the new earth was more or less confirmed by the work of Nilson (*B.* 13, 1433), and of Soret (*C. R.* 89, 251). In 1880 Cleve said he had isolated *thulia*, and described it as a white earth, giving an emission spectrum characterised by two bright lines 5896 and 5306, and forming solutions of salts which showed two absorption bands 6840 and 4645. To this earth Cleve assigned the formula Tm_2O_3, and he determined the maximum value of the atomic weight of the supposed element to be Tm = 170·7. In 1888 Krüss a. Nilson declared that thulium consists of two distinct elements (*B.* 21, 1681).

The absolute homogeneity of thulia has been by no means established (*v.* Metals, rare, vol. iii. p. 245). M. M. P. M.

THYME OIL. The essential oil from garden thyme, *Thymus vulgaris*, contains lævorotatory thymene $C_{10}H_{16}$ (160°–165°), thymol $C_{10}H_{14}O$ and a little cymene (Lallemand, *A.* 102, 119; *A. Ch.* [3] 49, 155). The oil from wild thyme, *Thymus serpyllum*, contains cymene, thymol, carvacrol, and a phenol coloured violet by $FeCl_3$ (Jahns, *Ar. Ph.* [3] 16, 277; Febre, *C. R.* 92, 1290; Buri, *Ar. Ph.* [3] 12, 485).

THYMO-ACRYLIC ACID *v.* Oxy-cymyl-acrylic acid.

THYMOHYDROQUINONE *v.* Hydrothymoquinone.

THYMOL $C_{10}H_{14}O$ *i.e.* $C_6H_3MePr.OH$ [5:2:1]. Mol. w. 150. V.D. 75·3 (calc. 75) (Eykman, *B.* 22, 2757). [49·5°] (Reissert, *B.* 23, 2242). (232°). S.G. $\frac{0}{0}$ ·9941. C.E. (0°–10°) ·00085. S. ·3. S.V. 188·9 (Pinette, *A.* 243, 46); 189·3 (Ramsay). $R_\infty = 76·56$ (Nasini a. Bernheimer, *G.* 15, 93). H.F.p. (liquid) 69,250; (solid) −3768. Occurs in essential oil of thyme (Doveri, *A.* 64, 374; Lallemand, *A. Ch.* [3] 49, 148; *A.* 102, 119), of horsemint, *Monarda punctata* (Arppe, *A.* 58, 42), of *Ptychotis ajowan* (Stenhouse a. Haines, *A.* 98, 307; H. Müller, *B.* 2, 130) of *Monarda Didyma*, of *Ammi Copticum* (Buri, *Ar. Ph.* [3] 12, 485), and in the oil from wild thyme (Jahns, *B.* 15, 819).

Formation.—By boiling diazo-*n*-cymene with water (Widman, *B.* 15, 170; 19, 245).

Preparation.—By extracting oil of thyme with NaOHAq, ppg. by HCl, and recrystallising from HOAc.

Properties.—Plates (from alcohol), v. sol. alcohol, ether, and HOAc, v. sl. sol. water. Has a slight odour of thyme and a peppery taste. When solid it is slightly heavier than water, when liquid it is lighter. Not ppd. by adding water to its alcoholic solution. Not dissolved by NH_3Aq, but absorbs NH_3, becoming liquid, but re-solidifying after the NH_3 has escaped. Sol. KOHAq. $FeCl_3$ does not colour its aqueous solution. Bromine-water only gives a milkiness. An aqueous solution (1 vol.) warmed first with HOAc (½ vol.) and then with H_2SO_4 (1 vol.) is coloured reddish-violet, the solution showing two absorption bands at E and D (Wolff, *Fr.* 22, 96). KOHAq followed by I in KI gives on warming a fugitive red tint (Itallie, *Fr.* 29, 205).

Estimation: Messinger, *B.* 23, 2754.

Reactions.—1. Decomposed by distilling with P_2O_5 into propylene and *m*-cresol.—2. P_2S_5 yields cymene (Fittica, *B.* 6, 938; *A.* 172, 305). 3. Oxidised by *chromic acid* to thymoquinone.—4. PCl_5 yields chloro-cymene. — 5. *Potash-fusion* yields several oxy-acids (Barth, *B.* 11, 567, 1571).—6. *Iodine* and *potash* yield a red amorphous pp. [110°] converted by heat or by boiling water into a yellow body [165°] (Messinger a. Vortmann, *B.* 22, 2316).—7. Boiling $POCl_3$ (1 mol.) acting on thymol (1 mol.) forms liquid $C_{10}H_{13}O.POCl_2$ (280°-285°) which is converted by water into liquid $C_{10}H_{13}O.PO(OH)_2$, which yields BaA'' 4aq and is decomposed by heat into thymol and HPO_3 (Discalzo, *G.* 15, 279).—8. Boiling $POCl_3$ acting on thymol (2 mols.) forms $(C_{10}H_{13}O)_2POCl$ (330°-340° at 320 mm.), a liquid which is converted by water into $(C_{10}H_{13}O)_2PO.OH$, which is insol. water and yields NaA' [74°] (Kreysler, *B.* 18, 1705) and BaA'_2 5aq. S. ·197 at 21°.—9. PCl_5 (1 mol.) acting on thymol (4 mols.) forms $(C_{10}H_{13}O)_3PO$ [59°] crystallising from alcohol in prisms (E. a. L.).—10. $SiCl_4$ forms $Si(OC_{10}H_{13})_4$ [48°] (450°) crystallising from $CHCl_3$ in prisms (Hertkorn, *B.* 18, 1693).—11. $Cl.CO.NH_2$ reacts forming $C_6H_3MePr.O.CO.NH.CO.NH_2$ [190°] (Gattermann, *A.* 244, 44).—12. $C_6H_4(NMe_2)(NH_2)$ [1:4] forms indothymol $C_6H_4(NMe_2).N{<}\genfrac{}{}{0pt}{}{C_6H_2MePr}{O}$ [69·5°] crystallising in needles, insol. water and alkalis, forming a blue solution in alcohol, a violet in ether, and a green in HOAc. HClAq decomposes indothymol into thymoquinone, dimethyl-aniline, and NH_3 (Bayrac, *Bl.* [3] 7, 97). 13. *Chloral* forms $C_{10}H_{11}OC_2HCl_3O$ [130°-134°] (Mazzara, *G.* 13, 272).—14. *Chloral*, conc. H_2SO_4, and HOAc yield $CCl_3.CH(C_{10}H_{12}.OH)_2$ (Jäger, *B.* 7, 1197).—15. Dilute H_2SO_4 gradually added to a mixture of benzoic aldehyde (1 mol.) and thymol (2 mols.) forms $C_6H_5.CH(C_{10}H_{12}.OH)_2$ [146°] which is sol. alkalis and yields a diacetyl derivative [126°] (Russanoff, *B.* 22, 1943).—16. $COCl_2$ passed into an aqueous solution of $C_{10}H_{13}ONa$ forms di-thymyl carbonate $(C_{10}H_{13}O)_2CO$ which crystallises from alcohol in needles [48°] (above 360°) and yields *o*-oxybenzoic acid when heated with NaOPh at 180° (Richter, *J. pr.* [2] 27, 505). According to Bender (*B.* 19, 2268), di-thymyl carbonate, prepared by heating thymyl ethyl carbonate at 300°, melts at 60°. $COCl_2$ also forms, as a by-product, $C_{10}H_{13}O.COCl$, which is converted by ammonia into $C_{10}H_{13}O.CO.NH_2$ [131°].—17. $Cl.CO_2Et$ acting in the cold upon $C_{10}H_{13}ONa$ forms $C_{10}H_{13}O.CO.OEt$ (c. 261°), an oil which yields *o*-oxy-benzoic acid, PhOEt, and thymol when heated with NaOPh (Richter).—18. Treatment with $ClCH_2.CO_2H$ and NaOHAq produces $C_{10}H_{13}O.CH_2.CO_2H$ [148°] which yields BaA'_2 2aq, PbA'_2, AgA', oily EtA' (290°), and an amide [97°] (Saarbach, *J. pr.* [2] 21, 159; Spica, *G.* 10, 342). 19. *a-Chloropropionic acid* and KOHAq yield $C_{10}H_{13}O.CHMe.CO_2H$ [48°] (Scichilone, *G.* 12, 50).—20. Thymol (10 g.) mixed with H_2SO_4 (70 g.) containing nitrous acid gives thymolchroïn $C_{40}H_{52}N_2O_5$, a dark-violet amorphous body which dissolves in alcohol, ether, $CHCl_3$, and benzene, forming red solutions with pale-green fluorescence. Alkalis turn its alcoholic solutions blue. Sublimes at 140°, giving off violet vapours. Yields brown amorphous $C_{40}H_{48}Ac_4N_2O_5$ (Brunner a. Chuit, *B.* 21, 252; *cf.* Liebermann, *B.* 7, 1100).—21. By heating with ammonium-zinc chloride it is converted into thymylamine $C_{10}H_{13}NH_2$ and di-thymylamine $(C_{10}H_{13})_2NH$.—22. *Cyanuric chloride* converts sodium thymol into $(C_{10}H_{13})_3C_3N_3O_3$ [151°] a yellow crystalline powder, insol. water, sl. sol. alcohol (Otto, *B.* 20, 2239).—23. Aqueous KOH and $K_2S_2O_7$ form $C_{10}H_{13}O.SO_2.OK$, which crystallises from alcohol in slender silky threads (Heymann a. Königs, *B.* 19, 3307). It is oxidised by alkaline $KMnO_4$ to oxycuminic acid $C_6H_3Pr(OH).CO_2H$ [4:3:1].

S a l t s. — $C_{10}H_{13}ONa$. Crystalline. Its aqueous solution is ppd. by $HgCl_2$ and $AgNO_3$.—$C_{10}H_{13}O.Hg.HgNO_3$.—$C_{10}H_{13}O.Hg.HgOAc$ (Merck, *G. P.* 48539; *Pharm. Zeit.* 1889, 625).—$(C_{10}H_{13}O)_2Hg_2O$ (Lallemand).—$(C_{10}H_{13}O)_3Al$. Decomposed by heat into propylene and $(C_6H_4Me.O)_3Al$, the *m*-cresylate then splitting up into alumina, *m*-cresol, di-*m*-tolyl oxide, and a body $C_{15}H_{14}O$ [200°] S. (alcohol) ·17 at 20°; 1 at 78°; S. (benzene) ·93 at 21°; S.G. 805; V.D. 208·8, crystallising in pearly plates (Gladstone a. Tribe, *C. J.* 39, 9; 41, 11).

Acetyl derivative $C_{10}H_{13}OAc$. (245°). S.G. $\frac{0}{0}$ 1·009.

Benzoyl derivative $C_{10}H_{13}OBz$. [32°]. H.F. 90,480 (Stohmann, *J. pr.* [2] 36, 9).

Methyl ether $C_{10}H_{13}OMe$. (216° cor.). S.G. $\frac{0}{0}$ ·9531. C.E. (0°-10°) ·00083. S.V. 214·3 (Pinette, *A.* 243, 47). H.F.p. 61,429 [C,O_2 = 94,000; H_2,O = 69,000] (Stohmann, *J. pr.* [2] 35, 26). Formed from thymol, KOH, and MeI (Engelhardt a. Latschinoff, *Z.* [2] 5, 43).

Ethyl ether $C_{10}H_{13}OEt$. (227°) (Pinette; *cf.* Jungfleisch, *Bl.* [2] 4, 17). S.G. $\frac{0}{0}$ ·9334. C.E. (0°-10°) ·00089. S.V. 240. H.F.p. 68,858 (Stohmann). Yields the ethyl derivative of oxyterephthalic acid on oxidation (Paterno a. Canzoneri, *G.* 9, 460). Decomposes at 360°-400° into thymol and ethylene (Bamberger, *B.* 19, 1820).

Propyl ether $C_{10}H_{13}OPr$. (243°). S.G. $\frac{0}{0}$ ·9276. C.E. (0°-10°) ·00088. S.V. 265·5.

Butyl ether $C_{10}H_{13}OC_4H_9$. (258°). S.G. $\frac{0}{0}$ ·9230. C.E. (0°-10°) ·00085. S.V. 289·2.

Isoamyl ether $C_{10}H_{13}OC_5H_{11}$. (238°-243°) (E. a. L.). Oil.

Heptyl ether $C_{10}H_{13}OC_7H_{15}$. (307°). S.G. $\frac{0}{0}$ ·9097. C.E. (0°-10°) ·00082. S.V. 368·7.

Octyl ether $C_{10}H_{13}OC_8H_{17}$. (320°). S.G. $\frac{0}{0}$ ·9026. C.E. (0°-10°) ·00075. S.V. 395·6 (Pinette).

Ethylene ether $(C_{10}H_{13}O)_2C_2H_4$. [99°]. Plates (from ether) (Paterno, *G.* 5, 13).

Nitroso-thymol *v.* *Oxim* of Thymoquinone.

Dithymol *v.* Di-oxy-dicymyl.

References.—*Amido-*, Bromo-amido-, Bromo-nitro-, Tri-chloro-, Iodo-, Iodo-amido-, and Nitro-thymol.

DI-THYMOL-ETHANE *v.* Di-oxy-di-cymyl-ethane.

THYMOL DICARBOXYLIC ALDEHYDE $C_{12}H_{14}O_3$ *i.e.* $C_6HMePr(OH)(CHO)_2$. [80°]. Formed as a by-product in the preparation of thymotic acid by the action of chloroform and NaOH on thymol (Kobek, *B.* 16, 2104). Needles. Gives a red colour with $FeCl_3$.

THYMOL (α)-SULPHONIC ACID $C_6H_2MePr(OH).SO_3H$. [92°] (Stebbins, *Am.* 3, 111). Formed from thymol by the action of

H_2SO_4 or $Cl.SO_2.OH$ at 50° (Engelhardt a. Latschinoff, *Z.* 1869, 44; 1871, 261). Pearly plates (containing aq), v. e. sol. water. $FeCl_3$ colours neutral solutions dark-violet. Yields thymoquinone on oxidation.

Salts.—KA' 2½aq. Efflorescent tables, v. e. sol. water.—NaA' 2½aq. [167°].—NH_4A' 2aq. [172°].—CaA'_2 2aq. [157°].—BaA'_2 4aq. Prisms, decomposing at 100°.—PbA'_2 4aq.

Benzoyl derivative $C_{10}H_{12}(OBz).SO_3H$. —KA' 2aq.—CaA'_2 4aq.—BaA'_2 5aq.—PbA'_2 5aq.

Ethyl derivative $C_{10}H_{12}(OEt)SO_3H$. Formed from the K salt, KOH, and EtI.—KA'. Thin plates.—BaA'_2 3aq. Plates, sl. sol. hot Aq.

Isoamyl derivative $C_{10}H_{12}(OC_5H_{11}).SO_3H$. —KA'. Needles, v. sol. water.—BaA'_2 3aq.

Thymol (β)-sulphonic acid $C_{10}H_{12}(OH).SO_3H$. Formed in small quantity by the action of H_2SO_4 on thymol.—KA'aq. Plates, sl. sol. cold water. Coloured violet-blue by $FeCl_3$.

Thymol (γ)-sulphonic acid $C_{10}H_{12}(OH).SO_3H$. Formed by heating thymol with fuming H_2SO_4 at 100° (E. a. L.).—KA'aq. Granular, v. sol. water.—$BaA'_2$3aq. Tufts of needles, more soluble than the (α)-isomeride. Not decomposed at 120°.

Benzoyl derivative $C_{10}H_{12}(OBz).SO_3H$.—KA' 3aq. Flat needles, sl. sol. cold water.

Ethyl derivative $C_{10}H_{12}(OEt).SO_3H$.—KA'. Flat needles.—BaA'_2 3aq. Six-sided tables.

Thymol-sulphonic acid

Ethyl derivative $C_6H_2MePr(OEt)SO_3H$ [1:4:3:6]. Formed by boiling diazo-cymene-sulphonic acid with absolute alcohol.—BaA'_2 3aq: white plates, sol. hot water, sl. sol. cold (Widman, *B.* 19, 247).

Thymol sulphonic acid. *Methyl derivative* $C_{10}H_{12}(OMe).SO_3H$. Formed, together with an isomeride, by sulphonation of the methyl ether of thymol (E. a. L.; Paterno a. Pisati, *B.* 8, 440).—KA': large tables.—$BaA'_2$3aq. Nodules, v. sol. hot water. S. 3·94 at 26°.

Thymol disulphonic acid $C_{10}H_{11}(OH)(SO_3H)_2$. Formed by sulphonating thymol.—K_2A'' 1½aq. Efflorescent needles (from alcohol), v. e. sol. water.

References. — AMIDO-, BROMO-, and IODO-THYMOL SULPHONIC ACID.

THYMOQUINONE $C_{10}H_{12}O_2$ *i.e.* $C_6H_2MePrO_2$ [2:5:4:1]. Mol. w. 164. [45·5°]. (232°). Formed by oxidation of thymol (Lallemand, *J.* 1854, 592), of the methyl ether of thymol (Paterno, *B.* 8, 440), of cymenol (Carstanjen, *J. pr.* [2] 3, 53; 15, 410), of di-oxy-di-cymyl-ethane (Steiner, *B.* 11, 289), of carvacrol *p*-sulphonic acid (Claus, *J. pr.* [2] 39, 356), and of amido-thymol (Andersen, *J. pr.* [2] 23, 172; Armstrong, *B.* 10, 297; Liebermann a. Ilinski, *B.* 18, 3194). Yellow crystals, with pungent odour, v. sl. sol. water, v. sol. alcohol and ether. Reduced by SO_2 to hydrothymoquinone. K_2SO_3 at 60° forms crystalline $C_{10}H_{13}O_5SK$. Phenyl cyanate forms $C_{10}H_{12}O:NO.CO.NHPh$ [132°], crystallising in large yellow needles (Goldschmidt a. Strauss, *B.* 22, 3106).

Oxim $C_6H_2MePrO(NOH)$ or $C_6H_2MePr(OH)(NO)$. *Nitroso-thymol.* [162°]. Formed by the action of nitrous acid on thymol (R. Schiff, *B.* 8, 1500; Widmann, *B.* 15, 170; Liebermann, *B.* 18, 3194). Formed also by the action of hydroxylamine hydrochloride on thymoquinone (Goldschmidt a. Schmid, *B.* 17, 2061). Slender monoclinic needles, *a:b:c* = 1·987:1:1·8941; β = 94° 57′ (Panebianco, *G.* 10, 78); sl. sol. hot water. Its alkaline solution is red. Oxidised by alkaline K_3FeCy_6 to nitro-thymol. Reduced by tin and HCl to amido-thymol (Liebermann, *B.* 10, 77). Does not react with SO_2 (Schmidt, *J. pr.* [2] 44, 521). Fuming HCl forms di-chloro-thymoquinone and chloro-amido-thymol (Sutkowski, *B.* 19, 2315). KOH and BzCl form $C_{10}H_{12}O(NOBz)$ [110°]. Hydroxylamine (3 mols.) in strongly alkaline solution forms, in 48 hours, a white substance which, if ppd. by HOAc, immediately dissolved in dilute NaOH, treated with an equal weight of a phenol, and exposed to the air, gives a deep-blue colour or pp. turned red by acids (Kehrmann a. Messinger, *B.* 23, 2818, 3557).

Di-oxim $C_{10}H_{14}N_2O_2$ *i.e.* $C_{10}H_{12}(NOH)_2$. Formed by boiling an alcoholic solution of nitroso-thymol (1 mol.) with hydroxylamine hydrochloride (2 mols.) and partially neutralising with alkali from time to time. Yellowish-white granules, decomposing at 235° without melting. Insol. water and NH_3Aq, sol. KOHAq.

Chlorimide $C_6H_2MePr<\genfrac{}{}{0pt}{}{O}{NCl}$. Formed by adding a solution of bleaching powder to a cold acidified solution of the hydrochloride of *p*-amido-thymol (Andresen, *J. pr.* [2] 23, 169). Pungent oil, volatilising even at 15°. Decomposes at 160°–170°. Volatile with steam. Decomposed by conc. HClAq into chloro-amido-thymol and mono- and di- chloro-thymoquinone. Conc. HBrAq behaves in a precisely similar way. Alcohol at 140° converts the chlorimide into thymoquinone. Conc. aqueous SO_2 reduces it in a few days to hydro-thymoquinone. Reduced by tin and HCl to *p*-amido-thymol, considerable quantities of hydrothymoquinone being formed at the same time.

Polymeride [201°]. Formed by the action of daylight on thymoquinone (Armstrong, *B.* 10, 297; Liebermann, *B.* 10, 2177; 18, 3193). Silky yellow needles (from alcohol), insol. ether. Changes to thymoquinone on distillation. Not attacked by SO_2 at 180°, but reduced by HI and P, or in alcoholic solution, by Zn and HClAq to hydrothymoquinone.

Phenyl hydrazide [249°]. Insol. benzene.

Oxim $(C_{10}H_{13}NO_2)_x$. [263°]. Crystalline, insol. water. Reduced by tin and HCl to amido-hydrothymoquinone.

Dioxim $(C_{10}H_{14}N_2O_2)_x$. [c. 290°]. Powder. May be reduced to di-amido-cymene.

References.—DI-AMIDO-, BROMO-, CHLORO-, IODO-, and OXY- THYMOQUINONE.

***o*-THYMOTIC ACID** $C_{11}H_{14}O_3$ *i.e.* $C_6H_2Me(C_3H_7)(OH).CO_2H$[6:3:2:1]. Mol. w. 194. [123°]. Formed by the action of CO_2 upon heated sodium-thymol (Kolbe a. Lautemann, *A.* 115, 205; Kobek, *B.* 16, 2101). Silky crystals, v. sol. alcohol, ether, and benzene, almost insol. cold water. Volatile with steam. Gives a deep-blue colour with $FeCl_3$. Yields thymol when distilled with baryta. PCl_5 acting on the Na salt forms thymotide $C_{11}H_{12}O_2$ [187°], which is reconverted into thymotic acid by potash fusion (Naquet, *Bl.* 4, 92).

***p*-Thymotic acid** $C_{11}H_{14}O_3$ *i.e.* $C_6H_2Me(C_3H_7)(OH).CO_2H$[6:3:4:1]. [157°]

Formed by heating thymol with aqueous NaOH and CCl_4 (Kobek). White plates, v. sol. alcohol, ether, and benzene, insol. cold water. Not coloured by $FeCl_3$.

Methyl derivative $C_6H_2Me(C_3H_7)(OMe).CO_2H$. [137°]. Silky needles (from dilute alcohol).—AgA′: pp.

p-**THYMOTIC ALCOHOL** $C_{11}H_{16}O_2$ *i.e.* $C_6H_2Me(C_3H_7)(OH).CH_2OH$. [120°–130°]. Formed by reducing thymotic aldehyde with sodium-amalgam (Kobek, *B.* 16, 2098). Amorphous powder, v. sol. alcohol and ether, insol. water.

p-**THYMOTIC ALDEHYDE** $C_{11}H_{14}O_2$ *i.e.* $C_6H_2Me(C_3H_7)(OH)CHO$[6:3:4:1]. [133°]. Formed, together with $C_6HMe(C_3H_7)(OH)(CHO)_2$ [6:3:4:5:1] [80°], by heating thymol with chloroform and NaOHAq (Kobek, *B.* 16, 2096). Silky needles, v. sol. alcohol, sl. sol. hot water. On heating with aniline it yields the compound $C_6H_2Me(C_3H_7)(OH).CH{:}NPh$ [142°] crystallising in yellow needles.

Methyl derivative $C_6H_2Me(C_3H_7)(OMe).CHO$. (278°). Formed by methylation of the aldehyde. Oil, yielding an anilide $C_6H_2Me(C_3H_7)(OMe).CH{:}NPh$ [80°] crystallising in transparent tables.

THYMYLAMINE $C_{10}H_{13}NH_2$. (230°). Formed, together with di-thymylamine, by heating thymol with ammoniacal $ZnBr_2$ or $ZnCl_2$ and NH_4Br or NH_4Cl at 350°-360°, the yield being 25 p.c. (Lloyd, *B.* 20, 1260). Colourless oil.—$B'_2H_2PtCl_6$: yellow needles.

Acetyl derivative $C_{10}H_{13}NAc$. [112°].

Isomeride *v.* CARVACRYLAMINE.

Di-thymyl-amine $(C_{10}H_{13})_2NH$. (340°–345°). Formed as above, the yield being 25 p.c. Oil. Its solution in P_2SO_4 is coloured blue by nitrites or nitrates.—$B'_2H_2PtCl_6$.

Acetyl derivative $(C_{10}H_{13})_2NAc$. [78°].

THYMYL CYANURIC ACID *v.* CYANIC ACID.

THYMYL MERCAPTAN $C_{10}H_{13}SH$. *Thiothymol.* (231°). S.G. ·989. Formed by heating thymol with P_2S_5 (Fittica, *A.* 172, 325; Bechler, *J. pr.* [2] 8, 167). Liquid with pungent odour. Oxidised by HNO_3 to sulpho-toluic acid. —$Hg(SC_{10}H_{13})_2$. Greenish rhombohedra [78°]. —PbA'_2: golden needles (from alcohol).

THYMYL PHOSPHATE $(C_{10}H_{13})_3PO_4$. [59°]. Formed by heating thymol with $POCl_3$, the yield being 75 p.c. of the theoretical amount (Kreysler, *B.* 18, 1705). Colourless needles.

THYMYL SILICATE $(C_{10}H_{13})_4SiO_4$. [48°]. (c. 450°). Formed by heating thymol with $SiCl_4$, the yield being 70 p.c. of the theoretical amount (Hertkorn, *B.* 18, 1692).

TIGLIC ACID $C_5H_8O_2$ *i.e.* $CH_3.CH{:}CMe.CO_2H$. *Methyl-crotonic acid.* Mol. w. 100. [65°]. (199° i.V.) (Kopp, *A.* 195, 84). Occurs as a glyceryl ether in croton oil (Geuther a. Fröhlich, *Z.* 1870, 549; Schmidt a. Berendes, *A.* 191, 94; *B.* 10, 835; *Ar. Ph.* [3] 13, 213), and as isoamyl ether in Roman oil of chamomile (Köbig, *A.* 195, 101).

Formation.—1. By the action of heat or of conc. H_2SO_4 on angelic acid (Demarçay, *B.* 9, 1933).—2. By reducing the dibromide of angelic acid with sodium-amalgam (Schmidt, *A.* 208, 253).—3. From $CEtMe(OH).CO_2Et$ (derived from oxalic ether, EtI, MeI, and Zn) by treatment with PCl_5 and saponification of the product (Frankland a. Duppa, *A.* 136, 9).—4. By distilling $CH_3.CH(OH).CHMe.CO_2H$ (Rohrbeck, *A.* 188, 235), or by heating it with HIAq (Rücker, *A.* 201, 61).—5. By reducing methyl-acetoacetic ether with sodium-amalgam and heating the resulting $CH_3.CH(OH).CHMe.CO_2H$ at 200° (Wislicenus, *A.* 250, 243).—6. By heating veratrine with alcoholic potash (Wright a. Luff, *C. J.* 33, 347).—7. By heating veratrine with conc. HClAq (Ahrens, *B.* 23, 2704).

Properties.—Triclinic plates, v. sol. hot water, alcohol, and ether. Smells like benzoic acid. Volatile with steam. Not attacked by sodium-amalgam. Forms with isovaleric acid the double salts $CaA'(C_5H_9O_2)\,4\frac{1}{2}aq$ and $AgA'C_5H_{10}O_2$.

Reactions.—1. Yields acetic aldehyde and acid on oxidation with $KMnO_4$ (Beilstein a. Wiegand, *B.* 17, 2261; Kondakoff, *J. R.* 20, 523).—2. *Potash-fusion* gives propionic and acetic acids.—3. Fuming HI forms an iodovaleric acid [87°] (Schmidt, *B.* 12, 252).—4. HI and P yield $CEtMeH.CO_2H$.—5. *Bromine* forms $C_5H_8Br_2O_2$ [88°] (Pückert, *A.* 250, 240; Wislicenus, *A.* 272, 21; 274, 99).—6. HOCl forms a mixture of $CH_3.CH(OH).CClMe.CO_2H$ [112°] and $CH_3.CHCl.CMe(OH).CO_2H$ [75°] (Melikoff, *Bl.* [2] 47, 166).

Salts.—KA′.—CaA'_2 3aq. S. (of CaA'_2) 6·4 at 17°.—BaA'_2 4aq. S. (of BaA'_2) 18·5 at 16°.—AgA′.

Ethyl ether EtA′. (155°). S.G. ^{9} ·942.

Isoamyl ether $C_5H_{11}A'$. (205°).

Reference.—*Chloro-tiglic acid.*

TIGLIC ALDEHYDE C_5H_8O. *Guaiol.* (118°). V.D. 2·92. Formed by distillation of gum guaiacum (Deville, *C. R.* 17, 1143; 19, 134; Völckel, *A.* 89, 346; Herzig, *M.* 3, 118). Formed also by heating acetic aldehyde (1 mol.) with propionic aldehyde (1 mol.) and aqueous (28 p.c.) NaOAc for 30 hours at 100° (Lieben a. Zeisel, *M.* 7, 53). Pungent oil, miscible with alcohol and ether. Oxidised by air to tiglic acid. Alkaline sodium nitroprusside gives a violet-red colour destroyed by HOAc (Von Bitto, *A.* 267, 376). Br forms di-bromo-valeric aldehyde. Iron and dilute (50 p.c.) acetic acid reduce it to valeric aldehyde (91°), an inactive amyl alcohol $CHMeEt.CH_2OH$ (129°) and tiglic alcohol $C_5H_{10}O$ (c. 130°). Reacts with phenyl-hydrazine, and combines with $NaHSO_3$. CrO_3 forms acetic acid (Gilm, *A.* 106, 379). Aqueous SO_2 at 0° forms oxy-pentane disulphonic acid (Haymann, *M.* 9, 1055).

TIGLYL ALCOHOL *v.* PENTENYL ALCOHOL.

TIN Sn. At. w. 118·8 (*v. infra*). Mol. w. not known with certainty (*v. infra*). Melts at 231·68° (Callendar a. Griffiths, *C. N.* 63, 1); for other data, giving m.p. from 220° to 235°, *v.* Carnelley's *Melting and Boiling-point Tables* (2, 12). Boils between the m.p.s of Ni and Fe, *i.e.* between 1450° and 1600° (Carnelley a. Williams, *C. J.* 35, 566). S.G. c. 7·3 (determinations vary from c. 7·0 to c. 7·5) (*v.* Clarke's *Table of Specific Gravities* [2nd ed.] 5). The so-called allotropic variety of tin seems to have S.G. from 5·8 to 6·1 (*v.* Schertel, *J. pr.* [2] 19, 322). S.H. (0°–100°) ·0559; so-called allotropic tin has S.H. ·0545 (0°–100°) (Bunsen, *P.* 141, 1); S.H. liquid tin (250°–350°) = ·0637 (Person, *A. Ch.* [3] 24, 129). C.E. (linear, 0°–100°) ·00002296 (Matthiessen, *Pr.* 15, 220; *v.* also Kopp, *A.* 81, 1; Fizeau, *C. R.* 68, 1125). T.C. 15·2 (Ag = 100) (Wiedemann, *P. M.* [4] 19, 243). E.C. (Hg at 0° = 1) at 15° = 8·823 (Kirchoff a. Hausemann, *W.* 13, 406); at 0° = 8·726, at 100° = 6·091 (Lorenz, *W.* 13, 422). Heat of fusion (for 1 kilo. tin) = 14,252 (Person, *A. Ch.* [3] 24, 129). For spectrum of tin *v.* Thalén (*A. Ch.* [4] 18, 237); Salet (*C. J.* [2] 9, 1147); also Hartley a. Adeney (*T.* 1884 [i.] 113).

Historical.—Tin was known long before the Christian era. Pliny distinguished *plumbum album* or *candidum* from *plumbum nigrum*; in the fourth century A.D. the former of these substances began to be called *stannum*, from which word the symbol Sn is derived.

Occurrence.—Tin has been found in Siberia and in South Australia. *Tinstone* or *cassiterite*, consisting essentially of SnO_2, is found in considerable quantities, both in veins and in alluvial deposits, in many parts of the world. *Tin pyrites*, containing SnS_2 with Cu_2S, FeS, and ZnS, is found in small quantities in various tin veins. Small quantities of SnO_2 occur in various *lithia-micas* (Sandberger, *J. M.* 1878. 291, 657). According to Lockyer (*Pr.* 27, 279), there are indications of the occurrence of tin in the sun.

Formation.—1. By ppn. from solution of $SnCl_2$ in HClAq by tin; or by tin and iron simultaneously, with a little Fe_2O_3 to neutralise excess of acid (Schultze, *B.* 23, 974).—2. By electrolysis of $SnCl_2$ in dilute HClAq.—3. By reduction of SnO_2 by heating with C.

Preparation.—Tinstone is cleansed by agitation with water; it is then sorted, stamped or rolled to a certain fineness, and washed. The washed ore is calcined in reverberatory calciners to remove sulphur from the sulphides of Fe that are present in most tin ores; the calcined ore is exposed to the air for some days to insure the oxidation of any sulphides that remain in the ore to sulphates, and it is then washed in water, whereby sulphates of Fe, Cu, &c., dissolve and the tin oxide sinks to the bottom of the vessels. The tin oxide is then separated into lighter and heavier parts by agitation with water; the heavier parts are mixed with charcoal or anthracite, some lime or fluorspar is added as a flux, and the mixture is smelted in a reverberatory furnace. The product of the smelting is purified by melting, when the tin runs off, leaving the less fusible foreign metals behind; this purified tin is again melted, the molten mass is stirred with billets of green wood for some hours, and is then allowed to partially solidify by cooling, when the metal separates into different strata, which are ladled into moulds: the upper stratum is the purest and the undermost is the least pure. Sometimes the smelting is conducted in a blast furnace. For details *v.* TIN in DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 834.

Commercial tin generally contains small quantities of As, Cu, Fe, and Pb, and occasionally traces of Sb, Bi, Mn, Mo, W, and Zn. To prepare pure tin, the purest commercial metal is granulated and dissolved in conc. HClAq; a little water is very slowly poured into the liquid so as to form two layers, and a plate of tin is placed in the liquid so that part of it is in the upper (less conc.) and part in the under (more conc.) layer. A slight electric current is thus produced, and crystals of pure tin are deposited on the plate (Hiller, *A.* 85, 253).

Pure tin was prepared by Bongartz a. Classen (*B.* 21, 2903) by heating the purest commercial tin (Banca tin) in dry Cl and so forming $SnCl_4$, distilling fractionally, and collecting that which passed over at 120°, adding to the $SnCl_4$ about four times its volume of water, and then crystallised Na_2S until the pp. of SnS_2 that formed was dissolved, then adding NaOHAq about equal to half the quantity of Na_2S used, allowing to stand for some days, drawing off the clear, almost perfectly colourless liquid into a Pt basin, and passing an electric current through this alkaline liquid, washing the ppd. tin with water, then with absolute alcohol, and drying at 100°. The current was arranged so that it produced c. 2 to 3 c.c. detonating gas per minute from water; c. 2 to 3 g. tin were obtained in 24 hours.

Properties.—Pure tin is a silver-white metal; the commercial metal generally has a slightly yellowish tinge. It is unchanged in pure air; but it tarnishes in the air of large towns from formation of a film of sulphide. Tin is one of the least tenacious metals; a wire 1·6 mm. diameter breaks with a weight of c. 14 kilos. Tin may be hammered into plates c. ·0254 mm. thick; the malleability varies much with temperature, at 200° the metal is so brittle that it crumbles when hammered. Tin readily crystallises; by fusing, allowing to cool partially, and pouring out the still fluid metal, fair-sized crystals are obtained. Crystals are formed by depositing tin by electrolysis. Stolba (*J.* 1873. 282) covers the outside of a Pt basin, all except a small portion, with wax, places the unwaxed surface of the basin on a plate of amalgamated zinc in a larger porcelain basin, fills the Pt basin with a dilute and not very acid solution of $SnCl_2$, and the porcelain basin with water containing c. $\frac{1}{20}$ part of HClAq; crystals of tin deposit on the bottom of the Pt basin. The forms of the crystals of tin are probably rhombic and quadratic (von Foullon, *J. M.* 1885 (11) *Ref.* 266). According to Frankenheim (*P.* 40, 456), the crystals belong to the regular system; Miller (*B. J.* 24, 133) obtained quadratic prisms by separating tin by electrolysis. If a piece of tin is brushed over with warm, dilute *aqua regia*, or with a mixture of warm dilute H_2SO_4Aq and HNO_3Aq, the surface becomes covered with a fretwork of crystals, from the facets of which light is unequally reflected, and the surface appears like watered silk. When a bar of tin is bent a crackling sound may be heard due to the crystals in the inner parts of the bar breaking against one another. When warmed, tin has a characteristic smell.

By exposure for some time to a very low temperature (c. −39°) tin crumbles to a grey powder (*v.* Fritzsche, *B.* 2, 112, 540); S.G. c. 5·8 to 6·1 (*v.* Schertel, *J. pr.* [2] 19, 322). Tin which had been kept for 300 to 400 years was found by Schertel (*l.c.*) to have become reddish-grey, and so brittle that it was crushed by pressure between the finger-nails; by immersion in boiling water the metal became more coherent and lighter in colour, and the S.G. increased to 7·3 (*cf.* Oudemanns, *P. M.* [5] 4, 470).

Tin remains lustrous in pure air at the ordinary temperature, and also in water; a greyish-white film of SnO_2 forms on the surface of tin kept molten in the air; when heated to whiteness in air the metal burns brightly to SnO_2. Tin dissolves in HClAq, forming $SnCl_2$ solution; dilute H_2SO_4Aq has only a slight action, conc. hot H_2SO_4 produces $SnSO_4$ and SO_2; dilute HNO_3Aq dissolves tin, with formation of $Sn(NO_3)_2Aq$ and NH_4NO_3Aq, conc. HNO_3 transforms the metal into SnO_2. Tin dissolves in hot conc. NaOHAq, forming Na_2SnO_3 solution and giving off H.

When haloid compounds of tin are volatilised in a stream of H and the gas is ignited, the flame shows two cones; the inner cone is blue with $SnCl_2$, green with $SnBr_2$, and yellow with SnI_2, and gives a continuous spectrum; the outer cone is carmine-red, and gives a spectrum with two characteristic lines (Salet, *C. J.* [2] 9, 1147).

Tin is metallic physically, and in most of its chemical relations. The oxide SnO_2 interacts towards several acids as a basic oxide, forming salts SnX_2 ($X = SO_4$, &c.); but with conc. KOHAq or NaOHAq this oxide reacts as an acidic oxide, forming salts M_2SnO_3. Tin is the third member of the odd-series family of Group IV. in the periodic classification of the elements; it is closely allied to Ge and Pb, and less closely to Si; it shows very marked analogies with Ti, Zr, Ce, and Th, which (with C) form the even-series family of Group IV. For details of the chemical relations of tin *v.* TIN GROUP OF ELEMENTS, this vol. p. 735.

The atom of tin is divalent in the gaseous molecule $SnCl_2$, and tetravalent in the gaseous molecule $SnCl_4$.

Supposed allotropic form of tin. The grey brittle powder formed by the action of great cold on tin, and also found in some very old specimens of the metal, is sometimes regarded as an allotropic variety of tin (*v. supra*). All the specimens of tin, however, which have been observed to undergo this change have contained small quantities of impurities; until the change has been effected with pure tin, and has been proved to occur without any change of mass, the existence of an allotropic variety of tin cannot be said to be established. According to von Foullon (*J. M.* 1885 [1] *Ref.* 266) there are three varieties of tin: (1) rhombic, S.G. 6·52 to 6·56; (2) quadratic, S.G. 7·196; (3) grey brittle tin, S.G. 5·781 to 5·809.

Atomic weight of tin. The at. w. has been determined (1) by oxidising Sn to SnO_2 by HNO_3 (Gay-Lussac, *A. Ch.* [2] 80, 163 [1812]; Berzelius, *P.* 8, 184 [1812]; Mulder, *A.* 72, 212 [1849]; Vlaanderen, *B. J.* 1858. 183 [1858]; Dumas, *A. Ch.* [3] 55, 134 [1859]; van der Plaats, *C. R.* 100, 52 [1885]; Bongartz a. Classen, *B.* 21, 2900 [1888]); (2) by ppg. Cl from $SnCl_2$ by $AgNO_3Aq$ (Dumas, *A. Ch.* [3] 55, 156 [1859]); (3) by electrolysing $SnCl_4.2NH_4Cl$ and $SnCl_4.2KCl$ (B. a. C., *l.c.* [1888]); (4) by electrolysing $SnBr_4$ (B. a. C., *l.c.*); (5) by reducing SnO_2 in H. (v. d. P., *l.c.* [1885]); (6) by determining S.H. of Sn (Bunsen, *P.* 141, 1 [1870]); (7) by determining V.D. of, and analysing, $SnCl_2$ and $SnCl_4$. The older determinations gave values from 115·9 to 117·8. The results of the determinations of B. a. C. are summarised by them (*l.c.*, p. 2909) as follows:—

Number of experiments	Method	At. weight	Diff. between min. and max. found
11	oxidation of Sn to SnO_2	118·7606	·459
16	electrolysis of $SnCl_4.2NH_4Cl$	118·8093	·228
10	electrolysis of $SnCl_4.2KCl$	118·7975	·163
10	electrolysis of $SnBr_4$	118·7309	·144

B. a. C. regard the second and third methods as the most trustworthy; in the oxidation of Sn to SnO_2 the Pt vessel was also slightly acted on, and there was the possibility of a very small loss in dissolving $SnBr_4$ in the last method. The mean of the results obtained by the electrolysis of the two double chlorides is 118·8 (O = 15·96).

Molecular weight of tin. As the V.D. of tin has not been determined the molecular weight is not known. Ramsay determined the depression of the vapour pressure of Hg caused by dissolving tin therein; assuming that equal volumes of dilute solutions contain equal numbers of molecules of the dissolved bodies, and that the mol. w. of liquid Hg is 200, the results obtained by R. gave the mol. w. of tin as 117·4 in one experiment and 149·5° in another.

Reactions and Combinations.—1. When tin is heated in *air* or *oxygen*, a film is formed on the surface, containing both SnO and SnO_2; when heated to whiteness tin burns brightly, forming SnO_2 (*v.* Emich, *M.* 14, 345).—2. Heated in *chlorine*, *bromine*, or *iodine*, the compounds SnX_2 and SnX_4 are formed, according to whether there is excess of tin or halogen. — 3. Tin combines with *sulphur*, and with *selenion*, to form SnS and SnSe, when heated with these elements.—4. Tin probably combines with *phosphorus* when heated in vapour of that element.—5. Tin forms alloys with many *metals* (*v.* TIN, ALLOYS OF, p. 720).—6. *Water* is decomposed by tin at a full red heat with formation of SnO and H.—7. *Sulphydric acid* has a slight action on tin, in moist air, forming a film of SnS.—8. *Hydrochloric acid* dissolves the metal, forming solution of $SnCl_2$ and giving off H; the reaction proceeds more rapidly with warm conc. HClAq.—9. *Pure conc. nitric acid*, S.G. c. 1·55, has no action on tin. When the acid is diluted the products of the reaction vary with the concentration and the temperature; according to Walker (*C. J.* 63, 845), both $Sn(NO_3)_2$ and $Sn(NO_3)_4$ are formed, the quantity of $Sn(NO_3)_4$ increasing as concentration increases at a fixed temperature; with very dilute acid an increase of temperature causes only a slight increase in the quantity of the stannic salt, but the effect of temperature is very marked with more conc. acid; the proportion of stannous to stannic salt formed is only slightly affected by changing the relative masses of tin and acid; when a fairly conc. solution of tin in HNO_3Aq is heated, hydrated stannic nitrates, varying in composition, are deposited (*v.* also Montemartini, *G.* 22, 384, 397, 426; abstract in *C. J.* 62, 1402; *v.* also Hay, *C. N.* 23, 298; Scott, *C. N.* 23, 322). Pure

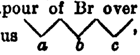
HNO_3 diluted sufficiently to start the reaction produces chiefly $SnO_2.xH_2O$ (*v. Hydrated stannic oxide*, under TIN OXIDES AND HYDRATED OXIDES, p. 725). When tin dissolves in HNO_3Aq, NH_4NO_3 is formed; the gases evolved are NO, N_2O, and N (*v.* Ackworth a. Armstrong, *C. J.* 32, 84).—10. A *mixture of nitric and sulphuric acids*, or *nitric and hydrochloric acids*, produces NH_2OH along with NH_3 (Divers, *C. J.* 43, 443; D. a. Shimidzu, *C. J.* 47, 597; *cf.* HYDROXYLAMINE, vol. ii. p. 734). With certain proportions of HNO_3Aq and H_2SO_4Aq, Bassett (*C. N.* 53, 172) obtained $Sn(NO_3)_2$ in solution, and almost pure N_2O.—11. *Dilute sulphuric acid* reacts slowly when warmed with tin, forming $SnSO_4$ if the tin is kept in excess, and chiefly $Sn(SO_4)_2$ if the acid is in excess, and giving off H. *Conc. sulphuric acid* reacts to form $SnSO_4$, or $Sn(SO_4)_2$, according to the proportion of tin to acid, and evolves H_2S or SO_2, or both, according to the concentration of the acid and the temperature; with pure hot H_2SO_4, SO_2 is given off, and S separates (*v.* Calvert a. Johnson, *C. J.* [2] 4, 435; also Pattison Muir a. Robbs, *C. N.* 45, 69).—12. *Aqua regia* dissolves tin, forming $SnCl_4$.—13. Tin reacts with *mercuric chloride* and *bromide*, when heated with these compounds, forming $SnCl_2$, or $SnBr_2$, and Hg.—14. With *sulphurous chloride*, $SnCl_2$ is formed, with production of much heat (Wöhler, *A.* 73, 374).—15. Tin dissolves in warm conc. *caustic potash*, or *soda*, solution, forming M_2SnO_3 and giving off H.—16. Fusion with *nitre* forms K_2SnO_3.

Detection and Estimation.—H_2S ppts. dark brown SnS from slightly acidified solutions of stannous salts; the pp. is soluble in warm yellow ammonium sulphide, forming $(NH_4)_2SnS_3Aq$, from which acids ppt. yellow SnS_2. $AuCl_3Aq$ produces a purple pp., a compound of Sn, Au, and O (*v. Purple of Cassius*, under TIN OXIDES AND HYDRATED OXIDES, p. 727). H_2S ppts. yellow SnS_2 from acidified solutions of stannic salts; the ppt. dissolves in warm yellow ammonium sulphide, and acids re-ppt. SnS_2 from this solution. Tin is generally estimated as SnO_2.

Tin, alloys of. Tin forms alloys with many metals. For a general account of the properties of different classes of tin alloys, *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 837. For alloys of tin with *antimony*, *v.* Karmarsch (*D. P. J.* 123, 267); Kestner (*Kast. Archiv*, 19, 424); Johnson (*Chem. Gazette*, 1855. 160); Chaudet (*A. Ch.* [2] 3, 376); with *bismuth and lead*, and with *bismuth, cadmium and lead*, *v.* vol. i. p. 511; with *cadmium*, *v.* vol. i. p. 655; with *cadmium and gold*, *v.* Heycock a. Neville (*C. J.* 59, 936); with *copper*, *v.* vol. ii. p. 254 (also DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 838); with *copper and lead*, *v.* vol. iii. p. 125 (also French, *S. C. I.* 8, 36); with *iridium, platinum, and rhodium*, *v.* Deville a. Debray (*C. R.* 81, 889); with *iron*, *v.* vol. iii. p. 53 (also Headden, *Am. S.* [3] 44, 464); with *gold*, *v.* Laurie (*P. M.* [5] 38, 94); with *lead*, *v.* vol. iii. p. 125; with *lead and zinc*, *v.* vol. iii. p. 125 (also Wright a. Thompson, *Pr.* 45, 461; 48, 25); with *mercury*, *v. infra*; with *platinum*, *v.* vol. iv. p. 288; with *silver*, *v.* W. a. T. (*Pr.* 48, 25); with *sodium*, *v.* Bailey (*C. N.* 65, 18). Tin alloys with *zinc* in all proportions; the alloys are harder than tin, but softer than zinc; they are less malleable than tin. Many varieties of bronze are alloys of tin with *zinc and copper* (*v.* Rudberg, *P.* 18, 240). *Amalgams of tin* are readily formed by immersing tin in Hg; the action is more rapid if the Hg is warmed (*v.* Böttger, *J. pr.* 1, 305; Joule, *Chem. Gazette*, 1850. 339, also *C. J.* 16, 384; Kupffer, *A. Ch.* [2] 40, 293).

Tin, bromides of. Tin combines with Br to form two compounds, $SnBr_2$ and $SnBr_4$. The V.D. of the latter has been determined, and the formula $SnBr_4$ is molecular; from the analogy of the chlorides it is probable that the formula $SnBr_2$ is molecular also. Watts a. Bell (*C. J.* 33, 442) obtained both $SnBr_2$ and $SnBr_4$ by heating SnO_2 in Br vapour mixed with CO.

STANNOUS BROMIDE $SnBr_2$. (*Dibromide of tin.*) Obtained by Balard (*A. Ch.* [2] 32, 337); more fully examined by Rayman a. Preis (*A.* 223, 323). Prepared by heating tin in HBr gas, allowing the oily liquid so obtained to cool, dissolving the crystals that form in dilute HBrAq, and purifying the solid that separates by distilling it in a stream of N. A crystalline, slightly yellow, transparent solid; melts at 215·5° to a transparent liquid, which solidifies at 215°. S.G. 5·117 at 17°. Carnelley a. Williams (*C. J.* 35, 563) say that $SnBr_2$ boils between 617° and 634°. Partly decomposed by water, with separation of an oxybromide of tin (R. a. P., *l.c.*). By crystallising a solution of tin in warm conc. HBrAq, R. a. P. (*l.c.*) obtained the *hydrate* $SnBr_2.xH_2O$ ($x = 1$ or 2), in colourless needles. By cooling a mixture of NH_4Cl and solution of tin in warm conc. HBrAq, the compound $SnBr_2.2NH_4Cl.H_2O$ was obtained in large rhombic, porcelain-like crystals (R. a. P., *l.c.*).

STANNIC BROMIDE $SnBr_4$. (*Tetrabromide of tin.*) Mol. w. 437·8. Melts at 30° (Carnelley a. O'Shea, *C. J.* 33, 55), at 33° (Rayman a. Preis, *A.* 223, 323). Boils at c. 201° (C. a. O'S., *l.c.*), at 203·3° (R. a. P., *l.c.*). S.G. 3·349 (R. a. P., *l.c.*). V.D. at 228°–260° = 227–230 (C. a. O'S., *l.c.*). Prepared by passing vapour of Br over melted tin in a tube shaped thus , the tin being at *b* and the Br at *a*. The tin burns in the Br vapour; the product is distilled backwards and forwards from *b* to *c* until the distillate is quite colourless. On cooling the liquid solidifies to colourless crystals of $SnBr_4$ (C. a. O'S., *l.c.*). R. a. P. (*l.c.*) prepared $SnBr_4$ by heating tin with Br, and crystallising from $SnCl_4$ or $SnBr_3Cl$. $SnBr_4$ forms white crystals, which are slowly decomposed in the air; according to R. a. P. (*l.c.*) the crystals deliquesce to a clear liquid, which when placed over H_2SO_4 deposits crystals of the *hydrate* $SnBr_4.4H_2O$. $SnBr_4$ is soluble in cold water; after some hours $SnO_2.xH_2O$ is deposited; boiling hastens this change; addition of HNO_3Aq to hot $SnBr_4Aq$ ppts. all the tin as $SnO_2.xH_2O$, with evolution of a little Br (C. a. O'S., *l.c.*). R. a. P. (*l.c.*) found that $SnBr_4$ absorbs NH_3; on heating some NH_3 was given off, and a yellow sublimate of $SnBr_4.2NH_3$ was obtained. According to Nicklès (*C. R.* 51, 869), $SnBr_4$ combines with *ether* to form $SnBr_4.Et_2O$.

Stannibromhydric acid $H_2SnBr_6.xH_2O$. (*Bromostannic acid. Hydrobromostannic acid.*) This compound was obtained by Seubert (*B.* 20, 194) by adding 74·1 parts HBrAq (50 p.c. HBr) to 100 parts $SnBr_4$ (*i.e.* in the ratio $2HBr:SnBr_4$). A yellow liquid was formed which solidified after a time to a mass of yellow, needle-shaped crystals; the small quantity of mother-liquor was removed by melting and allowing to solidify partially. It is doubtful whether the acid crystallises with 7 or $9H_2O$. The acid forms amber-yellow needles, probably triclinic; it is very deliquescent; fumes in air, giving off HBr. By adding Na_2CO_3 to H_2SnBr_6Aq, and allowing to evaporate, Seubert (*l.c.*) obtained *sodium stannibromide*, $Na_2SnBr_6.6H_2O$, in yellow needles. Several other stannibromides are described by Rayman a. Preis (*A.* 223, 323); their composition is $MSnBr_6.xH_2O$, where $M = (NH_4)_2$, Ba, Ca, Fe, Mg, Mn, Ni, Na_2, Sr, and x is 6, 8, or 10.

Tin, bromochlorides of. Rayman a. Preis (*A.* 223, 323) obtained a compound to which they gave the formula $SnBr_3Cl$ by heating tin in Br that contained some Cl, and repeatedly distilling. The compound is a liquid boiling between 181° and 190°. It dissolves $SnBr_4$, which crystallises out unchanged. By adding Br to excess of $SnCl_2$ Ladenburg (*A. Supplbd.* 8, 60) obtained indications of the formation of bromochlorides, probably $SnBr_3Cl$ and $SnBrCl_3$.

Tin, chlorides of. Tin and Cl combine to form two compounds, $SnCl_2$ and $SnCl_4$. Both formulæ are molecular.

STANNOUS CHLORIDE $SnCl_2$. (*Dichloride of tin. Tin-salt.*) Mol. w. 189·54; perhaps 379·08 ($=Sn_2Cl_4$) in the liquid state (*v. infra*). Melts at 249·3° (Carnelley a. Williams, *C. J.* 35, 63). Boils between 617° and 628° (C. a. W., *l.c.*); at 606° (Biltz a. Meyer, *Z. P. C.* 2, 184). V.D. *v. infra.* H.F. $[Sn,Cl^2] = 80{,}790$; $[Sn,Cl^2,Aq] = 81{,}140$; $[Sn,Cl^2,2H^2O] = 86{,}520$ (*Th.* 3, 327).

Preparation.—1. By heating a mixture of equal parts tin filings and $HgCl_2$; Hg sublimes and leaves $SnCl_2$.—2. By heating tin in HCl gas.—3. By dissolving tin in warm, fairly conc. HClAq, evaporating to the crystallising point, drying the crystals of $SnCl_2.2H_2O$ that separate, heating them in a capacious crucible so long as gases are given off, pouring the liquid into a small crucible, pounding when cold, and distilling from a retort; the first portions of the distillate are said to be pure $SnCl_2$ (Capitaine, *J. Ph.* 25, 552).

Properties.—A semi-transparent, white solid; melts at c. 250° and boils at incipient redness (*v. supra*). Heated to bright redness, out of air, some $SnCl_4$ is given off, then $SnCl_2$. Heated in air gives $SnCl_4$ and SnO_2. $SnCl_2$ dissolves in a little water; the solution is decomposed by much dilution, with separation of a hydrated oxychloride $SnCl_2.SnO.2H_2O$. According to Michael a. Kraft (*A. Ch.* [3] 41, 471), 1,000 c.c. saturated $SnCl_2Aq$ contains, at 15°, 1,333 g. $SnCl_2$ and 494 g. water, and the S.G. is 1·827. Gerlach (*D. P. J.* 186, 131) gives the following data for a solution of the hydrate $SnCl_2.2H_2O$:—

P.c. $SnCl_2.2H_2O$	S.G. of solution	P.c. $SnCl_2.2H_2O$	S.G. of solution
5	1·0331	45	1·3850
10	1·0684	50	1·4451
15	1·1050	55	1·5106
20	1·1442	60	1·5823
25	1·1855	65	1·6598
30	1·2300	70	1·7452
35	1·2779	75	1·8399
40	1·3298		

An aqueous solution of $SnCl_2$ generally becomes turbid from ppn. of Sn_2OCl_2; digestion with tin and a little HClAq dissolves the pp.; addition of tartaric acid, or NH_4Cl, stops the solution from becoming turbid, the former by dissolving the oxychloride, the latter by forming a double salt $SnCl_2.2NH_4Cl$, which is very soluble in water.

Mallet (*C. J.* 35, 524) obtained a semi-transparent, jelly-like solid from an aqueous solution of $SnCl_2$ which had stood in a loosely closed bottle for a year or two; the solid dried to a substance like gum arabic; it reddened litmus; the composition of the substance was $SnO_2.HCl$. Mallet writes the formula as $SnO.OH.Cl$, and suggests the name *chlor-stannic acid.*

Molecular weight of stannous chloride. The V.D. of the gas obtained by heating $SnCl_2$ has been determined repeatedly. The following table presents the results:—

Calculated for $SnCl_2$	Calculated for Sn_2Cl_4		Temp., and Observers	
94·7	189·4			
	103·7	? temp.		Rieth, *B.* 3, 668 [1870].
		185·9	at 619°	V. a. C. Meyer, *B.* 12, 1195 [1879].
		189·2	,, 697°	
	104·5		,, 800°	
	104·5		,, 800°	Meyer a. Züblin, *B.* 13, 811 [1880].
96·5			,, 880°	
90·1			,, 970°	
	123·7		,, 639°	Biltz a. Meyer, *Z. P. C.* 2, 184 [1888].
	123·7		,, 675°	
	122·9		,, 699°	
	119·5		,, 760°	
	111·4		,, 790°	
	102·7		,, 1113°	

From their determinations, Biltz a. Meyer concluded that molecules of the composition Sn_2Cl_4 do not exist in the gaseous state, and that the mol. w. of the gas comes to a constant value, corresponding with the formula $SnCl_2$, only at a temperature very much above the b.p. of the liquid ($SnCl_2$ boils at 606°). In some of the earlier determinations at c. 800° partial decomposition occurred, with production of Cl. The results, taken as a whole, seem to be explained by assuming that the molecules of the liquid, near to the b.p., have the composition Sn_2Cl_4, that some of these are dissociated to $2SnCl_2$ at c. 30° above the b.p., and that this process of dissociation continues slowly, and is not completed at even 500° above the b.p.

Reactions.—1. *Heated strongly in air*, $SnCl_4$ is given off, and SnO_2 remains. Heated to its b.p. in a retort, $SnCl_2$ and $SnCl_4$ distil, and the oxychloride Sn_2OCl_2 remains (Capitaine, *J. Ph.* 25, 552).—2. When *sulphur* is added to molten $SnCl_2$ the products are $SnCl_4$ and SnS; with *selenion* the products are $SnCl_4$ and SnSe (Schneider, *P.* 127, 624).—3. Many *salts* are reduced by $SnCl_2Aq$, either to lower salts or to metals. Au, Hg, and Ag are ppd. from solutions of their salts; ferric and manganic salts are reduced to ferrous and manganous salts; $CuCl_2Aq$ to Cu_2Cl_2.—4. The *higher oxides* of Bi, Cr, Pb, Mo, W, &c., are reduced to the lower oxides of these metals.—5. *Arsenious oxide* is reduced to As by a considerable excess of $SnCl_2Aq$.—6. According to Böttger (*Polytech. Notizbl.* 35, 96), a mixture of 2 pts. $SnCl_2$ rubbed with 1 pt.

potassium chlorate **gets hot, and produces an oxychloride of tin, $KClO_4$, oxide of chlorine, and H_2O.** For reactions with *water v. supra, Properties*; also *infra, Combinations*, No. 1.

Combinations.—1. With *water* to form the hydrate $SnCl_2.2H_2O$. This compound is prepared by dissolving tin in warm conc. HClAq and evaporating to the crystallising point, in contact with tin to prevent formation of $SnCl_4$. $SnCl_2.2H_2O$, commonly known by the name of *tin-salt*, forms large white, monoclinic crystals (Marignac, *J.* 1856. 394); melts at c. 37·7°; S.G. 2·71 at 15·5° (solid), 2·588 at 37·7° (liquid) (Penny, *C. J.* 4, 239). H.F. $[Sn,Cl^2,2H^2O]$ = 86,520 (*Th.* 3, 327). When gradually heated to 100°, most of the water is removed; when rapidly heated, H_2O and HCl are given off and Sn_2OCl_2 remains, which gives off $SnCl_2$ when more strongly heated. $SnCl_2.2H_2O$ decomposes slowly on exposure to the air, forming Sn_2OCl_2 and $SnCl_4$.—2. With *ammonia*, forming $SnCl_2.NH_3$.—3. According to Engel (*C. R.* 106, 1398), a compound of $SnCl_2$ with *hydrogen chloride* is formed by passing HCl gas over $SnCl_2.2H_2O$ at 0°; the liquid thus formed solidifies at 27°, forming crystals of $SnCl_2.HCl.3H_2O$, which melt at 40°.—4. With *chlorides of the alkali and alkaline earth metals*, to form $MCl_2.SnCl_2.xH_2O$, where $M = (NH_4)_2$, K_2, Ba, or Sr (*v.* Marignac, *C. R.* 55, 650; Rammelsberg, *Krystall. Chemie*, 211; Richardson, *Am.* 14, 89). Poggiale (*C. R.* 20, 1180) described a salt $SnCl_2.4NH_4Cl.3H_2O$. Richardson (*l.c.*) obtained $SnCl_2.KCl.H_2O$ as well as $SnCl_2.2KCl.2H_2O$. These double salts are perhaps best regarded as *stannochlorides*, derived from the acid $HSnCl_3$ (*v. Combinations*, No. 3) and the hypothetical acid H_2SnCl_4.

STANNIC CHLORIDE $SnCl_4$. (*Tetrachloride of tin.*) Mol. w. 260·28. Boils at 113·9° at 760 mm. (Thorpe, *C. J.* 37, 372); at 114·1° at 760 mm. (Young, *C. J.* 59, 912). Solidifies at −33° (Besson, *C. R.* 109, 940). S.G. $\frac{0^\circ}{4^\circ}$ 2·27875; 1·97813 at b.p. (Thorpe, *l.c.*). V.D. 133·1 at 124° (Dumas, *A. Ch.* [2] 33, 385). S.H. ·1402 (10°–15°) (Regnault, *A. Ch.* [3] 9, 332). Heat of vaporisation = 30,530 (gram-units for 1 kilo.) (Andrews, *C. J.* 1, 27). H.F. $[Sn,Cl^4]$ = 127,250; $[Sn,Cl^4,Aq]$ = 157,170; $[SnCl^2,Cl^2]$ = 46,460; $[SnCl^2Aq,Cl^2]$ = 76,030 (*Th.* 3, 327). C.E. (cubical, 0°–100°) ·00130244 (Thorpe, *l.c.*). S.V. 131·07 (Thorpe, *l.c.*; for S.V. from 0° to 280° *v.* Young, *C. J.* 59, 933, 935). For vapour pressures from −10° to 319° *v.* Young (*l.c.*, p. 927). Critical temperature = 318·7°; critical pressure = 28080 mm. (Y., *l.c.*, p. 928).

Formation.—1. By heating tin in excess of Cl.—2. By heating 1 pt. tin filings intimately mixed with 4 or 5 pts. $HgCl_2$.—3. By heating a mixture of $Sn(SO_4)_2$ and NaCl.—4. By passing vapour of CCl_4 over heated SnO_2 (Watts a. Bell, *C. J.* 33, 442).—5. By adding fuming sulphuric acid to tin, and then passing in HCl gas and distilling (Heumann a. Köchlin, *B.* 15, 416).

Preparation.—Dry Cl is led over tin filings heated in a retort connected with a dry flask, which is kept cold; the distillate is distilled from tin filings, and then repeatedly redistilled in a current of dry CO_2. A solution of $SnCl_4$ is obtained by passing Cl into $SnCl_2Aq$ until no pp. is produced with $HgCl_2Aq$, or by dissolving tin in dilute HClAq containing a little HNO_3.

Properties.—A thin, mobile, colourless, fuming, very corrosive liquid. Solidifies at −33° to small white crystals (Besson, *C. R.* 109, 940). $SnCl_4$ dissolves crystalline S, also P, I, Br, CS_2, &c. (Girardin, *C. R.* 51, 1057). $SnCl_4$ does not conduct electricity, even at its b.p.; addition of absolute alcohol forms crystals, probably ($SnCl_4.5EtOH$), which conduct when dissolved; ether behaves similarly to alcohol (Coldridge, *P. M.* [5] 29, 383, 480). $SnCl_4$ withdraws moisture from the air, probably forming $SnCl_4.3H_2O$ (*v. infra, Hydrates of stannic chloride*). $SnCl_4$ dissolves in water, with production of heat $[SnCl^4,Aq]$ = 29,920 (*Th.* 3, 327), and considerable contraction of volume (*v.* also *Reactions*, No. 1). Gerlach (*D. P. J.* 178, 49) gives the following table:—

Pcntge. $SnCl_4$	S.G. $SnCl_4Aq$	Vol. of 100 pts. by wt. of solution; vol. of 100 pts. water = 100	Vol. of mixture of $SnCl_4$ and water; vol of sum of constituents = 100
0	1·000	100·00	100·00
10	1·082	92·42	97·82
20	1·174	85·18	95·76
30	1·279	78·19	93·72
40	1·404	71·12	91·42
50	1·556	64·26	88·78
60	1·743	57·37	85·81
70	1·973	50·68	82·63
100	2·234	44·76	100·00

Hydrates of stannic chloride.—Various hydrates have been isolated: (1) $SnCl_4.3H_2O$, by exposing $SnCl_4$ to air (Casselmann, *A.* 83, 272); also by adding 18 pts. water to 260 pts. $SnCl_4$, when $\frac{2}{3}$ of the $SnCl_4$ remains unchanged, and $\frac{1}{3}$ forms the hydrate, which sinks in the excess of $SnCl_4$ (Gerlach, *D. P. J.* 178, 49); also by dissolving 260 pts. $SnCl_4$ in 54 pts. water, and letting the solution cool to 60° (G., *l.c.*); (2) $SnCl_4.2H_2O$, by keeping the trihydrate *in vacuo* (Scheurer-Kestner, *C. R.* 50, 50); also by drying the pentahydrate over H_2SO_4 (Lewy, *A. Ch.* [3] 16, 303); (3) $SnCl_4.5H_2O$, by dissolving $SnCl_4$ completely in water and evaporating (G., *l.c.*; L., *l.c.*); (4) $SnCl_4.8H_2O$, by strongly cooling dilute $SnCl_4Aq$ (G., *l.c.*); (5) $SnCl_4.9H_2O$, obtained by Nöllner (*Z.* [2] 1, 445) by treating $SnCl_2Aq$ with *aqua regia*, and exposing the solution to a winter temperature. Gerlach (*l.c.*) gives a table (*v.* next page), showing the S.G. and percentage composition of solutions of the pentahydrate.

Reactions.—1. With *water*: $SnCl_4$ dissolves in water (*v. supra*) with production of much heat. Vignon (*C. R.* 108, 1049; 109, 372) found that H_2SnO_3 ppd. from freshly prepared $SnCl_4Aq$, from $SnCl_4Aq$ after keeping, and from $SnCl_4Aq$ after heating, showed markedly different heats of neutralisation by potash. He concluded that $SnCl_4Aq$ contains HClAq and H_2SnO_3Aq, and that the H_2SnO_3 in solution gradually polymerises. Dilute $SnCl_4Aq$ gradually decomposes, giving HClAq and $SnO_2.xH_2O$ (Casselmann, *A.* 83, 272). Heating in a sealed tube with a little water is said to give SnO_2.—2. With conc. ***nitric*** *acid* $SnCl_4$ forms $SnO_2.xH_2O$.—3. **Dry *hydrogen sulphide* forms white crystals of $SnCl_4.5H_2S$, which gives off H_2S and HCl when heated, and**

Pcntge. $SnCl_4.5H_2O$	S.G. of solution at 15°	Pcntge. $SnCl_4.5H_2O$	S.G. of solution at 15°
0	1·000	48	1·347
1	1·006	49	1·357
2	1·012	50	1·3661
3	1·018	51	1·376
4	1·024	52	1·386
5	1·0298	53	1·396
6	1·036	54	1·406
7	1·042	55	1·4154
8	1·048	56	1·426
9	1·053	57	1·437
10	1·0593	58	1·447
11	1·066	59	1·458
12	1·072	60	1·4684
13	1·078	61	1·480
14	1·084	62	1·491
15	1·0905	63	1·503
16	1·097	64	1·514
17	1·104	65	1·5255
18	1·110	66	1·538
19	1·117	67	1·550
20	1·1236	68	1·563
21	1·130	69	1·575
22	1·137	70	1·5873
23	1·144	71	1·601
24	1·151	72	1·614
25	1·1581	73	1·627
26	1·165	74	1·641
27	1·173	75	1·6543
28	1·180	76	1·669
29	1·187	77	1·683
30	1·1947	78	1·698
31	1·202	79	1·712
32	1·210	80	1·7271
33	1·218	81	1·743
34	1·226	82	1·759
35	1·2338	83	1·775
36	1·242	84	1·791
37	1·250	85	1·8067
38	1·259	86	1·824
39	1·267	87	1·842
40	1·2755	88	1·859
41	1·284	89	1·876
42	1·293	90	1·8939
43	1·302	91	1·913
44	1·310	92	1·932
45	1·3193	93	1·950
46	1·329	94	1·969
47	1·338	95	1·9881

leaves SnS_2 (Coldridge, *P. M.* [5] 29, 383, 480).—4. $SnCl_4$ dissolves *stannous oxide*, forming $SnCl_2$ and a solution of $SnO_2.H_2O$ in excess of $SnCl_4$ (Scheurer-Kestner, *C. R.* 50, 50).

Combinations.—1. With *hydrogen chloride.* By passing dry HCl over $SnCl_4.5H_2O$, then saturating the liquid so formed with dry HCl at 28°, and cooling to 0°, Engel (*C. R.* 103, 213) obtained white crystalline leaflets of the compound $SnCl_4.2HCl.6H_2O$, melting at c. 20°, and giving off HCl when more strongly heated. The same compound was prepared by Seubert (*B.* 20, 793) by adding to $SnCl_4$ such a quantity of conc. HClAq that the ratio of water in the acid was to the $SnCl_4$ as $6H_2O:SnCl_4$ (100 pts. $SnCl_4$ require 62·15 pts. of 33 p.c. HClAq), and after a little passing in c. 8 pts. dry HCl; the whole then solidified to a crystalline mass, melting at 19·2°. This compound is best called ***stannichlorhydric acid***; it has also been called *chlorostannic acid* (Mallet gave the name *chlor-stannic acid* to SnO.OH.Cl, *v.* STANNOUS CHLORIDE, *Properties*, p. 721), and *hydrochlorostannic acid.* Chassevant (*A. Ch.* [6] 30, 5) has described a compound $SnCl_4.HCl.3H_2O$.—2. With several *metallic chlorides.* The double salts of $SnCl_4$ and alkali and alkaline earth chlorides have the composition $MSnCl_6.xH_2O$, where M = $(NH_4)_2$, K_2, Na_2, Ba, Ca, Mg, or Sr; these salts are best named *stannichlorides* (for details, *v.* Bolley, *A.* 39, 101; Lewy, *J. pr.* 37, 479; Rammelsberg, *Krystall. chemie*; Wittstein, *R. P.* 64, 7; Topsoë, *W. A. B.* 69 [2] 261; Morel, *C. C.* 1891 [1] 492; Chassevant, *A. Ch.* [6] 30, 5). Cleve (*Bl.* [2] 31, 195) obtained double salts of the form $xSnCl_4.2MCl_3.sH_2O$, where M = Ce, Di, La, or Y, x = 2 and 5, and s had large values (from 18 to 45).—3. With certain *nonmetallic chlorides*; the compound $SnCl_4.2SCl_4$ is said to be obtained by the interaction of Cl and SnS (H. Rose, *P.* 44, 320; Casselmann, *P.* 42, 517); the compound $SnCl_4.PCl_5$ was obtained by Casselmann (*l.c.*) by heating a mixture of $SnCl_4.2SCl_4$ and PCl_3 in a stream of HCl.—4. With certain *nonmetallic oxychlorides*: (1) $SnCl_4.POCl_3$, formed by the reaction of $POCl_3$ and $SnCl_4$ (Casselmann, *A.* 91, 248; 98, 213); (2) $SnCl_4.2SeOCl_2$, by combining the constituent compounds (Weber, *B. B.* 1865. 154); (3) $SnCl_4.2NOCl$, by passing the dry vapour from *aqua regia* over $SnCl_4$ (Hampe, *A.* 126, 43), also by subliming $SnCl_4.N_2O_3$ formed by the action of N_2O and NO_2 on $SnCl_4$ (Weber a. Hampe, *P.* 118, 471).—5. With *hydrogen sulphide* to form $SnCl_4.5H_2S$; decomposed by heating to SnS_2, H_2S, and HCl (Coldridge, *P. M.* [5] 29, 383).—6. With *hydrogen cyanide*, to form crystals that are decomposed in moist air (Klein, *A.* 74, 85). 7. With *ammonia*, to form $SnCl_4.2NH_3$ according to H. Rose (*P.* 24, 163), to form $SnCl_4.4NH_3$ according to Grouvelle a. Persoz (*A. Ch.* [2] 44, 322).—8. With *phosphorus trihydride*, to form $3SnCl_4.2PH_3$ (H. Rose, *P.* 24, 159); heated to 100° in CO_2 there are formed HCl and $Sn_3P_2Cl_8$, according to Mahn (*J. Z.* 5, 160).—9. With certain *nonmetallic oxides*: (1) with SO_3 to form a solid [? composition] (H. Rose, *P.* 44, 320); (2) with NO a compound is formed, according to Kuhlmann (*A.* 39, 319), but no action occurs according to Hampe (*A.* 126, 43); (3) with N_2O_3 to form $SnCl_4.N_2O_3$, produced by passing NO_2 and N_2O over $SnCl_4$ (Hampe, *l.c.*).—10. With *ethylic alcohol*, to form $SnCl_4.5EtOH$ (Coldridge, *P. M.* [5] 29, 383, 480).—11. With *amylic alcohol*, to form $SnCl_4.2C_5H_{11}(OH)$ (Bauer a. Klein, *Z.* [2] 4, 370) 12. With *ether*, to form $SnCl_4.2Et_2O$ (Coldridge, *l.c.*).—13. With various *nitriles*, forming crystallisable compounds (Lewy, *C. R.* 21, 371).

Tin, chlorobromides of, *v.* TIN BROMOCHLORIDES, p. 721.

Tin, chloro-iodide of; *v.* TIN IODOCHLORIDE, p. 724.

Tin, chlorosulphide of; *v.* TIN THIOCHLORIDE, p. 733.

Tin, ferricyanides of; *v.* vol. ii. p. 340.

Tin, ferrocyanides of; *v.* vol. ii. p. 337.

Tin, fluorides of. Only one fluoride, SnF_2, has been isolated; double salts of stannic fluoride (SnF_4) are known.

Stannous fluoride SnF_2. (*Difluoride of tin.*) Formed, in small opaque, lustrous, prisms, by dissolving $SnO.xH_2O$ in HFAq, and evaporating; heated in air it forms the oxyfluoride $SnOF_2$ ($= SnF_4.SnO_2$) (Marignac, *Ann. M.* [5] 15, 221; Fremy, *A. Ch.* [3] 47, 37). By dissolving freshly ppd. $SnO.xH_2O$ in solutions of alkali fluorides acidified by HFAq, Wagner (*B.* 19, 896) obtained *stannofluorides* of the form $xSnF_2.2MF.yH_2O$, where $x = 1$ and 3, $y = 1$ and 2, and M was NH_4, K, and Na.

Stannic fluoride. This compound has not been isolated; a solution of $SnO_2.xH_2O$ in HFAq coagulates when heated, but does not yield any definite compound; when evaporated in air HF is given off, and an oxyfluoride, $SnOF_2$, is deposited (Marignac, *l.c.*).

Stannifluorides. A series of these salts, $MSnF_6.xH_2O$, where M = one atom of a divalent metal or two atoms of a monovalent metal, has been obtained by Marignac (*Ann. M.* [5] 15, 221). The salts are isomorphous with the corresponding silicofluorides and titanifluorides; they are generally obtained by saturating the stannates with HFAq and evaporating, some are formed by double decomposition from the Pb or Ag salt. The following salts have been obtained: $MSnF_6.xH_2O$; $M = NH_4$, Ba, Cd $x = 6$, Ca $x = 2$, Cu $x = 4$, Pb $x = 3$, Li $x = 2$, Mg $x = 6$, Mn $x = 6$, Ni $x = 6$, K $x = 1$, Ag $x = 4$, Na, Sr $x = 2$, Zn $x = 6$.

Tin, haloid compounds of. Tin and the halogens combine to form two series of compounds, SnX_2 and SnX_4 (SnF_4 has not been isolated). The V.D.s of $SnCl_2$, $SnCl_4$, and $SnBr_4$ have been determined; it is probable that the simplest formula in every case is molecular. One or two compounds of the forms SnXX′ and $SnXX_3'$ are known, where X and X′ are different halogens. A few oxyhaloid compounds are known, and probably also one or two thiohaloid compounds. The compounds $SnBr_4$ and $SnCl_4$ combine with HBr and HCl respectively, forming acids H_2SnBr_6 and H_2SnCl_6, from which series of salts, stannibromides and stannichlorides, are derived; stannifluorides are also known. An acid $HSnCl_3$ has also been isolated, and a few stannochlorides—M^ISnCl_3 and $M^I_2SnCl_4$—are known, as also some stanno-iodides.

Tin, hydrosulphide of. The compound SnS_3H_2, which has probably been isolated, may be called hydrosulphide of tin (*v.* Tin, thio-acids and salts of, p. 733).

Tin, hydroxides of, *v.* Tin oxides and hydrated oxides, p. 725; also Tin, oxyacids and salts, p. 727.

Tin, hydroxyl chloride of, SnO.OH.Cl, *v.* *Chlor-stannic acid*, under Stannous chloride, *Properties*, p. 721.

Tin, iodides of. Two compounds are formed by combining tin and I; they correspond in composition with the two bromides and the two chlorides. The V.D.s of the iodides have not been determined, but the simplest formulæ are probably molecular.

Stannous iodide SnI_2. (*Di-iodide of tin.*) Formula probably molecular.

Preparation.—1. Tin and I are heated together in the ratio Sn:2I (1 pt. tin to 2·14 pts. I); the brown crystalline solid so formed (a mixture of SnI_2 and SnI_4) is mixed with tin filings and heated, when orange-red SnI_4 sublimes, and SnI_2 remains as a red crystalline solid mixed with particles of tin, which are easily separated (Henry, *T.* 1845. 363).—2. Conc. KIAq is added to warm conc. $SnCl_2Aq$; the yellow crystalline pp. is dried and melted, out of contact with air, and a red crystalline mass of SnI_2 is formed on cooling (Boullay, *A. Ch.* [2] 34, 372).—3. Tin foil is heated for some hours with fairly conc. HIAq in a sealed tube at 120°–150° (Wöhler a. Dünhaupt, *A.* 86, 374); SnI_2 separates, on cooling, in shining yellow-red prisms.

Properties and Reactions.—A red, crystalline solid. Melts at 316° (Carnelley a. Williams, *C. J.* 35, 564). Slightly soluble in cold, more soluble in hot, water, without decomposition (Boullay, *l.c.*). According to Personne (*C. R.* 54, 216), SnI_2 is decomposed by a large quantity of water, forming HIAq and several oxyiodides (*q. v.*). SnI_2 is soluble in $SnCl_2Aq$. When heated out of contact with air, SnI_2 melts without decomposition, but when heated in the air it is decomposed to an oxyiodide, which remains in the vessel, and SnI_4, which sublimes.

Combinations.—1. With *stannous chloride* to form $SnI_2.SnCl_2$ (*v. Iodochloride, infra*).—2. With *stannous oxide* to form several oxyiodides (*q. v.*).—3. With *ammonia*, probably forming $SnI_2.2NH_3$ (Rammelsberg, *P.* 48, 169).—4. With *alkali iodides* and with *iodides of the alkaline earth metals* to form *stanno-iodides*; these salts have the composition $M_2SnI_4.xH_2O$ and $MSnI_3.xH_2O$, corresponding with the stanno-chlorides (*v.* Stannous chloride, *Combinations*, p. 722); $M = NH_4$, K, Na, also $\frac{1}{2}$Ba and $\frac{1}{2}$Sr. The stanno-iodides are formed by mixing solutions of the constitutent salts, or by adding $SnCl_2Aq$ to excess of the alkaline iodide in solution; the salts must be crystallised from alcohol, as they are decomposed by water, forming stannous oxy-iodides (*v.* Boullay, *l.c.*; Personne, *l.c.*).

Stannic iodide SnI_4. (*Tetra-iodide of tin.*) Formula probably molecular. This compound is probably formed by heating tin with 4·2 pts. I, and subliming from the product (Henry, *T.* 1845. 363). Schneider (*P.* 127, 624) recommends to add 6 pts. CS_2 to 1 pt. tin filings, and then to add gradually, cooling frequently, 4 pts. I, and to allow the yellow liquid to evaporate.

SnI_4 crystallises in orange-red octahedra; melts at 146°, sublimes at 180°, and boils at 295° (Personne, *C. R.* 54, 216). S.G. 4·696 at 11° (Bödeker, *Die Beziehungen zwischen Dichten u. Zusammensetzung bei festen u. liquiden Stoffen* [Leipzig, 1860]). Solubility in CS_2 at 15° = 145 (Schneider, *l.c.*); it is also soluble in $CHCl_3$, EtOH, Et_2O, and C_6H_6. Decomposed by water to $SnO_2.xH_2O$ and HIAq. Combines with ammonia to form $SnI_4.xNH_3$, where $x = 3$, 4, and 6 (Personne, *l.c.*), also = 8 (Rammelsberg, *P.* 48, 169). SnI_4 is said not to combine with alkali iodides.

Tin, iodochloride of, SnICl ($= SnI_2.SnCl_2$). According to Henry (*T.* 1845. 363) the addition of I to conc. $SnCl_2Aq$ causes ppn. of SnI_2, and on evaporating the mother-liquor (which contains $SnCl_2$, $SnCl_4$, and SnI_2) straw-yellow crystals are deposited that have the composition $SnI_2.SnCl_2$. The crystals are decomposed by water, with separation of SnI_2.

Tin, iodosulphide of, *v.* TIN THIO-IODIDE, p. 733.

Tin, oxides and hydrated oxides of. Two oxides have been isolated, SnO and SnO_2; various compounds of these oxides with H_2O seem to exist, but their composition readily undergoes change with variation of temperature. Both oxides interact with acids to form corresponding salts, SnX_2 and SnX_4, where $X = NO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. Some of the hydrates of SnO_2 also react as weak acids, especially $SnO_2.H_2O$ ($= H_2SnO_3$), from which is derived a series of *stannates* $MSnO_3$, $M = Na_2$, Ca, Pb, &c.; and $xSnO_2.xH_2O$ ($= xH_2SnO_3$), x probably $= 5$, from which a series of *metastannates*, $xMSnO_3$ is derived. Stannic and metastannic acids and salts derived from them are described under the heading TIN OXYACIDS AND SALTS AND DERIVATIVES THEREOF (p. 727). The oxides SnO and SnO_2 are described in this section of the article TIN, and a brief account is also given of the experiments on the hydrates of these oxides other than stannic and metastannic acids.

When tin is strongly heated in air or oxygen a film forms on the surface consisting of SnO and SnO_2; at a full red heat, or incipient white heat, tin burns to SnO_2. According to Vignon (*C. R.* 107, 734), tin ppd. by zinc from neutral $SnCl_2Aq$ or $SnCl_4Aq$ oxidises easily in air; after being exposed to the air for some days it contains from 20 to 33 p.c. SnO. Emich (*M.* 14, 345) found that the surface of tin that was kept molten in the air became covered with crystalline nodules of SnO_2.

STANNOUS OXIDE SnO. (*Protoxide of tin.*) Mol. w. not known.

Formation.—1. By heating finely-divided tin in the air; the metal becomes covered with a film of SnO (Vignon, *C. R.* 108, 96). Also by exposing tin ppd. by zinc from $SnCl_2Aq$ or $SnCl_4Aq$ to the air at ordinary temperatures (V., *C. R.* 107, 734).—2. By dehydrating $SnO.xH_2O$, ppd. from $SnCl_2Aq$ by alkali carbonates, either by heating in a stream of CO_2, or by boiling with water containing a little KOH.—3. By dissolving $SnO.xH_2O$ in cold KOHAq, and allowing the solution to stand in the air (Ditte, *A. Ch.* [5] 27, 145).—4. By heating SnC_2O_4 in a tube of hard glass without free access of air (Liebig, *A.* 95, 116).—5. By ppg. a stannous salt by KCNAq, and boiling the pp. for some days with KCNAq (Varenne, *C. R.* 89, 360).

Preparation.—$SnCl_2Aq$ is ppd. by Na_2CO_3Aq, the white pp. of $SnO.H_2O$ is thoroughly washed with cold water, and is then boiled with water containing a little KOHAq or NaOHAq (less than sufficient to dissolve the pp.), when the $SnO.xH_2O$ is gradually dehydrated, and small black, lustrous crystals of SnO are obtained (Fremy, *A. Ch.* [3] 12, 460).—2. Tin is dissolved in warm HClAq, the solution is evaporated, in contact with tin, until it solidifies to $SnCl_2$ on cooling; 7 parts, or rather more, $Na_2CO_3.10H_2O$ are then added for each part of $SnCl_2$ in the basin, and the liquid thus formed is heated with constant stirring until it becomes black, and is then allowed to cool; the brownish-black powder, SnO, thus obtained is thoroughly washed with cold water, and dried at 100° (Sandall, *J. pr.* 14, 254).—3. A solution of $SnCl_2$ is ppd. by a slight excess of KOHAq in the cold, the pp. is thoroughly washed and dissolved in cold KOHAq (c. 1 part KOH in 10 parts H_2O); the solution, which should be saturated with $SnO.xH_2O$, is allowed to stand in the air, when SnO is gradually ppd. as small, blue-black, shining crystals (Ditte, *A. Ch.* [5] 27, 145).

Properties and Reactions.—Prepared by any of the methods described above, SnO forms small, black, lustrous, regular crystals (for crystalline form *v.* Nordenskjöld, *P.* 114, 612). S.G. 6·1 (N., *l.c.*); 6·6 at 0° (Berzelius; Ditte, *A. Ch.* [5] 27, 145).

According to Fremy (*A. Ch.* [3] 12, 460), another modification of SnO is obtained by heating the black crystals (prepared by the first process given above) to 258°; the crystals are said to swell up and change into soft, olive-green laminæ, without any change in weight.

By evaporating very dilute NH_4ClAq, holding $SnO.xH_2O$ in suspension, until NH_4Cl began to crystallise, Fremy (*A. Ch.* [3] 12, 460) obtained a cinnabar-red powder, which he took to be a third form of SnO. Retl (*A.* 60, 214) obtained red, crystalline SnO by digesting $SnO.xH_2O$, at 56°, with a solution of $SnO.xH_2O$ in acetic acid; the solution containing a little free acetic acid, and having S.G. 1·06.

For the S.G. and appearance of SnO prepared in various ways *v.* also Ditte (*l.c.*).

SnO is unchanged in air at ordinary temperatures. According to Ditte (*A. Ch.* [5] 27, 145), SnO that separates from an alkaline solution is unchanged at 300°–310°; when heated to redness it is partly decomposed to Sn, and SnO_2 which combines with unchanged SnO to give $2SnO.SnO_2$. SnO is readily converted into SnO_2 by heating with oxidising agents; the change is effected by heating to 500° in NO (Sabatier a. Senderens, *C. R.* 114, 1429). SnO dissolves in acids to form stannous salts, SnX_2, $X = NO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; it is not acted on by NH_3Aq; boiled with fairly conc. KOHAq or NaOHAq it gives a solution of an alkali stannate (M_2SnO_3) and tin; heated in Cl forms $SnCl_4$ and SnO_2; mixed with S and strongly heated, SnS_2 and SO_2 are produced; SnO is reduced to tin by heating to redness in H or with C.

HYDRATED STANNOUS OXIDE. The white pp. formed by adding an alkali carbonate to solution of a stannous salt, washing with air-free cold water, and drying at a temperature not above 80°, is said to have the composition $2SnO.H_2O = Sn_2O(OH)_2$. According to Ditte (*A. Ch.* [5] 27, 145) the pp. formed by adding KOHAq or NaOHAq to $SnCl_2Aq$, washing thoroughly, and drying *in vacuo* at 14° is $SnO.2H_2O$ ($= SnO_2H_2.H_2O$). Stannous hydroxide is a yellowish white amorphous powder. It is dehydrated, to SnO, by heating in CO_2; also by the action of boiling water containing a little KOH, or a trace of HCl, or acetic acid—HNO_3Aq and H_2SO_4Aq form stannous salts; also by boiling with NH_4ClAq (Ditte, *l.c.*). The hydroxide is gradually oxidised by exposure to air to $SnO_2.xH_2O$. Boiled with conc. KOHAq it gives K_2SnO_3Aq and tin. Many metallic salts are reduced, to lower salts or to the metals, by the action of $SnO.xH_2O$ (for details of the interaction with CuO in presence of alkali *v.* Lenssen, *J. pr.* 89, 90).

STANNIC OXIDE SnO_2. (*Dioxide of tin.*) Mol.

is unknown; probably at least $Sn_{10}O_{20}$ (*v.* Carnelley a. Walker, *C. J.* 53, 92).

Occurrence.—Tinstone is more or less pure SnO_2; the percentage of the oxide varies from c. 85 to c. 99, the other constituents are generally SiO_2, and oxides of Al, Fe, and Mn. Tinstone crystallises in quadratic forms. Crystalline SnO_2 has been found in the fused slag from a furnace used for casting gun-metal (Abel, *C. J.* 10, 119).

Formation.—1. By exposing molten tin to the action of the air (Emich, *M.* 14, 345).—2. By heating to c. 600° $SnO_2.xH_2O$ formed by the interaction of tin and HNO_3Aq, or of alkalis and stannic salts, or of alkali stannates and dilute acids.—3. By strongly heating SnO or $SnO.xH_2O$.—4. By passing a mixture of vapour of $SnCl_4$ and steam through a red-hot tube.—5. By heating SnC_2O_4, in small quantities, in contact with the air (Vogel, *C. C.* 1855. 413).—6. By passing a little CO_2 into a dilute solution of an alkali stannate (Ditte, *A. Ch.* [6] 30, 282).

Preparation.—A. Crystalline stannic oxide.—1. Molten tin is kept in contact with the air until the surface becomes covered with crystalline nodules of SnO_2 (Emich, *M.* 14, 345). 2. A stream of CO_2 is passed through $SnCl_4$, and then through a red-hot porcelain tube through which a current of steam is passed at the same time (Daubrée, *C. R.* 29, 227).—3. Amorphous SnO_2 is strongly heated in a rapid current of dry HCl (Deville, *C. R.* 53, 161).—4. SnC_2O_4 is strongly heated, in small quantities at a time, in an open porcelain or silver dish (Vogel, *C. C.* 1855. 413).

B. Amorphous stannic oxide.—5. The hydrated stannic oxide obtained by ppg. a stannic salt by an alkali, decomposing an alkali stannate solution by dilute acid, or by treating tin with HNO_3Aq, is thoroughly washed and dried, and then heated to c. 630°, at which temperature dehydration is complete (Carnelley a. Walker, *C. J.* 53, 83).

Properties.—Crystalline stannic oxide is a hard, lustrous, white solid. It is dimorphous. Prepared by heating the amorphous oxide in HCl gas, SnO_2 crystallises in quadratic forms isomorphous with *tinstone* and *anatase* (TiO_2) (Daubrée, *C. R.* 29, 227); prepared by decomposing vapour of $SnCl_4$ by steam, it crystallises in trimetric prisms isomorphous with *brookite* (TiO_2). S.G. of crystalline SnO_2 = 6·7 to 6·85 (Playfair a. Joule, *C. J.* 1, 137; Mallet, *J.* 3, 705; Bergemann, *J.* 10, 661; Daubrée, *C. R.* 29, 227). The crystals obtained by long continued heating molten tin in air had S.G. 7·0096 at 4° (Emick, *M.* 14, 345). Crystalline SnO_2 is hard enough to scratch glass. The amorphous oxide has S.G. 6·6 to 6·9 (P. a. J., *l.c.*; Herapath, *P. M.* 64, 321; Boullay, *A. Ch.* [2] 43, 266). It is a hard, yellowish-white powder. SnO_2 has not been fused. It is not acted on by acids (but *v. Reactions*, No. 6). Fusion with KOH or NaOH forms M_2SnO_3 which dissolves in water. The product of fusion with $KHSO_4$ dissolves in water, but addition of more water ppts. all the tin as $SnO_2.xH_2O$.

Mallet (*C. J.* 35, 524) obtained a compound $SnO_2.HCl$, to which he gave the formula SnO.OH.Cl, and the name *chlor-stannic acid*, by keeping $SnCl_4$ for a year or two in a loosely closed bottle.

Reactions.—1. Fusion with *sulphur* produce SnS_2 and SO_2.—2. When strongly heated i *chlorine* $SnCl_4$ is formed.—3. SnO_2 is reduced t tin by heating to a high temperature in *hydrogen*, or with *potassium*, *sodium*, or *carbon*, or i *carbonic oxide*.—4. Fusion with *caustic potash* o *caustic soda* forms alkali stannate (M_2SnO_3), which dissolves in water.—5. Heating with *phosphorus trichloride* to 160° forms $SnCl_2$, $SnCl_4$, and P_2O_5 (Michaelis, *J. Z.* 6, 239; 7, 110).—6. According to Ditte (*C. R.* 104, 172), SnO_2 dissolves very slowly in hot *sulphuric acid* (1 acid to 8 water), and on concentrating till not more than 3 or 4 vols. water are present to 1 vol. H_2SO_4 crystals of $SnO_2.2H_2SO_4$ separate.

HYDRATED STANNIC OXIDE. Carnelley a. Walker (*C. J.* 53, 60, 68, 83) examined the dehydrating action of heat on $SnO_2.xH_2O$, obtained by decomposing Na_2SnO_3Aq by cold dilute HClAq and drying the pp. in the air for five months. The pp. lost less and less weight for each increase of c. 10° from 50° to c. 110°, at which temperature rather less water was present than corresponded with the formula $SnO_2.H_2O$, the loss of weight for each rise of 10° was then approximately constant up to c. 360°, at which temperature the composition was nearly that required by the formula $3SnO_2.H_2O$; at a little above 360° the solid changed colour from brown to pale yellow, and at the same time lost weight at a rate nearly three times as great as during the previous rise of 100°; after changing colour the solid had the composition $7SnO_2.2H_2O$; the loss of weight, per 10° increase, then decreased very much for the next 30° or 40°, and after that dehydration continued irregularly until at 630°–635° the oxide SnO_2 remained. From these results, considered with results obtained by the same method for other hydrated oxides, C. a. W. concluded that probably a large number of hydrates of SnO_2 exists, but that none of these is stable through more than a very small range of temperature. The results of J. van Bemmelen (*B.* 13, 1466) on the dehydration by heat of stannic hydrates, obtained by oxidising tin by HNO_3Aq, and by decomposing $SnCl_4Aq$ by $CaCO_3$, and on the rehydration of the products obtained by heat, by placing them in air more or less saturated with moisture, at different temperatures, show that the quantity of water of hydration varies with variations in temperature, in the molecular states of the solids, and in the moistness of the surrounding air. Not only does the quantity of water of hydration vary with variations in the molecular state of the hydrates, but the firmness or looseness wherewith the water is held also varies much as the molecular condition varies. According to J. van B. the loosely held water is given up in dry air; and when the product is placed in moist air water is taken up until a state of equilibrium is attained wherein as many molecules of water are taken up as are lost in the unit of time.

The following compositions have been given to different hydrates of SnO_2.

I. *Hydrates obtained by decomposing soluble stannates by dilute acids*: (1) $8SnO_2.7H_2O$, by drying in a stream of dry air (Fremy, *A. Ch.* [3] 12, 462); (2) $SnO_2.2H_2O$, by drying in the air at the ordinary temperature (Weber, *P.* 122, 358); (3) $SnO_2.H_2O$, by drying *in vacuo* (Fremy, *l.c.*); (4) $8SnO_2.2H_2O$, by drying at 140° (Fremy, *l.c.*); to these should probably be added (5) $7SnO_2.2H_2O$, by drying at c. 365° (Carnelley a. Walker, *l.c.*).

II. *Hydrates obtained by oxidising tin by* HNO_3Aq: (6) $5SnO_2.10H_2O$, by drying at the ordinary temperature (Fremy, *l.c.*); (7) $5SnO_2.5H_2O$, by drying at the ordinary temperature (Thomson, *Ann. Phil.* 1817. 149), by drying over H_2SO_4 (Weber, *l.c.*), by drying *in vacuo*, or at 100° (Fremy, *l.c.*); (8) $5SnO_2.4H_2O$, by drying at 130° (Fremy, *l.c.*); (9) $5SnO_2.3H_2O$, by drying at 160° (Fremy, *l.c.*); (10) $2SnO_2.H_2O$, by drying at 55° (Thomson, *l.c.*).

The hydrates obtained by decomposing stannates by dilute acids, or by ppg. stannic salts by $CaCO_3$ or $BaCO_3$, differ in properties from the hydrates obtained by oxidising tin by HNO_3Aq; the former are generally distinguished as *stannic hydrates*, and the latter as *metastannic hydrates*. The stannic hydrates, dried in air, form hard, semi-transparent lumps, like gum arabic; soluble in the stronger acids, forming stannic salts SnX_4, where $X = NO_3, \frac{1}{2}SO_4$, &c.; soluble in alkali solutions, forming stannates $M^{I}_2SnO_3$ (*v. Stannates*, under TIN OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, *infra*). Metastannic hydrates are white solids (? crystalline) that do not dissolve in HNO_3Aq, or H_2SO_4Aq (*v. infra*). These hydrates interact with HClAq, and the product is soluble in water but insoluble in conc. HClAq; according to Weber (*P.* 122, 358), the solution gives $SnCl_4.3SnO_2.5H_2O$, when evaporated over H_2SO_4; by prolonged boiling, with fresh additions of water, all the tin in the solution is ppd. as metastannic hydrate (Fremy, *A. Ch.* [3] 12, 463; 23, 393). Metastannic hydrates dissolve in KOHAq and NaOHAq, forming metastannates $M_2H_8Sn_5O_{15}$ (*v. Metastannates*, under TIN OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 730).

According to Ditte (*C. R.* 104, 172), both stannic and metastannic hydrates dissolve in warm H_2SO_4Aq (1 part acid and 8 parts water), and on concentrating till not more than 3 to 4 vols. water are present to 1 vol. H_2SO_4 the solution deposits white crystals of $SnO_2.2H_2SO_4$: these crystals are very deliquescent; they are decomposed by water; if so much water is added that not more than 43 g. H_2SO_4 are present in 1,000 c.c. of the liquid, a pp. of $SnO_2.xH_2O$ is formed. By dissolving stannic or metastannic hydrate in warm H_2SeO_4Aq, and concentrating, D. (*l.c.*) obtained crystals of $SnO_2.2H_2SeO_4$.

For further details of reactions of stannic and metastannic hydrates *v.* TIN OXYACIDS, AND SALTS AND DERIVATIVES THEREOF (*infra*).

OXIDES OF TIN OTHER THAN STANNOUS AND STANNIC OXIDES. Oxides which are most simply regarded as $xSnO.ySnO_2$ seem to exist.

According to Fuchs (*J. pr.* 5, 318), a greyish-white, slimy solid, having the composition $SnO.SnO_2 (= Sn_2O_3)$, is obtained by diffusing freshly ppd. $Fe_2O_3.xH_2O$ in $SnCl_2Aq$ free from acid, and boiling

$$(2SnCl_2Aq + Fe_2O_3 = SnO.SnO_2 + 2FeCl_2Aq).$$

This oxide is said to dissolve completely in NH_3Aq, and also in HClAq.

By digesting $SnO_2.xH_2O$, ppd. by alkali from $SnCl_4Aq$, with $SnCl_2Aq$, Schiff (*A.* 120, 53) obtained an orange-yellow solid, to which he gave the composition $SnO.6SnO_2.5H_2O$; by digesting $SnO_2.xH_2O$, formed by oxidising tin with HNO_3Aq, with $SnCl_2Aq$ Schiff (*l.c.*) obtained a yellow powder, said by him to be $SnO.6SnO_2.9H_2O$, or when dried at 85° to be $SnO.6SnO_2.4H_2O$ (*v.* also Tschermak, *C. C.* 1862. 305).

PURPLE OF CASSIUS. A purple-coloured solid is obtained by adding solution of a stannous salt to dilute $AuCl_3Aq$; this solid has been examined by many chemists, who have generally assigned to it formulæ which represent it as a compound of SnO_2, sometimes of $SnO.SnO_2$, and AuO. According to the most recent investigations the composition varies according to the conditions of preparation, and all that can be said with certainty is that the purple solid is a compound of tin, gold, and oxygen (*v.* Buisson, *J. Ph.* 16, 629; Bohlen, *Ar. Ph.* 57, 277; Capaun, *J. pr.* 22, 153; Fuchs, *J. pr.* 5, 318; Wächter, *A.* 68, 116; Figuier, *Ph. C.* 1844. 724; Debray, *C. R.* 100, 1035; Müller, *J. pr.* [2] 30, 252; and, for a bibliography (to 1866), Fischer, *D. P. J.* 182, 39).

Tin oxyacids, and salts and derivatives thereof. Some of the hydrates of SnO_2 interact with alkalis to produce salts wherein tin forms part of the acidic radicle; compounds are also known the acidic radicles whereof contain tin in combination with other negative elements besides oxygen, or tin in combination with both metallic and nonmetallic elements.

The reactions of the hydrates of SnO_2 ppd. from solutions of stannates by dilute cold acids, or ppd. from stannic salts by alkalis, are distinctly different from the reactions of the hydrates of SnO_2 obtained by oxidising tin by HNO_3Aq, or by ppn. by dilute acids from solutions of another class of salts which have the same composition as stannates, except that they always contain H and O in the ratio 2H:O in addition to the constituents of stannates. It is therefore usual to distinguish the acidic hydrates of SnO_2 as *stannic* and *metastannic acids*; to the former is given the composition $H_2SnO_3 (= SnO_2.H_2O)$, and to the latter the composition $H_{10}Sn_5O_{15} (= 5SnO_2.5H_2O)$. Neither of these formulæ is to be regarded as more than an attempt to connect the differences in the chemical behaviour of two compounds having identical percentage compositions (if the H_2O in one class is omitted) with differences in the complexities of their interacting atomic aggregates; the molecular weight of neither compound is known. It is, indeed, doubtful whether a compound with the composition xH_2SnO_3 can exist apart from other hydrates of the composition $ySnO_2.zH_2O$; it is certain that the composition of the hydrates of SnO_2 varies with very small variations of temperature, by whatever methods these hydrates are prepared (*v.* p. 726, HYDRATED STANNIC OXIDE).

That the hydrates of SnO_2, obtained respectively by ppg. solution of stannates by dilute acids and by oxidising tin by HNO_3Aq, differed in their reactions, was noticed by Berzelius in 1811 (*v. Lehrbuch* [5th ed.] 2, 596). Berzelius regarded these compounds as hydrates of two different modifications of stannic oxide; he called the oxide supposed to be a constituent of the hydrates obtained by ppg. solutions of stannates ***stannic oxide***, and designated it as $aSnO_2$; the other oxide he called *metastannic oxide*, and designated it as $bSnO_2$. Gmelin called the hydrate from stannates *ordinary stannic acid*, and the other hydrate *abnormal stannic acid.*

STANNIC ACID H_2SnO_3.

Preparation.—By adding cold dilute HClAq to an aqueous solution of K_2SnO_3, prepared by fusing SnO_2 with KOH, or by heating tin with KOH and KNO_3 (*v.* POTASSIUM STANNATE, p. 730), a gelatinous pp. is obtained which, when washed and dried *in vacuo*, has the composition $SnO_2.H_2O = H_2SnO_3$ (Fremy, *A. Ch.* [3] 12, 463). The same hydrate is formed, according to F. (*l.c.*), by adding $CaCO_3$ or $BaCO_3$ to excess of $SnCl_4Aq$, washing, and drying *in vacuo.* (For details regarding the results obtained by different chemists who have examined the compositions of the stannic hydrates, *v.* HYDRATED STANNIC OXIDE, p. 726). Graham (*T.* 1861. 213) obtained colloidal stannic acid (no analyses are given) by dissolving $SnO_2.xH_2O$ ppd. from a stannic salt (? by alkali from $SnCl_4Aq$) in $SnCl_2Aq$, and dialysing until all the Cl had passed into the dialysate. Colloidal forms of stannic acid are also obtained (1) by dialysing a solution of the ppd. acid in HClAq or in an alkali; (2) by the action of CO_2, or of air, on an alkaline solution of the ppd. acid (J. van Bemmelen, *R. T. C.* 7, 87; *abstract* in *C. J.* 54, 1160 [1888]; the results of experiments on the dehydration of the colloidal acid are given).

Properties and Reactions.—A gelatinous, amorphous solid, drying (in air or *in vacuo*) to hard, semi-transparent lumps, like gum arabic. Reddens litmus paper. Vignon (*C. R.* 108, 1049) found that the heat of neutralisation, by KOHAq, of stannic acid formed by ppg. $SnCl_4Aq$ by KOHAq, decreased when the ppd. acid was kept in contact with water for some days, and decreased more rapidly when the acid was heated with water in a sealed tube for some hours. J. van Bemmelen (*J. pr.* [2] 23, 324) found that when stannic acid is shaken with solutions of HCl, or H_2SO_4, or with solutions of certain salts, such as KCl or K_2SO_4, a definite number of molecules of the acid or salt is taken up by the stannic acid so as to form a loose combination therewith; and that the number of molecules thus absorbed varies with the proportion between the quantities of stannic acid and the acid or salt in the solution used, and also with the concentration of the solution used. The loose compounds thus formed are called *absorption-compounds* by J. van B. Dissolves in the stronger acids (HNO_3, H_2SO_4, HCl, &c.). According to Ditte (*C. R.* 104, 172), when a solution of stannic acid in warm H_2SO_4Aq (1 part acid to 8 parts water) is evaporated until not more than 3 to 4 vols. water are present to 1 vol. H_2SO_4, and allowed to cool, it yields white deliquescent crystals of $SnO_2.2H_2SO_4$; and a solution of stannic acid in warm H_2SeO_4Aq yields a similar crystalline compound $SnO_2.2H_2SeO_4$. Dissolves in excess of caustic alkali solutions, forming stannates (*q. v.* p. 730) M_2SnO_3. According to J. van. B. (*l.c.*) colloidal stannic acid does not form any compound when shaken with dilute cold KOHAq, but only complex molecular aggregates, the composition of which varies considerably with temperature and concentration. Stannic acid, dried at the ordinary temperature by pressure, is gradually changed to metastannic acid by heat; the change begins at c. 55° (J. van B., *l.c.*; *v.* also *infra*, *Change of stannic to metastannic acid, and vice versâ*). For other reactions of stannic acid *v. infra*, *Distinctions between stannic and metastannic acids.*

METASTANNIC ACID $H_{10}Sn_5O_{15}$.

Preparation.—Tin, in thin pieces or granulated, is heated with HNO_3Aq, S.G. c. 1·35, until the metal is converted into a greyish-white powder, which is washed with dilute HNO_3Aq, and then with water, and dried. The solid is said to have the composition $H_{10}Sn_5O_{15}$ ($= 5SnO_2.5H_2O$) when dried *in vacuo* (Fremy, *A. Ch.* [3] 12, 463), when dried over H_2SO_4 (Weber, *P.* 122, 358), or when dried at the ordinary temperature (Thomson, *Ann. Phil.* 1817. 149). For details of the results obtained by different chemists who have examined the compositions of the metastannic hydrates *v.* HYDRATED STANNIC OXIDE (p. 726); *v.* also J. van Bemmelen, *R. T. C.* 7, 87 (*abstract* in *C. J.* 54, 1160 [1888]). It should be noted that the empirical formula assigned to metastannic acid dried *in vacuo* (Fremy), or dried over H_2SO_4 (Weber), is the same as that assigned to stannic acid dried *in vacuo* (Fremy); this formula is $SnO_2.H_2O$. The different reactions of the two compounds show that if both have the same empirical formula one must be an isomeride or a polymeride of the other. Metastannic acid is also obtained by decomposing an aqueous solution of the sodium salt (*v.* p. 730, *Metastannates*) by boiling. Graham (*T.* 1861. 213) obtained colloidal metastannic acid by adding a little HClAq to the acid obtained by the action of HNO_3Aq on tin, dissolving the solid so formed in water, and dialysing. Vignon (*C. R.* 108, 1049) found that the heat of neutralisation of metastannic acid by KOHAq decreased when the acid was dried at 110°, and decreased very considerably when the acid was heated with water, for some hours, at 250° in a sealed tube.

Properties and Reactions.—A white powder. Insol. in nitric acid. Contact with conc. HClAq for a short time produces a compound (according to J. van Bemmelen, *R. T. C.* 7, 87; *abstract* in *C. J.* 54, 1160 [1888], no definite compound is formed, but only complex molecular aggregates of metastannic acid and HCl) which dissolves in water, but is insol. in HClAq. According to Barfoed (*J. pr.* 101, 268), the compound with HCl is quite insol. in HClAq S.G. 1·1, and may be purified by washing with acid of that concentration. The solution of this substance in water gives off HCl and H_2O, with a very little $SnCl_4$, when distilled; and metastannic acid separates out (Fremy, *A. Ch.* [3] 12, 463; 23, 393; H. Rose, *A.* 68, 272). Evaporation of the aqueous solution over H_2SO_4 is said to give an oxychloride $3SnO_2.SnCl_4.5H_2O$ (Weber, *P.* 123, 358). Metastannic hydrate dissolves in conc. HClAq after prolonged boiling, forming $SnCl_4$ solution (Löwenthal, *J. pr.* 77, 321). Barfoed (*l.c.*) says that conc. HClAq gradually converts recently ppd. and moist metastannic acid into stannic acid, and that the quantity of metastannic acid thus changed increases with the quantity of conc. HClAq, the time of contact, and the temperature. J. van Bemmelen (*J. pr.* [2] 23, 324) found that metastannic acid forms *absorption compounds* with HCl, H_2SO_4, KCl, K_2SO_4, &c.

(*cf.* Stannic acid, *Properties*, p. 728). For other reactions of the solution in water of the product of the action of HClAq on metastannic acid *v. infra*, *Distinctions between stannic and metastannic acids*. According to Ditte (*C. R.* 104, 172), metastannic acid dissolves in warm H_2SO_4Aq (1 pt. acid to 8 pts. water), forming a solution which gives crystals of $SnO_2.2H_2SO_4$ when evaporated until not more than 3 to 4 vols. water are present for one vol. H_2SO_4; the crystals are decomposed by water, with ppn. of $SnO_2.xH_2O$ (?metastannic hydrate), when sufficient water is added to insure that not more than 43 g. H_2SO_4 are present in 1,000 c.c. of the liquid. A similar compound was obtained with selenic acid, viz. $SnO_2.2H_2SeO_4$ (D., *l.c.*). Allen (*C. J.* 25, 274) found that metastannic acid dissolved in boiling conc. H_2SO_4, forming $Sn(SO_4)_2$ solution; by pouring this solution into water some of the tin was ppd., after a time, as stannic acid, but on boiling the whole of the tin came down as metastannic acid. Metastannic acid is said to dissolve slowly in fairly dilute cold KOHAq or NaOHAq; addition of conc. KOHAq or NaOHAq is said to ppt. K or Na metastannate; when the solution in KOHAq or NaOHAq stands in the air metastannic acid gradually deposits. According to J. van Bemmelen (*l.c.*), colloidal metastannic acid does not form any definite compound with KOH when shaken with KOHAq of different concentrations. By fusing metastannic acid with $KHSO_4$ or $NaHSO_4$, Allen (*C. J.* 25, 274) obtained a product which dissolved partially in water; the aqueous solution gave a pp. of metastannic acid on boiling.

Distinctions between stannic and metastannic acids (*v.* Fremy, *A. Ch.* [3] 12, 462; 23, 393; H. Rose, *P.* 75, 1; 105, 561; Löwenthal, *J. pr.* 77, 321; Barfoed, *J. pr.* 101, 368; J. van Bemmelen, *R. T. C.* 7, 87; *abstract* in *C. J.* 54, 1160 [1888]).—Stannic acid is soluble in dilute HNO_3Aq, H_2SO_4Aq, or HClAq; metastannic acid is insol. in these acids. Cold conc. HClAq dissolves stannic acid, and the solution gives the reactions of $SnCl_4$; cold conc. HClAq forms a compound (?molecular aggregates) with metastannic acid, which is insol. HClAq of S.G. 1·1, or greater S.G., but dissolves in cold water.

The following reactions apply to solutions of stannic acid in HClAq on the one hand, and to solutions in water of the substance formed by the action of HClAq on metastannic acid on the other hand. Stannic acid solution, if conc., does not become turbid on boiling; long continued boiling, with additions of water, ppts. all the acid. Metastannic acid solution, even when conc., goes turbid on boiling; long-continued boiling, accompanied by dilution, ppts. all the acid. Stannic acid solution, when distilled, gives off H_2O, with a little HCl and $SnCl_4$; and a little stannic acid separates. According to Barfoed (*J. pr.* 101, 368), when a solution of stannic acid in HClAq S.G. 1·1 is distilled, the whole of the tin passes over as $SnCl_4$. Metastannic acid solution, when distilled, gives off H_2O, with some HCl and a very little $SnCl_4$, and the meta- acid separates in the retort. Addition of tartaric acid to the stannic solution, followed by gradual addition of NH_3Aq, excess of NH_3Aq being avoided, produces no pp. Treatment of the metastannic solution with tartaric acid and NH_3Aq (not in excess) ppts. the meta- acid. $SnCl_4$Aq gives no pp. with the stannic solution; $SnCl_2$Aq gives a yellowish pp. (? $SnO.6SnO_2.9H_2O$) with the metastannic solution. Addition of dilute H_2SO_4Aq to the stannic solution produces no pp., unless the stannic solution is very much diluted. Dilute H_2SO_4Aq produces a pp. even in very dilute metastannic solution; by washing this pp. with hot water, metastannic acid remains (*cf.* Ditte's experiments are described under both Stannic acid and Metastannic acid, pp. 728, 729). The stannic solution is not ppd. by conc. HClAq. The metastannic solution, if nearly neutral, is ppd. by conc. HClAq. Addition of K_4FeCy_6Aq to the stannic solution, in the ratio $K_4FeCy_6:Sn$ present, ppts. all the tin as $SnFeCy_6$. To ppt. all the tin from the metastannic solution, the K_4FeCy_6Aq must be added in c. the ratio $19K_4FeCy_6:Sn$ present; the pp. is not $SnFeCy_6$, it is said by some observers to be metastannic acid; J. van B. (*l.c.*) calls it an *absorption compound* of metastannic acid and K_4FeCy_6. The stannic solution gives no pp. with excess of fairly conc. NaOHAq. The metastannic solution is completely ppd., as sodium metastannate, by excess of fairly conc. NaOHAq.

Change of stannic to metastannic acid and vice versâ. A solution of stannic acid in HClAq gradually changes to metastannic acid; the change is the more rapid and complete the more dilute the solution (H. Rose, *l.c.*; Barfoed, *l.c.*); by boiling for some time with repeated additions of water the whole of the stannic acid may be converted into metastannic acid. A very conc. solution of stannic acid in HClAq remains unchanged (*cf.* reaction of meta- acid with conc. HClAq, *infra*). According to Löwenthal (*l.c.*), the change from stannic to metastannic acid is stopped by addition of tartaric acid, even when the solution of stannic acid in HClAq is dilute; the amount of change to the meta- acid may be determined (according to L., *l.c.*) by finding the quantity of K_4FeCy_6Aq required to completely ppt. the tin in solution. Barfoed (*l.c.*) says the best way to measure the amount of change is to add excess of fairly conc. NaOHAq, which ppts. all the meta- acid (as a sodium salt) but none of the stannic acid.

Stannic acid is converted into the meta- acid by heat (H. Rose, *l.c.*). J. van Bemmelen (*l.c.*) found that stannic acid dried by pressure at the ordinary temperature is completely soluble in conc. HClAq, but that by heating to c. 55°, or by heating with water to below 100°, some metastannic acid is formed which is insoluble in conc. HClAq.

A solution of stannic acid in excess of KOHAq gradually deposits metastannate of K on exposure to air, with formation of K_2CO_3Aq.

Metastannic acid is gradually changed to stannic acid, according to Barfoed (*l.c.*), by contact with conc. HClAq; the quantity of stannic acid produced increases with the quantity of HClAq used, the time of contact, and the temperature.

Stannic acid is said to be obtained from the meta- acid by fusing the latter with a large excess of KOH, dissolving in water, and ppg. by cold dilute HClAq (H. Rose, *l.c.*; Fremy, *l.c.*).

Oxyacids of Tin other than Stannic and Metastannic. (1) $H_2Sn_2O_7$. Spring (*Bl.* [3] 1,

180) obtained a colloidal solid, drying at 100° to a white mass with the composition $H_2Sn_2O_7$, by adding excess of $BaO_2.xH_2O$ to a solution of $SnCl_4$ in HClAq, and dialysing the turbid liquid until $BaCl_2$ ceased to pass into the dialysate. S. regarded the new compound as an acid of the hypothetical perstannic oxide SnO_3, analogous to CeO_3, TiO_3, and (?) ZnO_2. (2) $H_4Sn_2O_6$ and $H_6Sn_3O_9$. The empirical formula of both these hydrates of stannic oxide is $SnO_2.H_2O$. According to Musculus (*C. R.* 65, 961), the hydrates differ somewhat in properties both from stannic and metastannic acids; they are said to be formed by keeping stannic acid under water, and to form K salts, $KH_3Sn_2O_6$ and $KH_5Sn_3O_9$.

Stannates, $M^{I}_2SnO_3$ and $M^{II}SnO_3$. The alkali stannates are obtained by dissolving stannic acid in MOHAq ($M = NH_4$, K, or Na), and evaporating over H_2SO_4; the stannates of the alkaline earth metals may be obtained by the interactions of solutions of the alkali stannates with MO_2H_2 or MCO_3 (M = Ba, Ca, Sr).

Ammonium stannate. A salt, said to have the composition $(NH_4)_2SnO_3.SnO_2.xH_2O$, is obtained, as a yellowish jelly, by evaporating a solution of stannic acid in NH_3Aq over H_2SO_4 (Moberg, *J. pr.* 28, 230). When K_2SnO_3Aq is added to NH_4ClAq, stannic acid is ppd. according to Ditte (*C. R.* 96, 701).

Barium stannate. The *normal salt* $BaSnO_3.6H_2O$ is said to be obtained by adding $BaCl_2Aq$ to K_2SnO_3Aq; it is described as a heavy, white powder (Moberg, *l.c.*). By adding K_2SnO_3Aq to excess of $BaCl_2Aq$, Ditte (*l.c.*) obtained a *basic salt* $BaSnO_3.BaO.10H_2O$ as lustrous leaflets.

Calcium stannate. Ditte (*l.c.*) obtained the *normal salt* $CaSnO_3.5H_2O$, in white crystals, by adding K_2SnO_3Aq to excess of $CaCl_2Aq$, washing, and drying at 100°. By heating for some hours a mixture of stannic acid and $CaCl_2Aq$, with a little CaO, D. obtained $CaSnO_3$ in regular crystals.

Potassium stannate $K_2SnO_3.xH_2O$. Prepared by dissolving stannic acid in KOHAq, or by fusing SnO_2 or metastannic acid with excess of KOH for some time and dissolving in water, and evaporating over H_2SO_4; transparent, rhombic prisms; crystallising with $4H_2O$ (Fremy, *A. Ch.* [3] 23, 393), with $3H_2O$ (Moberg, *l.c.*). Marignac (*Ann. M.* [3] 15, 277) obtained the salt, in rhombohedral crystals, by gradually heating 3 pts. metastannic acid with 8 pts. KOH till the mixture boiled, allowing to cool, dissolving in water, filtering, and evaporating. Ordway (*Am. S.* [2] 40, 173) prepared the pure salt by adding an equal volume of absolute alcohol to a solution of the commercial salt (*v. infra*), repeatedly treating the syrupy layer that separated with alcohol, drying the pasty mass so obtained by pressure, dissolving in water, evaporating *in vacuo*, and washing the crystals with alcohol. K stannate dissolves easily in water; O. (*l.c.*) gives S. at 10° = 106·6, and at 20° = 110·5; solution reacts alkaline. Insoluble in alcohol. By adding a dilute acid solution sufficient to neutralise $\frac{3}{4}$ of the alkali, a white flocculent pp. of K metastannate is said to be produced (O., *l.c.*); excess of cold dilute acid ppts. stannic acid. $K_2SnO_3.xH_2O$ is dehydrated at a red heat.

Commercial stannate of potash solution is prepared (1) by fusing tinstone with K_2S, KOH or KNO_3 and dissolving in water; (2) by boiling tinstone with KOHAq; (3) by fusing tin with KNO_3 and K_2CO_3, or boiling the metal with KOHAq containing KNO_3 and KCl (*v.* Haeffely, *D. P. J.* 144, 66; Vaughan, *B.* 5, 396; and Dictionary of Applied Chemistry, vol. iii. pp. 843–4).

Sodium stannate $Na_2SnO_3.xH_2O$. Prepared similarly to the K salt. Crystallises in hexagonal plates with $3H_2O$ (M., *l.c.*; O., *l.c.*). Marignac (*l.c.*) obtained rhombohedral crystals. Jonas (*C. C.* 1865. 607) obtained rhombic crystals of $Na_2SnO_3.9H_2O$ by recrystallising the commercial salt. Haeffely (*D. P. J.* 144, 66) obtained crystals of $Na_2SnO_3.3H_2O$ by heating an aqueous solution of S.G. 1·3; on allowing to cool again the crystals dissolved, the S.G. became 1·35, and after a time crystals of $Na_2SnO_3.8H_2O$ were deposited. Scheurer-Kestner (*Bl.* [2] 8, 839) obtained crystals of the composition $Na_2SnO_3.10H_2O$ by evaporating a dilute solution of the ordinary salt, free from excess of NaOH, at a low temperature. $Na_2SnO_3.3H_2O$ is more soluble in cold than in hot water; O. (*l.c.*) gives S. at 0° = 67·4, and at 20° = 61·3. Insoluble in alcohol. According to H. (*l.c.*), an aqueous solution of the octohydrate gives a crystalline pp. of Na metastannate when heated, or when left at the ordinary temperature for some weeks. *Commercial stannate of soda solution* is prepared similarly to the solution of the potash salt (*v. supra*).

Strontium stannate. A *basic salt* $2SrSnO_3.SrO.10H_2O$ was obtained by Ditte (*C. R.* 96, 701), in lustrous octahedra, by adding K_2SnO_3Aq to excess of $SrCl_2Aq$.

Metastannates. Only alkali metastannates have been prepared. The empirical formula of these salts is $M_2O.5SnO_2.4H_2O$; as they are decomposed by removing water, the formula is generally written as $M_2H_8Sn_5O_{15}$ (*cf.* Metastannic acid, p. 728). Metastannic acid dissolves slowly in KOHAq or NaOHAq; on adding conc. MOHAq the salts are ppd. The salts are better obtained by adding conc. MOHAq to a solution in water of the substance obtained by the interaction of metastannic acid and conc. HClAq (Barfoed, *J. pr.* 101, 368). Dilute acid solutions ppt. metastannic acid from solutions of metastannates. Metastannates heated with excess of MOH give stannates. For more details regarding $M_2H_8Sn_5O_{15}$ (M = K or Na) *v.* Fremy (*A. Ch.* [3] 23, 393); Weber (*P.* 122, 358); Haeffely (*D. P. J.* 144, 66).

ARSENIO-STANNATES. A compound $Na_2O.2As_2O_5.6SnO_2.5H_2O$ was obtained by Haeffely (*D. P. J.* 140, 290) by adding excess of HNO_3Aq to a boiling solution of Na_2SnO_3 and Na_3AsO_4, and treating the gelatinous pp. with excess of NaOHAq.

OXALO-STANNATES. The compound $2KHC_2O_4.SnO_2.5H_2O$ was obtained, in lustrous leaflets, by Péchard (*C. R.* 116, 1513) by dissolving stannic acid in hot KHC_2O_4Aq and allowing to cool.

PLATINO-STANNATES. Compounds of SnO and SnO_2 with PtO_2, derived from the acids $H_2Sn_2Pt_2O_6$ and $H_2Sn_2Pt_2O_4$ (*v.* Platino-stannates, this vol. p. 285).

PLATINO-SELENO-STANNATES *v.* this vol. p. 285.

SILICO-STANNATES. Bourgeois (*Bl.* [2] 47, 97) obtained the salt $CaO.SiO_2.SnO_2$ in monoclinic, lustrous crystals, by fusing SiO_2 and SnO_2 with excess of $CaCl_2$, and extracting with water.

In connection with stannic and metastannic acids and their derivatives, *v. Chlor-stannic acid*, under STANNOUS CHLORIDE (p. 721); TIN, OXIDES AND HYDRATED OXIDES OF (p. 725); and TIN, THIO-ACIDS AND SALTS OF (p. 735).

Tin, oxybromides of. By adding pieces of tin to the mother-liquor from $BaSnBr_6$ (*v. Stannibromides*, under STANNIC BROMIDE, p. 720). Rayman a. Preis (*A.* 223, 323) obtained colourless, prismatic crystals to which they gave the formula $Sn_3OBr_6.12H_2O$; and from the mother-liquor from this compound fine, colourless needles of $Sn_3O_2Br_8.10H_2O$ separated after a time.

Tin, oxychlorides of. According to Ditte (*A. Ch.* [5] 27, 145), when $SnO.xH_2O$, obtained by ppg. a stannous salt by NH_3Aq, is boiled with water containing a trace of $SnCl_2$, a gelatinous oxychloride is obtained having the composition $Sn_2OCl_2.6H_2O$ ($=SnO.SnCl_2.6H_2O$); and when this compound is boiled with a little more dilute $SnCl_2Aq$ another oxychloride, $Sn_5O_3Cl_4.6H_2O$ ($=3SnO.2SnCl_2.6H_2O$) is formed in small, white, pearly tablets.

The oxychloride $SnOCl_2$ is obtained, according to Scheurer-Kestner (*A. Ch.* [3] 47, 1), by evaporating $SnCl_4Aq$ at 50° to 60°; also by heating 100 pts. $SnCl_2.2H_2O$, dissolved in 50 pts. water, with HNO_3Aq containing 16 pts N_2O_5.

An oxychloride is also formed by treating metastannic acid with conc. HClAq, pouring off the excess of acid, dissolving in water, and evaporating over H_2SO_4 and CaO; to this oxychloride, which is an amorphous, white solid, Weber (*P.* 122, 358) gave the formula $Sn_4O_6Cl_4.5H_2O$ ($=3SnO_2.SnCl_4.5H_2O$). Tschermak (*W. A. B.* 44, 2) obtained a crystalline oxychloride $Sn_8O_8Cl_{14}$ ($=4SnO_2.3SnCl_4.SnCl_2$) by dissolving moist metastannic acid in hot conc. $SnCl_2Aq$ containing HCl.

Mallet (*C. J.* 35, 524) obtained a semi-transparent, jelly-like solid from $SnCl_2Aq$ which had been kept in a loosely-stoppered bottle for a year or two; to this solid he gave the formula $SnO_2.HCl$ ($=SnO.OH.Cl$).

Tin, oxyfluoride of. When SnF_2 is heated in air it is said to form the oxyfluoride $SnOF_2$ ($=SnO_2.SnF_4$) (Fremy, *A. Ch.* [3] 47, 37; Marignac, *Ann. M.* [5] 15, 221).

Tin, oxyiodides of. According to Personne (*C. R.* 54, 216), various oxyiodides are formed by decomposing SnI_2 by much water; P. analysed four compounds, to which he assigned the compositions $Sn_3O_2I_2$ ($=2SnO.SnI_2$), Sn_2OI_2 ($=SnO.SnI_2$), Sn_3OI_4 ($=SnO.2SnI_2$), and Sn_4OI_6 ($=SnO.3SnI_2$).

Tin, phosphides of. By heating finely divided tin in vapour of P, Schrötter (*W. A. B.* 1849. 301) obtained a silver-white, brittle solid to which he gave the formula SnP; S.G. 6·56; easily acted on by HClAq, but not by HNO_3Aq. Other crystalline solids have been obtained by heating tin and P together, but their compositions are not determined with certainty (*v.* Pelletier, *S.* 55, 106; Berthier, *A. Ch.* [2] 33, 180; H. Rose, *P.* 24, 326; Lüpke, *C. C.* 1890 [ii.] 643). Natanson a. Vortmann (*B.* 9, 1459) obtained a phosphide of tin by heating glacial phosphoric acid with C and tin; HClAq gave off PH_3 and left SnP.

Tin, salts of. Tin forms two classes of salts by replacing the H of acids; the *stannous* salts SnX_2 and the *stannic* salts SnX_4 ($X=ClO_3$, NO_3, $\frac{1}{2}CO_3$, $\frac{1}{2}SO_4$, $\frac{1}{3}P_4O$, &c.). The chief salts of oxyacids are the following: (1) ***Stannous salts:*** *antimonate, arsenate, borate, carbonate, chlorate, chromate, iodate, nitrate, phosphates, phosphite, sulphates*, and *sulphite*. (2) ***Stannic salts:*** *antimonate, arsenate, bromate, chlorate, iodate, molybdate, nitrate, phosphates, phosphite, selenate, selenite, sulphates*, and *tungstates* (*v.* NITRATES, SULPHATES, &c.).

Tin, selenides of. Tin and Se form two compounds, SnSe and $SnSe_2$. The former can be prepared by the direct union of the elements; the latter does not seem to be obtained by this method. Both selenides dissolve in alkali solutions, and in solutions of alkali sulphides.

STANNOUS SELENIDE SnSe. (*Tin monoselenide or protoselenide.*) Mol. w. unknown. Obtained by melting together Se and tin (Berzelius; Welsmann, *A.* 116, 122). With excess of Se the disulphide $SnSe_2$ was said to be formed (Little, *A.* 112, 213), but this was probably a mistake (Schneider, *P.* 127, 624). Also formed by adding powdered Se to molten $SnCl_2$, heating till $SnCl_4$ is volatilised, and allowing to cool, when SnSe crystallises; excess of $SnCl_2$ is removed by washing with dilute HClAq (Schneider, *l.c.*). Steel-grey, lustrous prisms; probably isomorphous with SnS; S.G. 5·24 at 15° (S., *l.c.*). Also obtained, as a black powder, by passing H_2Se into $SnCl_2Aq$, washing, and drying at 100°. SnSe prepared by ppn. is soluble in alkali solution; the crystals prepared by heating Se with $SnCl_2$ are insoluble, even in boiling alkali solutions. Both crystalline and amorphous SnSe are soluble in solutions of alkali sulphides or selenides. SnSe is insoluble in HClAq; oxidised by HNO_3Aq to $SnO_2.xH_2O$, H_2SeO_3, and H_2SeO_4. Heated with I, forms SnI_4 and $SnSe_2$; or, with an excess of I, SnI_4 and Se; reacts similarly with Br. SnSe is not reduced by heating in H. Heated in air it is gradually oxidised to SnO_2 and SeO_2 (S., *l.c.*). According to Ditte (*C. R.* 96, 1790), SnSe can be sublimed in a stream of H at a red heat; D. says S.G. is 6·179 at 0°.

STANNIC SELENIDE $SnSe_2$. (*Tin diselenide.*) Mol. w. unknown. Not formed by heating together tin and Se, as excess of Se over that required to form SnSe sublimes; Little's statement that $SnSe_2$ is formed by directly combining tin and Se by heat (*A.* 112, 213) is probably wrong (Schneider, *P.* 127, 624). Prepared by rubbing 5 pts. I and 8 to 10 pts. crystallised SnI_2 (the SnI_2 is used to enable the I to be thoroughly powdered), adding 4 pts. powdered SnSe, then sufficient CS_2 to form a pasty mass (stirring constantly), and then adding more CS_2 to dissolve SnI_4, and washing with CS_2, when $SnSe_2$ remains as a dark, red-brown, indistinctly crystalline powder, which becomes darker when dried at 100° (Schneider, *l.c.*). S.G. 4·85. According to Welsmann (*A.* 116, 122), $SnSe_2$ is obtained, as a dark reddish-brown powder, by passing H_2Se into $SnCl_4Aq$; heated in H, this powder gives off Se and leaves SnSe.

$SnSe_2$ is not acted on by water, or by dilute acids; it is slowly attacked by conc. boiling HClAq; *aqua regia*, or conc. HNO_3Aq, oxidises it to SnO_2, H_2SeO_3 and H_2SeO_4; it dissolves in hot conc. H_2SO_4, and when the olive-green solution is poured into water Se separates and $Sn(SO_4)_2$ remains dissolved. $SnSe_2$ is easily soluble in caustic alkali solutions, including NH_3Aq, forming blood-red liquids. Heated with I, in the ratio $SnSe_2$:4I, SnI_4 and Se are formed; Br reacts similarly to I (Schneider, *l.c.*).

Tin, silicides of. No definite compound has been isolated. Substances which seem to be of the nature of alloys are formed by heating together tin and Si; treatment with HClAq dissolves tin from these bodies, and separates Si along with SiO_2 (*v.* Winkler, *J. pr.* 91, 193).

Tin, silicofluoride. According to Berzelius (*Lehrbuch* [5th ed.] 3, 767), the salt $SnSiF_6$ separates (? from solution of $SnO.xH_2O$ in H_2SiF_6Aq) in prismatic crystals, which are readily crystallised from water.

Tin, sulphides of. Two sulphides of tin are known, SnS and SnS_2: the former is readily obtained by heating tin and S; the latter by heating tin with an excess of S and some substance (*e.g.* NH_4Cl) which readily volatilises, and so removes heat, which would else drive off the S above that required to form SnS. Both sulphides are also formed by ppn. by H_2S from corresponding salts in solution. Both sulphides dissolve in solutions of alkali polysulphides, forming *thiostannates*, M_2SnS_3.

STANNOUS SULPHIDE SnS. (*Tin monosulphide* or *protosulphide.*) Mol. w. unknown.

Preparation.—1. Finely divided tin is heated with c. equal parts of S; the product is powdered, and repeatedly heated with S in a closed vessel. Ditte (*C. R.* 96, 1790) recommends to sublime the SnS thus prepared, by heating to redness in a porcelain tube in a stream of H.—2. H_2S is passed into a solution of a stannous salt until the liquid smells strongly of H_2S; the brownish black pp. of amorphous SnS is washed and dried, and is then added, little by little, to molten $SnCl_2$ as long as it is dissolved thereby; after cooling, $SnCl_2$ is dissolved out by dilute HClAq, and any dark-brown powder that is present is washed away from the heavier, greyish, lustrous, crystalline particles of SnS (Schneider, *P.* 95, 167).

Properties.—A dark, lead-grey, crystalline solid; S.G. 4·85° (Karsten, *S.* 65, 394), 5·27 (Boullay, *A. Ch.* [2] 43, 266). Ditte (*l.c.*) describes SnS, after sublimation in H, as crystallising in thin, lustrous squares with an angle of c. 90°; with a grey-blue, metal-like lustre; soft and friable; S.G. 5·0802 at 0°. Crystalline SnS melts at a red heat; it expands considerably on cooling (Ditte, *l.c.*). Prepared by ppn. SnS is a brownish-black, amorphous solid.

Reactions.—1. SnS, prepared by heating together tin and S, may be sublimed in *hydrogen* at a red heat (Ditte, *C. R.* 96, 1790); but continued heating in H is said to reduce it to tin, H_2S being given off.—2. Heated in *air* SnS is gradually converted into SnO_2 and SO_2.—3. Reacts with *chlorine*, even at the ordinary temperature, to form $SnCl_4$ and $SnCl_4.2SCl_4 = (SnS_2Cl_{12})$ (H. Rose, *P.* 47, 517).—4. Fusion with *potassium cyanide* produces tin and KCNS.—5. SnS dissolves gradually in boiling *hydrochloric acid*, forming $SnCl_2$ solution and giving off H_2S (for details of interaction with HClAq of different concentration, and with HCl gas, *v.* Ditte, *C. R.* 97, 42).—6. Gradually oxidised to SnO_2 by heating with *nitric acid*.—7. Dissolves in solutions of *alkali polysulphides*, forming alkali thiostannates M_2SnS_3.—8. SnS is generally said to be nearly insoluble in solutions of *alkali monosulphides* (M_2S). According to Ditte (*C. R.* 94, 1419, 1470), SnS is not acted on by K_2SAq at the ordinary temperature if the concentration of the solution does not exceed $20K_2S:100H_2O$; but a more conc. solution of K_2SAq, out of contact with air, gradually converts the SnS into a grey, spongy mass of tin; and still more conc. K_2SAq dissolves this, forming K_2SnS_3Aq and giving off H: if air is admitted the reactions are more complex.

STANNIC SULPHIDE SnS_2. (*Tin disulphide.*) Mol. w. not known.

Preparation.—1. By saturating $SnCl_4Aq$ containing a little HClAq with H_2S, warming, again saturating with H_2S, warming gently for some hours, collecting the pp., washing with dilute H_2SAq, drying, and heating to above 100° out of contact with air. Pure SnS_2 can scarcely be prepared in this way; there seems to be always some $SnO_2.xH_2O$ present in the pp. (Kühn, *A.* 84, 110; Barfoed, *J. pr.* 101, 368).—2. By passing the mixed vapours of $SnCl_4$ and H_2S through a red-hot porcelain tube, or by passing H_2S into $SnCl_4$ and heating the white crystals of $SnCl_4.5H_2S$ so obtained (Coldridge, *P. M.* [5] 29, 383).—3. A mixture of finely-divided tin and S, or of SnS and S, with some substance that gradually volatilises and so removes heat, is slowly heated to redness in a glass retort, or a loosely covered flask, imbedded in sand; the volatile substance gradually passes off, then the excess of S is volatilised and the SnS_2 remains, partly on the sides and partly on the bottom of the vessel. If tin is heated with S only, the heat produced in the reaction is so great that the SnS_2 formed is resolved into SnS and S. Various mixtures have been employed by different chemists; the following give good results: (1) equal parts sifted tin-filings, S, and NH_4Cl (Pelletier); (2) 4 parts tin-filings, 3 parts S, 2 parts NH_4Cl (Woulfe); (3) a pulverised amalgam of 12 parts tin and 6 parts Hg, with 7 parts S, and 6 parts NH_4Cl (W.); (4) 5 parts SnS and 8 parts $HgCl_2$ (W.).

References.—Pelletier (*Crell's Chem. Ann.* 1797 [1] 46); Woulffe (*ibid.* 1, 149); Bullion (*ibid.* 1793 [1] 89); Proust (*Gehlen's Journ. f. Chem. und Phys.* 1, 250).

According to Gmelin (*Handbuch* [5th ed.] 3, 75) if NH_4Cl is heated with tin and S there is formed a compound of NH_4Cl and $SnCl_2$, which then interacts with the S, forming SnS_2 (? $2Sn + 8NH_4Cl = 2(2NH_4Cl.SnCl_2) + 2H_2 + 4NH_3$;
$2(2NH_4Cl.SnCl_2) + 2S$
$= SnS_2 + 2NH_4Cl.SnCl_4 + 2NH_4Cl$).

Properties.—Prepared by sublimation, SnS_2 is a soft golden-yellow, lustrous, crystalline solid; S.G. 4·6 (Karsten, *S.* 65, 394), 4·42 (Boullay, *A. Ch.* [2] 43, 266). Crystalline SnS_2 is known as *mosaic gold* (*v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 845).

Reactions and Combinations.—1. *Heated in a closed vessel* gives SnS and S, and a sublimate of SnS_2.—2. *Heated in air* SnO_2 and SO_2 are formed.—3. *Chlorine* liquefies SnS_2, on cooling yellow crystals of $SnCl_4.2SCl_4$ are formed (H. Rose, *P.* 42, 517). — 4. The compound SnS_2I_4(= $SnSI_2.SI_2$) is said to be formed by heating SnS_2 with *iodine* in a stream of CO_2 (Schneider, *J. pr.* 79, 419; *v.* also Tin, thio-iodide, *infra*). According to Schneider (*l.c.*) a boiling alcoholic solution of I does not act on SnS_2 prepared by sublimation, but with amorphous SnS_2 prepared by ppn. it gives SnS_2I_4.—5. Amorphous, but not crystalline, SnS_2 is slowly decomposed by boiling conc. *hydrochloric acid*, H_2S being given off and $SnCl_4$ solution formed.—6. The amorphous sulphide is slowly oxidised by hot *nitric acid*; *aqua regia* oxidises both amorphous and crystalline SnS_2 to SnO_2 and H_2SO_4Aq.—7. Fusion with *lead monoxide* produces a mixture of sulphides and oxides of tin and lead; with excess of PbO, SO_2 is given off and lead remains.—8. SnS_2 was said by Dumas (*S.* 66, 409) to combine with *stannic chloride*, forming $SnS_2.2SnCl_4$; the compound being produced by the interaction of $SnCl_4$ and H_2S. According to Coldridge (*P. M.* [5] 29, 383) this compound does not exist, the product of the reaction being $SnCl_4.5H_2S$.—9. SnS_2 dissolves in *alkali sulphide solutions*, forming thiostannates (*q.v.*, *infra*), M_2SnS_3. — 10. In *alkali solutions* SnS_2 dissolves, probably forming stannates and thiostannates (? $3SnS_2 + 6KOHAq = K_2SnO_3Aq + 2K_2SnS_3Aq + 3H_2O$).

Tin Sesquisulphide. Berzelius (*Lehrbuch* [5th ed.] 2, 600) gave the formula Sn_2S_3 to a greyish-yellow, lustrous solid obtained by heating a mixture of 3 parts SnS and 1 part S in a retort; the substance was almost certainly a mixture of SnS and SnS_2.

Tin, sulphochlorides of; *v.* Tin thiochlorides, *infra.*

Tin, sulpho-iodide of; *v.* Tin thio-iodide, *infra.*

Tin, sulphocyanide of; *v.* vol. ii. p. 352.

Tin, telluride of, SnTe. A grey, lustrous, metal-like, crystalline solid; S.G. 6·478 at 0°; obtained by heating together tin and Te, and slowly subliming in a stream of H (Ditte, *C. R.* 96, 1790).

Tin, thio-acids and salts of. It is doubtful whether a thio- acid of tin has been isolated with certainty; a few salts derived from the acid H_2SnS_3 have been obtained.

Thiostannic acid. (*Sulphostannic acid.*) Kühn (*A.* 84, 110) obtained an olive-brown pp. by adding HClAq or $H.C_2H_3O_2$Aq to a conc. solution of $Na_2SnS_3.Na_2S.12H_2O$ (*v. infra*); after washing, and drying at 100°, the pp. was a leaden-grey, lustrous solid having the composition H_2SnS_3. Storch (*M.* 10, 255), repeating Kühn's experiments, always obtained brown pps., which did not contain more S than required by the ratio Sn:S = 1:2·19. S. concluded that the pps. were mixtures of H_2SnS_3 and SnS_2. By adding dilute oxalic acid solution to solution of Na_2SnS_3 (prepared by saturating Na_2SnO_3Aq with H_2S) in quantity just sufficient to combine with the Na present, S. (*l.c.*) obtained a deep-yellow liquid which remained clear for hours; after removing the H_2S by a current of air S. found that the liquid contained tin and S in the ratio Sn:3S; he concluded that H_2SnS_3 was present in the liquid. The liquid was decolourised by NH_3Aq, KOHAq, Na_2CO_3Aq, $(NH_4)_2CO_3$Aq, and NH_4ClAq; strong acids gave brownish pps. containing rather more S than required by the formula SnS_2.

Thiostannates (Kühn, *l.c.*; Höring, *Hirsel's Zeit. für Pharm.* 1851. No. 8). The alkali salts are obtained by dissolving SnS_2 in alkali sulphide solutions, M_2SAq; the alkaline earth salts are formed by double decomposition from the alkali salts.

Potassium thiostannate $K_2SnS_3.10H_2O$. Obtained by dissolving SnS_2 in K_2SAq, and adding alcohol, when the salt separates as a dark brown heavy oil; all H_2O is given off at 100°.

Sodium thiostannates. The *normal salt* $Na_2SnS_3.2H_2O$ is obtained, in yellow, glassy, regular crystals, by adding tin, little by little, to molten Na_2S_5, treating the fused mass with water, and evaporating at a low temperature. A solution of SnS and S in Na_2SAq deposits colourless, monoclinic crystals of the *basic salt*, which, when dried over H_2SO_4, has the composition $Na_2SnS_3.Na_2S.12H_2O$. The stronger acids (HCl, H_2SO_4, $CHCl_2.CO_2H$) ppt. SnS_2 at once from Na_2SnS_3Aq; but weak acids (H_3PO_4, $H_2C_2O_4$, $CH_2Cl.CO_2H$, &c.) form brown-yellow solutions from which red-brown pps. separate more or less slowly (Storch, *M.* 10, 255). Kühn (*l.c.*) gives the reactions of the two Na thiostannates with solutions of several metallic salts; many of the pps. were doubtless thiostannates of the metals employed.

PLATINO-THIOSTANNATES. Schneider (*Z.* [2] 5, 629; 6, 270, 613) obtained salts to which he gave the composition $M_2Pt_3SnS_6$ (= $M_2S.3PtS.SnS_2$), where M = K or Na, by fusing SnS_2, Pt, M_2CO_3, and S, and lixiviating with water.

Tin, thiochlorides of. A compound SnS_2Cl_{12} (= $SnCl_4.2SCl_4$) is said to be formed, along with $SnCl_4$, by the interaction of Cl and SnS or SnS_2 (H. Rose, *P.* 42, 517). Dumas (*S.* 66, 409) described a compound $Sn_2S_2Cl_4$(= $SnS_2.SnCl_4$) as obtained by passing H_2S into $SnCl_4$; but according to Coldridge (*P. M.* [5] 29, 383) this compound is not formed. C. (*l.c.*) says that the passage of H_2S into $SnCl_4$ produces white crystals of $SnCl_4.5H_2S$, which are decomposed by heat, giving off HCl and H_2S, and leaving SnS_2.

Tin, thio-iodide of. By melting together crystalline SnS_2 and I, in the ratio SnS_2:4I, allowing the liquid to cool, and either heating in a stream of CO_2, or dissolving in CS_2 and crystallising, Schneider (*J. pr.* 79, 419) obtained brown, lustrous crystals of SnS_2I_4 (= $SnSI_2.SI_2$). This thio-iodide is dissolved unchanged by CS_2 or $CHCl_3$; alcohol separates S; water, or a solution of a caustic alkali, produces SnS_2, S, and HIAq (or MIAq); HClAq or HNO_3Aq decomposes it, with separation of S. The compound SnS_2I_4 is also produced by the interaction of a solution of I in CS_2 and ppd., dried SnS_2 (S., *l.c.*). M. M. P. M.

TIN ORGANIC COMPOUNDS.

Stannic methide $SnMe_4$. (78°). S.G. 1·313. V.D. 6·00 (calc. 6·15). Got by heating an alloy of tin and sodium (14 p.c.) with MeI (¾ pt.) at 100°–120° (Ladenburg, *A. Suppl.* 8, 74; *cf.* Cahours, *A.* 111, 236; 114, 372). Oil, with ethereal odour. Reduces alcoholic $AgNO_3$.

Stannic tri-methylo-iodide $SnMe_3I$. (170°). S.G. ^{0} 2·143. Formed by the action of I on $SnMe_4$. Oil. Yields crystalline $SnMe_3OH$ and the salts $(SnMe_3)_2SO_4$, $SnMe_3.O.CO.H$, and $SnMe_3.OAc$. Forms the compounds $SnMe_3OEt$ (Ladenburg, *B.* 3, 358) and $SnMe_3I2NH_3$ (Cahours, *A.* 122, 56).

Stannic di-methylo-di-iodide $SnMe_2I_2$. [30°]. (228°). S.G. ^{22} 2·872. Formed by heating tinfoil with MeI at 150° (C.). Monoclinic crystals (from ether-alcohol). Converted by ammonia into amorphous $SnMe_2O$, which is insol. water, but dissolves in acids forming the following crystalline salts: $SnMe_2Cl_2$ [90°] (189°), forming trimetric crystals; *a*:*b*:*c* = ·834:1: ·941.—$SnMe_2PtCl_6$ 7aq, forming trimetric crystals; *a*:*b*:*c* = ·888:1:·977. — $SnMe_2Br_2$. (209°). — $SnMe_2SO_4$, forming monoclinic crystals (Hjortdahl, *C. R.* 88, 584).

Stannic ethide $SnEt_4$. Mol. w. 234. (181°). S.G. ^{23} 1·187. Formed from $SnEt_2I_2$ and EtI (Buckton, *A.* 109, 218; 112, 223; Frankland, *A.* 111, 44). Formed also, together with tin and ZnEtCl, by adding fused $SnCl_2$ to cooled $ZnEt_2$ and then distilling (Frankland a. Lawrance, *C. J.* 35, 134). Prepared by heating powdered tin with EtI and the zinc-copper couple; and also by heating ZnEtI with powdered tin at 160° (Letts a. Collie, *C. J. Proc.* 2, 166). Oil. Has no action at 180° on Al, Na, or Mg. Slowly absorbs sulphur dioxide, forming crystalline $SO_2(OSnEt_3)_2$, insol. ether and an oil $SnEt_3.SO_3Et$, sol. ether. Hot conc. HClAq forms ethane and $SnEt_3Cl$. Iodine forms $SnEt_3I$ and IEt.

Stannous ethide $SnEt_2$. S.G. ^{15} 1·558. Formed by adding zinc to a warm solution of $SnEt_2Cl_2$ (Frankland). Oil. Decomposed at 150° into $SnEt_4$ and tin. Br forms $SnEt_2Br_2$.

Distannic hexa-ethide Sn_2Et_6. (265°–270°). S.G. ^{0} 1·412. V.D. 14·8 (calc. 14·7). Got by distilling $SnEt_3I$ with sodium (Ladenburg, *A. Suppl.* 8, 66; *B.* 3, 647). Pungent oil. I forms $SnEt_3I$. Conc. HClAq forms $SnEt_2Cl_2$, ethane, and hydrogen.

Stannic tri-ethylo-iodide $SnEt_3I$. (231°). S.G. ^{22} 1·833. Formed by the action of EtI on an alloy of tin and sodium (Ladenburg, *A. Suppl.* 8, 60; *B.* 3, 353, 647; *cf.* Löwig, *A.* 84, 308). Liquid. Combines with NH_3 (2 mols.). On distilling with KOHAq it yields $SnEt_3OH$ crystallising from ether in prisms [43°] (271°) converted by heat into oily $(SnEt_3)_2O$, which recombines with water forming the hydroxide. NaOEt converts the iodide into $SnEt_3OEt$ (191°) S.G. ^{0} 1·263, which is at once changed by water into the hydroxide. The hydroxide $SnEt_3OH$ is sol. water, strongly alkaline, absorbs CO_2 from the air, and is converted by acids into the salts:—$SnEt_3Cl$. [c. 0°]. (209°). S.G. ^{8} 1·428.—$(SnEt_3)_2PtCl_6$.—$SnEt_3PtCl_5$.—$SnEt_3Br$. (223°) (Cahours). — $SnEt_3Cy$. — $SnEt_3CyO$.—$SnEt_3NO_3$.—$(SnEt_3)_2SO_4$. Hexagonal prisms terminated by pyramids (Hjortdahl).—$(SnEt_3)_2S$. — $SnEt_3SH$. — $(SnEt_3)H_2PO_4$. — $SnEt_3.OAc$. — $SnEt_3OBz$. — $(SnEt_3)_2CO_3$. — $(SnEt_3)_2C_2O_4$ aq. — Formate $(SnEt_3)CHO_2$.— Butyrate $(SnEt_3)C_4H_7O_2$. — Tartrates $(SnEt_3)_2C_4H_4O_6$ aq.—$(SnEt_3)HC_4H_4O_6$ aq.

Stannic di-ethylo-di-iodide $SnEt_2I_2$. [44·5°]. (245°). Formed from tin and EtI by exposure to sunlight or by heating with EtI at 150° (Frankland, *A.* 85, 329; Löwig, *A.* 84, 308; Cahours a. Riche, *A.* 84, 333). Needles (from alcohol), sl. sol. cold water. May be sublimed. Alcoholic NH_3 forms $SnEt_2O$, which is an amorphous powder, insol. water, converted by acids into the following salts: $SnEt_2Cl_2$. [85°]. (220°), forming trimetric crystals; *a*:*b*:*c* = ·839:1: ·943. — $SnEt_2Cl.OH$: plates.—$SnEt_2Br_2$ (233°). V.D. 11·6 (calc. 11·7).—$SnEt_2(NO_3)_2$.—$SnEt_2ICy$.—$SnEt_2(SCy)_2$. — $SnEt_2S$. — $SnEt_2SO_4$. — Crystals. $SnEt_2(OAc)_2$. — $SnEt_2C_2O_4$. — Formate $SnEt_2(CHO_2)_2$.

Stannic ethylo-trimethide $SnEtMe_3$. (125°–128°). Formed from $SnMe_3I$ and $ZnEt_2$ (Cahours, *A.* 122, 59). Oil; converted by I into EtI and $SnMe_3I$.

Stannic di-ethylo-di-methide $SnEt_2Me_2$. (145°). S.G. ^{0} 1·260. V.D. 6·84 (calc. 7·14). Formed from $SnEt_2I_2$ and $ZnMe_2$ (Frankland, *A.* 111, 50; Morgunoff, *A.* 144, 157). Oil.

Stannic methylo-tri-ethide $SnMeEt_3$. (163°). V.D. 6·72 (calc. 6·65). Formed from $SnEt_3I$ and $ZnMe_2$ in the cold (C.). Heavy oil.

Stannic tetrapropylide $SnPr_4$. (224°). S.G. ^{14} 1·179. Formed from $SnPr_3I$ and $ZnPr_2$ (Cahours, *C. R.* 76, 133). Pungent oil.

Stannic tripropylo-iodide $SnPr_3I$. (261°). S.G. ^{10} 1·692. Formed from PrI and an alloy of Na and tin (Cahours a. Demarçay, *C. R.* 88, 725, 1112). Oil, converted by moist Ag_2O into crystalline $SnEt_3OH$.

Stannic di-propylo-di-iodide $SnPr_2I_2$. (272°). Formed from tin and PrI. Oil. Converted by alkalis into amorphous $SnPr_2O$, insol. water, which yields $SnPr_2Cl_2$ [81°].

Stannic tri-isopropylo-iodide $SnPr_3I$. (257°). Got in like manner.

Stannic di-isopropylo-di-iodide $SnPr_2I_2$. (267°). Yields $SnPr_2Cl_2$ [57°].

Stannic tri-isobutylo-iodide $Sn(C_4H_9)_3I$. (285°). S.G. ^{15} 1·540. Formed from CH_2PrI and a 9 p.c. alloy of Na in tin (Cahours a. Demarçay, *C. R.* 89, 68). Pungent oil, converted by KOH into $Sn(C_4H_9)_3OH$ (313°).

Stannic di-isobutylo-di-iodide $Sn(C_4H_9)_2I_2$. (290°–295°). Formed by heating tinfoil with isobutyl iodide at 125°. Liquid, converted by alkalis into amorphous $Sn(C_4H_9)_2O$, and by HCl into $Sn(C_4H_9)_2Cl_2$ [c. 6°] (261°).

Stannic tetra-isoamylide $Sn(C_5H_{11})_4$. Formed from isoamyl iodide and an alloy of Na (1 pt.) and tin (6 pts.) (Grimm, *A.* 92, 383). Liquid.

Stannic tri-isoamylo-iodide $Sn(C_5H_{11})_3I$. (304°). Accompanies the preceding compound (C. a. D.). Converted by potash into oily $Sn(C_5H_{11})_3OH$ (337°).

Stannic tetraphenylide $SnPh_4$. [226°]. (over 420°). Formed by heating bromo-benzene with a tin-sodium alloy and acetic ether (Polis, *B.* 22, 2915). Colourless prisms, insol. ligroïn, v. sl. sol. alcohol, v. sol. boiling benzene.

Stannic tri-phenylo-chloride $SnPh_3Cl$. [105°]. Formed by the action of $NaNO_2$ on a solution of $SnPh_2Cl_2$ in HOAc, the yield being 85 p.c. of that represented by the equation $3SnPh_2Cl_2 = 2SnPh_3Cl + SnCl_4$ (Aronheim, *B.* 12, 509). Converted by potash into $SnPh_3OH$ 1$\frac{1}{2}$aq [118°].

Stannic di-phenylo-dichloride $SnPh_2Cl_2$. [42°]. (335°). Prepared by boiling $HgPh_2$ with $SnCl_4$ and ligroïn (Aronheim, *B.* 10, 2228;

11, 2285; *A.* 194, 145). Triclinic prisms; $a:b:c = \cdot588:1:1\cdot067$; $\alpha = 62°\ 47'$; $\beta = 76°\ 48'$; $\gamma = 94°\ 8'$. Sol. alcohol and ligroïn, miscible with ether. Converted by means of water into $SnPh_2Cl.OH$, an amorphous insoluble powder [187°]. Potash forms $SnPh_2O$. Ether, alcohol, and sodium-amalgam form $SnPh_2(OEt)_2$ [124°].

Stannic di-phenylo-di-bromide $SnPh_2Br_2$. [c. 38°]. (230° at 42 mm.). Formed from $SnPh_4$ and Br (Polis), and from the oxide and HBr (A.).

Stannic di-phenylo-chloro-bromide $SnPh_2BrCl$ [39°]. Crystalline. Formed from $SnPh_2Cl(OH)$ and HBr.

Stannic di-phenylo-chloro-iodide $SnPh_2ClI$. [69°]. Yellow monoclinic crystals (from ether), decomposed by water.

TIN GROUP OF ELEMENTS. Group IV. in the periodic classification of the elements contains the following members:—

Even series	2	4	6	8	10	12
	C	Ti	Zr	Ce	—	Th
Odd series	3	5	7	9	11	
	Si	Ge	Sn	—	Pb	

Subdividing this group in accordance with the chemical similarities of the elements we get the following families:—

Carbon family: C and Si.
Titanium family: Ti, Zr, Ce, —, Th.
Tin family: Ge, Sn, —, Pb.

The *carbon family* is considered in the article CARBON GROUP OF ELEMENTS (vol. i. p. 682); and that article also gives a sketch of the chemical relations of all the members of the group. The elements of the *titanium family* are considered under the heading TITANIUM GROUP OF ELEMENTS (this vol., p. 749). The *tin family* is considered in the present article.

Ge occurs in small quantities, as sulphide, in a very few rare minerals. Tin and lead are found native in not very large quantities. The chief ore of tin is *tinstone*, which contains SnO_2; SnS_2 is also found in *tin pyrites*; and various *micas* contain more or less SnO_2. *Galena*, containing PbS, is the chief ore of lead; sulphate, carbonate, phosphate, &c., are also found in considerable quantities. Ge is obtained by heating its ore with Na_2CO_3 and S, dissolving in water, decomposing Na_2S by H_2SO_4Aq, ppg. Ag (Ag_2S is a constituent of the ore) by HClAq, then ppg. GeS_2 by H_2S, oxidising the GeS_2 to GeO_2 by HNO_3, and reducing the GeO_2 by heating in H or with C. Tin is obtained by calcining *tinstone*, washing, and reducing the SnO_2 by heating with C. To obtain lead, *galena* is roasted in such a quantity of air that it is partially oxidised, both PbO and $PbSO_4$ being formed; by then heating out of contact with much air the PbS, PbO, and $PbSO_4$ interact to form SO_2 and lead. Tin and lead have been known from very early times. Ge was isolated in 1885.

The table on page 736 presents some of the principal physical and chemical properties of the tin elements.

General formulæ and characters of compounds. **Oxides**:—MO, MO_2; also Pb_3O_4 and Pb_2O_3: various hydrates of most of these oxides are known. **Sulphides**:—MS, MS_2 (?PbS_2). **Haloid compounds**:—MX_2 and MX_4. **Acids**:—H_2MX_6, where M = Ge or Sn, and X = either Br, Cl, F, or I; also H_2PbI_4; H_2SnO_3 and $H_2.H_8Sn_5O_{15}$; ?H_2SnS_3. **Salts**:—MX_2 and MX_4, where M = Sn or Pb and X = NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. **Salts containing M in the acidic radicle**:—$R^I_2MX_6$, where M = Ge, Sn, (?Pb), and X is a halogen; $R^I_2MO_3$, where M = Sn, or Pb; also $R^I_4PbO_4$; also $R^I_2.H_8Sn_5O_{15}$; also $R^I_2SnS_3$.

The *oxides* MO are basic; they react with acids to form salts MX_2, X = NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c. (no salts of GeO have yet been isolated). PbO also dissolves in molten KOH, forming K_2PbO_2. The oxides MO_2, where M = Sn or Pb, are both basic and acidic; they react with some acids to form salts MX_4; several of these salts have been isolated when M = Sn, very few when M = Pb: they also react with molten KOH or NaOH ($SnO_2.xH_2O$ also with MOHAq) to form salts K_2(orNa_2)MO_3; when M = Sn two classes of salts are known, *stannates* M_2SnO_3, and *metastannates*, probably $M_2.H_8Sn_5O_{15}$. GeO_2 dissolves in acids, also in molten KOH or K_2CO_3, but the products of these reactions have not yet been examined. Pb_3O_4 reacts with dilute strong acids to form PbO_2, and PbX_2 which dissolves; with glacial acetic acid Pb_3O_4 forms $Pb(C_2H_3O_2)_2$ and $Pb(C_2H_3O_2)_4$. Pb_2O_3 probably reacts with dilute strong acids to give PbO_2 and a salt of PbO. The hydrates of MO and MO_2 react similarly to the oxides. Some of the hydrates $SnO_2.xH_2O$ are acidic; one class of these is probably polymeric with the other. There are indications of the existence of an oxide MO_3 in the case of tin; this oxide seems to be acidic.

The *sulphides* of Ge have not been much investigated; GeS_2 dissolves in alkali sulphide solutions, and is probably acidic. GeS has been gasified and V.D. determined. The sulphides of tin are both basic and acidic; with hot conc. HClAq they give $SnCl_2$ and $SnCl_4$ respectively; both dissolve in alkali sulphide solutions to form *thiostannates* M_2SnS_3. PbS is basic; with acids it gives salts PbX_2, and H_2S; there are indications of the existence of a higher sulphide, perhaps PbS_2, which will probably form thioplumbates with the sulphides of strongly positive metals.

The *haloid compounds* MX_2 (none isolated yet when M = Ge) may be formed by the direct union of the elements, and by the other usual methods. $SnCl_2$ and $PbCl_2$ have been gasified, and the formulæ are molecular; molecules of the composition Sn_2Cl_4 probably exist, but are decomposed at c. the boiling-point of the compound. Several salts are known of the form M_2SnX_4, where X = Br, Cl, F, or I; and an acid $HSnCl_3.xH_2O$ and some salts $MSnI_3$ are also said to exist. H_2PbI_4 and salts M_2PbI_4 have been isolated; and also several salts coming under the general formula $xPbX_2.yNH_4Cl$, where X = Br or Cl. The haloid compounds MX_4 have been gasified, and V.D.s determined, when M = Ge and X = Cl or I, and when M = Sn and X = Br or Cl. $PbCl_4$ has not been isolated with certainty, but salts of the form M_2PbCl_6 are known, and also some salts $xPbCl_4.yNH_4Cl$. The acids H_2GeF_6, H_2SnBr_6, and H_2SnCl_6 have been obtained, and also salts derived from these acids; salts M_2SnF_6 and M_2PbCl_6 are also known. $GeHCl_3$ has been isolated. Many *oxyhaloid compounds* $x.MO.yMX_2$ and $xMO_2.yMX_4$ are known.

The *oxyacids* of tin, H_2SnO_3, and (probably) $H_2.H_8Sn_5O_{15}$, are to be classed with the weak

—	GERMANIUM.	TIN.	LEAD.
Atomic weights.	72·3	118·8	206·4
	One or more compounds of each element have been gasified. Specific heats have also been determined directly. There is some evidence in favour of the conclusion that the molecules of tin and lead, in solution in Hg, are monatomic.		
Melting-points. (approx.).	900°	232°	330°
Boiling-points. (approx.).	—	1,450°–1,600°	1,450°–1,600°
Spec. gravs. (approx.).	5·5	7·3	11·4
Spec. heats.	·0737	·0559	·0315
Atom. wts. / *Spec. gravs.* (approx.).	13·2	16·3	18·1
Occurrence and preparation.	Double sulphide of Ge and Ag occurs as a rare mineral. GeO_2 also found in some specimens of *euxenite*, with oxides of Nb, Ta, and Y. Prepared by reducing GeO_2 by H or C.	Metal found in small quantities. SnO_2 occurs in tolerable quantities widely distributed. Prepared by reducing SnO_2 by C.	Small quantities of lead found. Chief ore contains PbS; widely distributed in considerable quantities. Prepared by interaction of PbS, PbO, and $PbSO_4$; also by reducing PbO by C.
Physical properties.	Greyish white, lustrous, very brittle. Crystallises in regular octahedra. Melts at c. 900°; slightly volatilised at 1,350° in N or H.	Silver-white, lustrous, malleable, but malleability varies with temperature; tenacity very small. Crystallises very easily in rhombic and quadratic forms. Melts easily (at 232°), and boils between 1,450° and 1,600°.	White, with tinge of blue; lustrous; very malleable and ductile; tenacity very small; very soft. Crystallises easily in regular octahedra. Melts easily (at 330°), but at higher temperature than tin, and boils between 1,450° and 1,600°.
Chemical properties.	Unchanged in air at ordinary temperature; oxidised to GeO_2 when heated in fine division. Combines readily with Br, Cl, and I when heated, forming GeX_4. Heated in HCl gas forms $GeHCl_3$. Dissolves in H_2SO_4Aq. No salts have yet been isolated by replacing H of oxyacids by Ge. GeO_2 dissolves in fused KOH or K_2CO_3. H_2GeF_6Aq and salts of this acid are known.	Unchanged in pure air at ordinary temperature. Heated in air gives SnO and SnO_2. Heated in Br, Cl, or I forms SnX_2 and SnX_4. Heated with S forms SnS and SnS_2; also forms SnSe and $SnSe_2$. Reacts with acids forming two series of salts, SnX_2 and SnX_4, $X = NO_3, \frac{1}{2}SO_4, \frac{1}{3}PO_4$, &c. Conc. HNO_3 produces $SnO_2.xH_2O$. SnO is basic; $SnO_2.xH_2O$ both basic and acidic, with strong acids forms salts SnX_4, and with caustic alkalis forms stannates M_2SnO_3. SnS_2 forms thio-stannates M_2SnS_3 with alkali sulphides. Stanni fluorides M_2SnF_6 are known; the acids H_2SnCl_6 and H_2SnBr_6 have been isolated. Mol. w. perhaps same as at. w. in solution in Hg. Valency of atom varies from 2 in $SnCl_2$ gas to 4 in $SnCl_4$ gas.	Tarnishes in air, film of oxide (? Pb_2O) forming on surface. Melted in air forms PbO and Pb_3O_4. Combines with halogens to form PbX_2; $PbCl_4$ also probably isolated. Combines with S and Se, forming PbS and PbSe; $PbS.xS$ also probably exists. Reacts with acids forming salts PbX_2, $X = NO_3, \frac{1}{2}SO_4, \frac{1}{3}PO_4$, &c. PbO is basic; PbO_2 feebly basic and feebly acidic; $Pb(C_2H_3O_2)_4$ has been isolated, and probably $PbCl_4$; with molten KOH, PbO_2 forms K_2PbO_3. No thioplumbates isolated. No acid H_2PbF_6, or salts thereof, isolated; but $3KF.HF.PbF_4$ probably exists. Mol. w. perhaps same as at. w. in solution in Hg. Atom is divalent in gaseous molecule $PbCl_2$, and tetravalent in gaseous molecule $PbMe_4$.

acids; the one is probably a polymeride of the other. The salts of these acids show very distinct differences: the acids themselves interact with strong acids to form salts containing tin in the positive radicles. Of *acids containing tin and halogens* the following have (probably) been isolated: $HSnCl_3$, H_2SnBr_6, and H_2SnCl_6. H_2GeF_6 is known, and H_2PbI_4 is said to exist. It is doubtful whether *thiostannic acid* H_2SnS_3 has been obtained pure, but salts of this acid have been isolated.

The salts of oxyacids containing these metals in the negative radicles are M_2SnO_3 and $M_2.H_8Sn_5O_{15}$, M_2PbO_2 and M_2PbO_3. These salts are generally easily decomposed. Oxyacids and salts of oxyacids of Ge have yet to be searched for.

Salts derived from oxyacids by replacing H by M are known when M = Sn or Pb; no Ge salts of oxyacids have yet been isolated. The tin salts belong to two classes, SnX_2 and SnX_4, where X = NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; both classes of salts readily undergo decomposition and show a general tendency to separate off SnO or SnO_2. Almost all the lead salts belong to the class PbX_2; they are more definite and less ready to split off oxide or decompose to basic salts than the corresponding salts of tin. $Pb(C_2H_3O_2)_4$ is the only lead salt of an oxyacid of the class PbX_4 that has been certainly isolated; it is decomposed by the least trace of moisture, giving a pp. of PbO_2.

The elements of the tin family are distinctly metallic in their physical properties, and in most of their chemical properties also; they exhibit, however, non-metallic characters in their highest salt-forming oxides, MO_2, which are acidic towards strong bases, while they also react as basic oxides towards several acids. The tin elements are less chemically metallic, on the whole, than the members of the even-series, or titanium family, of Group IV.; the two distinctly non-metallic elements of the group are the first member of the even series – carbon, and the first member of the odd series – silicon.

In considering the chemical analogies of the tin elements, the position of the members of the family in their respective series should be looked to (*v.* table in vol. iii. p. 811). Ge comes in series 5; it is preceded by Ga, Zn, and Cu, and succeeded by As, Se, and Br: tin comes in series 7; it is preceded by In, Cd, and Ag, and succeeded by Sb, Te, and I: lead comes in series 11; it is preceded by Tl, Hg, and Au, and succeeded by Bi and two unknown elements. The highest salt-forming oxides of the elements preceding and succeeding the tin elements in the series are: *series* 5, CuO, ZnO, Ga_2O_3; GeO_2; As_2O_5, SeO_3, —; *series* 5, Ag_2O, CdO, In_2O_3; SnO_2; Sb_2O_5, TeO_3, ? I_2O_7 — *series* 11, Au_2O, HgO, Tl_2O_3; PbO_2; Bi_2O_5, —, —. The preceding oxides GeO_2 are, on the whole, more basic than the oxides preceding SnO_2 or PbO_2; and the oxides succeeding GeO_2 are on the whole more acidic than the oxides succeeding SnO_2 or PbO_2. Hence we should expect the three oxides, GeO_2, SnO_2, and PbO_2 to be about equally acidic and equally basic; SnO_2, perhaps, being the most acidic of the three. Looking at the position of the tin elements in the general periodic system, we may express the relationship of these odd-series elements to the first member of the odd series of their group (Si) by the following statements: (1) Pb:Si = Tl:Al = Hg:Mg = Au:Na = Bi:P. — (2) Sn:Si = In:Al = Cd:Mg = Ag:Na = Sb:P. — (3) Ge:Si = Ga:Al = Zn:Mg = Cu:Na = As:P. On the whole, Bi is more unlike P than Tl is unlike Al, Hg is unlike Mg, or Au is unlike Na; Sb is more unlike P than In is unlike Al, Cd is unlike Mg, or Ag is unlike Na; and As is more unlike P than Ga is unlike Al, Zn is unlike Mg, or Cu is unlike Na. Hence the differences between Pb and Si, tin and Si, and Ge and Si, respectively, will be very decided. If the relations expressed in the preceding statements are worked out in detail, they show that the differences between Pb and Si will be more marked than those between tin and Si, and still more marked than those between Ge and Si; but at the same time there will not be any very great differences between these three pairs of differences. Lead, then, will on the whole be the most metallic, and Ge the least metallic, of the tin elements. But the three elements will resemble each other closely in so far as their general positive or negative character is concerned. Then, considering the resemblances and differences between consecutive pairs of elements in (1) series 3 and 5 (*i.e.* Si and Ge series), and (2) series 5 and 7 (*i.e.* Ge and tin series), and (3) series 7 and 11 (*i.e.* tin and lead series), it is evident that Ge and Si will be more alike than Ge and tin, and that Ge and tin will more closely resemble one another than tin and lead. Hence, on the whole, we may expect that Ge will form several compounds wherein the element acts distinctly as a non-metal; it is possible that GeH_4 may be isolated ($GeHCl_3$ exists). Ge will form volatilisable organic compounds; GeO_2 will probably be found to be di- or trimorphous.

In connection with this article *v.* CARBON GROUP OF ELEMENTS, vol. i. p. 682; and TITANIUM GROUP OF ELEMENTS, this vol. p. 749.

M. M. P. M.

TITANATES, *and derivatives of*, *v.* p. 747.

TITANIC ACIDS *v.* p. 746.

TITANIFLUORHYDRIC ACID H_2TiF_6 *v.* TITANIC FLUORIDE, *Combinations*, No. 1, p. 742.

TITANIFLUORIDES M_2TiF_6 *v.* TITANIC FLUORIDE, *Combinations*, No. 2, p. 742.

TITANIUM. At. w. 47·9. Mol. w. not known. Has not been fused. S.G. $\frac{0^\circ}{4^\circ}$ 3·5888 (K. Hofmann, *B.* 26, 1025); some older determinations gave S.G. c. 5·3 (*v.* Fritz, *M.* 1892. 772; Wilson, *Pr.* 32, 457 [1881]). S.H. 0° to 100° ·1135, 0° to 211° ·1288, 0° to 301° ·1485, 0° to 440° ·162 (Nilson a. Pettersson, *Z. P. C.* 1, 34); Fritz (*M.* 1892. 772) gives ·13. S.V.S. 13·4.

Historical.—In 1791 Gregor found indications of a new element in a Cornish ironsand called *menaccanite*, from the village near which it was found (*Crell's Ann.* 1791 [1] 40, 103). The element was called *menachin* by Kirwan. In 1795 Klaproth found a compound of a new element in a mineral known as '*rother Schoerl zu Boinik in Hungarn*,' and called the element *titanium* (derived from *Titan*). In 1797 K. recognised that the chief constituent of the Hungarian mineral was the same as the characteristic constituent of *menaccanite* examined by

Gregor (K., *Beiträge zur Kentniss der Mineralkörper*). The element was isolated for the first time by Berzelius in 1824 (*P.* 4, 3).

Occurrence.—Ti never occurs native. The chief ore of Ti is more or less pure TiO_2, which occurs in different crystalline forms as *rutile* and *anatase* (tetragonal) and *brookite* (rhombic). Various minerals contain TiO_2, combined with SiO_2 and alkaline earths, *e.g.* *titanite* or *sphene* and *ferrotitanite*; compounds of titanates and niobates are found in some rare minerals, *e.g.* *polycrase*, *euxenite*, and *pyrochlore*. Varying quantities of TiO_2 occur in many *titaniferous iron ores*. The ores of Ti are found in small quantities. Some of them, especially the titaniferous iron ores, are widely distributed (for analyses of Ti ores *v.* H. Rose, *P.* 3, 163; 14, 501; 15, 276; Mosander, *P.* 19, 211; Hermann, *J.* 25, 368; Berzelius, *J. pr.* 43, 50; Rammelsberg, *P.* 1858. 507; Scheerer, *P.* 64, 489; Groth, *Tabellarische Uebersicht der Mineralien* [2nd ed.] 35; O. v. d. Pfordten, *B.* 22, 1485). Mazade (*C. R.* 34, 952) found traces of Ti compounds in the mineral spring of Negrac in France. For analyses and descriptions of *anatase*, *brookite*, and *rutile* *v.* Klein (*J. M.* 1875. 337); G. vom Rath (*ibid.* 1876. 64); Schrauf (*ibid.* 1877. 403); Koch (*ibid.* 1878. 652). Cornu (*C. R.* 86, 101, 983) obtained spectroscopic indications of the occurrence of Ti in the sun's atmosphere. The bright-reddish crystals that are often found in blast furnaces wherein titaniferous iron ore has been smelted were supposed for many years to be Ti; but Wöhler (*A.* 73, 34) showed that they contain C and N besides Ti (*v.* TITANIUM CARBONITRIDE, p. 739).

Formation.—1. By heating K_2TiF_6 with K or Na, out of contact with air (*v. Preparation*).—2. By heating $TiCl_4$ with Na in a closed iron crucible heated in a wind furnace (Nilson a. Pettersson, *W.* 4, 554; *cf.* Kern, *C. N.* 33, 57). According to Robinson a. Hutchings (*Am.* 6, 74), Ti is formed by heating $TiCl_4$ with Na to 130° in a sealed tube; but O. v. d. Pfordten (*A.* 237, 201) says that very little, if any, Ti is obtained, and that the main product is $TiCl_2$.—3. By fusing K_2TiF_6 with an equal weight of iron filings, and dissolving away the iron by HClAq (Wehrlin a. Giraud, *C. R.* 85, 288).—4. By heating $TiCl_4$ to 180° with Ag obtained by reducing a salt of Ag; Ti_2Cl_6 is also formed (Friedel a. Guérin, *A. Ch.* [5] 7, 24).

Preparation.—Finely-powdered *rutile* is mixed with double its weight of K_2CO_3, and the mixture is fused in a Pt crucible placed inside an earthenware crucible. The fused mass is powdered and dissolved in the necessary quantity of HFAq in a Pt dish; water is added to dissolve K_2TiF_6 which begins to separate, the liquid is boiled and filtered while boiling; the K_2TiF_6, which separates from the filtrate in lustrous crystalline crusts, is pressed between filter-paper, washed repeatedly with cold water, again pressed, and recrystallised several times from boiling water (Wöhler, *A.* 74, 212). The dry K_2TiF_6 is placed in a porcelain boat in a porcelain (or hard glass) tube connected with a supply of pure dry H; another boat, containing Na, is also placed in the tube; H is passed through the apparatus, and the Na is gradually vaporised and driven over the K_2TiF_6, which is heated. When the action is completed and the tube has cooled (the H stream being maintained), the solid is treated with water, which dissolves out KF, NaF, and Na (W. a. Deville, *A.* 103, 230). The Ti is finally washed with ether and dried over H_2SO_4 (*v.* Kern, *C. N.* 33, 57). Merz (*P.* 73, 48) prepared Ti by heating a mixture of six pts. K_2TiF_6 and three pts. NaCl with two pts. Na in a glass bulb placed in a sand-bath, while a stream of H was passed through the bulb, then adding zinc-powder and fusing, and dissolving out the zinc by cold dilute HClAq.

Properties.—A dark-grey or black lustrous powder; has not been obtained crystallised. Ti resembles iron reduced from Fe_2O_3 by H at a low temperature.

According to Junot (*J.* 1853. 336), Ti was obtained by him as a silver-white lustrous deposit by electrolysing a solution prepared by dissolving titanate of K in boiling H_2SO_4Aq, evaporating to a syrup, and extracting with Na_2SO_4Aq. J.'s experiments do not seem to have been repeated. Lévy (*C. R.* 110, 1368) obtained hard, steel-white, cubicle crystals, which he took to be nearly pure Ti, by passing $TiCl_4$ vapour over Si, B, or several metals heated to bright redness. L. found only 80 p.c. Ti in the crystals. Ti burns brilliantly in a flame. When heated to redness in O, it is oxidised with production of an intensely brilliant white light. Ti also burns in Cl. It decomposes water at 100°. Warm HClAq dissolves Ti easily; it is also at once dissolved by HFAq. Heated by electric sparks, Ti gives an emission-spectrum very rich in lines (*v.* Thalen, *A. Ch.* [4] 18, 239; Troost a. Hautefeuille, *C. R.* 73, 620; Cornu, *C. R.* 86, 101, 983; Liveing a. Dewar, *Pr.* 32, 402).

The atomic weight of Ti has been determined (1) by analyses of $TiCl_4$ (H. Rose, *P.* 15, 145 [1829]; Pierre, *A. Ch.* [3] 20, 257 [1847]; Thorpe, *C. J.* 47, 108 [1885]); (2) by determining the weight of TiO_2 got from a determinate weight of $TiCl_4$ (H. Rose, *l.c.*; Thorpe, *l.c.*); (3) by analyses of $TiBr_4$ (Thorpe, *l.c.*); (4) by determining the weight of TiO_2 got from a determinate weight of $TiBr_4$ (Thorpe, *l.c.*); (5) by measuring S.H. of Ti (Nilson a. Pettersson, *Z. P. C.* 1, 34); (6) by determining V.D. of $TiCl_4$ and TiI_4 (*v.* these compounds). Rose's determinations gave values for the at. w. of Ti varying from 47·92 to 48·32; Pierre's values varied from 50·2 to 50·29. The very accurate series of determinations made by Thorpe has settled the at. w. to be almost exactly 48 (48·01 if O = 16; 47·9 if O = 15·96).

The atom of Ti is tetravalent in the gaseous molecules $TiCl_4$ and TiI_4. Ti is metallic in many of its chemical properties; it decomposes water, giving off H; the oxides Ti_2O_3 and TiO_2 form corresponding salts; the chloride and iodide (and ? also bromide) can be gasified without decomposition; the sulphide TiS_2 does not show any acidic characters so far as it has been examined. The chlorides give pps. of corresponding hydrated oxides by reacting with alkalis, &c. On the other hand, Ti exhibits distinctly non-metallic or chlorous properties; hydrates of TiO_2 act as feeble acids, producing salts wherein Ti forms part of the negative radicle. The acids H_2TiF_6 and $H_2TiO_2F_4$ are known, and also salts derived therefrom. $TiCl_4$ is very easily decomposed by

water, giving HClAq and $TiO_2.xH_2O$, &c. As might be expected from the two-sided character of the reactions of Ti, most of the salts obtained by replacing the H of oxyacids by Ti are basic salts. The oxide TiO_3 has been isolated; it is probably a superoxide. Ti is closely related to Zr, Ce, and Th; these elements, with Ti, form the even-series family of Group IV. (*v.* TITANIUM GROUP OF ELEMENTS, p. 749). Ti is also closely related to Ge, Sn, and Pb, which form the odd-series elements of Group IV. (*v.* TIN GROUP OF ELEMENTS, p. 735). Ti also shows distinct relationships to C and Si, which are the first and second members of Group IV. (*v.* CARBON GROUP OF ELEMENTS, vol. i. p. 682). The similarity between Ti and Si is shown very distinctly in the titanic and silicic acids, the relations between which may be expressed by such a general equation as $nMH_4O_4 - mH_2O = M_nH_{4n-2m}O_{4n-m}$ (M = Ti or Si). Ti is the only element of Group IV. which is known to form compounds of the type $M_2TiO_2F_4 = Ti(OM)_2F_4 = TiX_6$.

Reactions and Combinations.—1. Heated in ***air*** or in *oxygen*, burns brilliantly to TiO_2.—2. Burns when heated in *chlorine*, forming Ti_4Cl.—3. TiI_4 is formed by passing vapour of *iodine* over hot Ti.—4. Combines with *nitrogen* when heated therewith (*v. Nitrides*, p. 743).—5. Ti is violently oxidised to TiO_2 by heating with *cupric oxide* or *red lead*.—6. Interacts with ***water*** at 100°, forming TiO_2 and H.—7. Dissolves in warm *hydrochloric acid*, forming Ti_2Cl_6 (Glatzel, *B.* 9, 1831; Rammelsberg, *B. B.* 1874. 490).—8. Ti dissolves easily in *hydrofluoric acid* (? forming Ti_2F_6); also in warm dilute *nitric* or *sulphuric acid*, according to Glatzel (*l.c.*), the solution in H_2SO_4Aq deposits crystals of $Ti_2(SO_4)_3$ on cooling. Conc. hot H_2SO_4 reacts with Ti, giving off SO_2 (? forming $Ti(SO_4)_2$); conc. hot HNO_3 oxidises Ti to metatitanic acid (*q. v.*, p. 747) according to Weber (*P.* 120, 287).

Detection and Estimation.—Compounds of Ti are not reduced to metal by heating on charcoal in the blowpipe flame. Ti compounds, if not containing elements which give a colour to microcosmic salt, form a colourless glass when melted in the microcosmic salt bead in the outer blowpipe flame; in the inner flame they give a glass which is colourless when hot, but becomes violet on cooling; the delicacy of the reaction is much increased by adding a little zinc to the bead (Riley, *C. J.* 12, 13). Solutions of $TiO_2.xH_2O$ in HClAq or H_2SO_4Aq give white pps. of $TiO_2.xH_2O$ on boiling; addition of a piece of tin to a solution of $TiO_2.xH_2O$ in HClAq causes evolution of H and produces a violet-blue solution which becomes rose-coloured on dilution with water (von Kobell, *P.* 62, 599). A solution of TiO_2xH_2O in HClAq gives a violet-red liquid (Ti_2Cl_6 solution) by digestion for some time with Cu (Fuchs, *A.* 56, 319). Ti is estimated as TiO_2, ppd. from solutions by a slight excess of NH_3Aq. Insoluble compounds of Ti are generally fused with $KHSO_4$, the fused mass is dissolved in water, and $TiO_2.xH_2O$ is ppd. by long continued boiling.

Titanium, alloys of. The alloys of Ti have not been much examined. Wöhler a. Michel (*A.* 113, 248; 115, 102) obtained an alloy with ***aluminium*** approaching in composition to $TiAl_3$ by heating a mixture of TiO_2, KCl, NaCl, and *cryolite*, and treating with HClAq. By heating a mixture of Ti and Al with KCl or NaCl in an earthenware crucible in a stream of H, Lévy (*C. R.* 106, 66) obtained brittle steel-grey crystals which he took to be an *isomorphous mixture* of $TiAl_4$ and $TiAl_4$. Ti alloys with *iron*; it is often present in pig-iron, but rarely in bar-iron or steel (*v.* Riley, *C. J.* 16, 387).

Titanium, bromides of. Only one bromide has been isolated, $TiBr_4$.

TITANIC BROMIDE $TiBr_4$. (*Titanium tetrabromide.*) Mol. w. has not been determined, but the formula is almost certainly molecular from analogy of $TiCl_4$ and TiI_4.

Prepared by passing Br vapour over a mixture of TiO_2 and charcoal heated to full redness, collecting the liquid that distils over and solidifies in the receiver, and redistilling it from Hg (to remove free Br) (Duppa, *Pr.* 8, 42). Also prepared by passing HBr gas over $TiCl_4$ kept a few degrees below its boiling-point in a distilling flask connected with an upright condenser; the whole of the Cl of the $TiCl_4$ is expelled (Thorpe, *C. J.* 47, 126). Thorpe used 350 g. $TiCl_4$, and continued the passage of HBr for three days. The HBr is conveniently obtained by the interaction of Br and amorphous P in a little water; it is freed from Br by passing through a U tube containing broken glass and amorphous P, and is dried by passing through another U tube containing $CaCl_2$.

$TiBr_4$ forms dark-yellow or orange crystals, S.G. 2·6, melting at c. 40°, and boiling at c. 229° (D., *l.c.*; T., *l.c.*). It is very hygroscopic, easily decomposed by water, forming a perfectly clear solution containing HBr and $TiO_2.xH_2O$.

Titanium, bromochlorides of. By adding Br to $TiCl_2$ (*q. v.*, p. 741) Friedel a. Guérin (*A. Ch.* [5] 8, 24) obtained a colourless liquid, fuming in the air, boiling at 176°, which they said was probably $TiBr_2Cl_2$; and by the reaction of Br with Ti_2Cl_6 they obtained a liquid boiling at 154°, probably $TiBrCl_3$.

Titanium, carbonitride of, Ti_5CN_4. (*Titanium nitrocyanide*, or *cyanonitride* $Ti_{10}(CN)_2N_6$.) This compound is often found in blast furnaces wherein titaniferous ironstone has been smelted. It was supposed by Wollaston to be Ti (*G. A.* 75, 220), and was for many years generally mistaken for the metal. In 1850 Wöhler (*A.* 73, 34) proved it to contain C and N besides Ti.

The compound is found in blast furnaces as lustrous, opaque, copper-coloured, prismatic crystals. By treating these crystals with conc. HClAq, then with conc. H_2SO_4, washing, treating with HFAq, and again washing, the compound is freed from admixed Fe, &c.; small leaflets of graphite generally remain mixed with the carbonitride. Ti_5CN_4 can be prepared by heating a mixture of dry K_4FeCy_6 and TiO_2 in a closed crucible for an hour or two at c. the melting-point of Ni (1400° to 1450°), dissolving out Fe, &c., by conc. HClAq, washing, and drying. By examining the brown powder thus obtained with a magnifying power of 300 diameters copper-coloured crystals of Ti_5CN_4 can be detected (Wöhler, *A.* 73, 34). It is also obtained by heating a mixture 1 part C and $5\frac{2}{3}$ parts TiO_2, in a closed carbon crucible for some hours at 1400° to 1450°; also by passing N over a mixture of C and TiO_2 in the ratio $1:5\frac{2}{3}$ heated in a carbon boat placed in a carbon tube to the melting-point of Pt (c. 1800°) (W. a. Deville, *A.* 103, 231).

When Ti_5CN_4 is fused with KOH it gives off NH_3; heated to redness in a stream of water vapour TiO_2 is formed, and H, NH_3, and HCN are given off (W., *l.c.*); heated in Cl it gives $TiCl_4$ and $TiCl_4.2HCN$ (W., *l.c.*; also p. 219); the compound is burnt by heating with PbO, CuO, or HgO, giving off CO_2 and leaving TiO_2 and Pb, Cu, or Hg (much heat is produced in the reaction) (W., *l.c.*).

The simplest formula that expresses the composition of Ti carbonitride is Ti_5CN_4 (W., *l.c.*; *cf.* Reinhardt, *Zeit. für anorgan. Chemie*, 1, 121). This formula is generally doubled and written $Ti(CN)_2.3Ti_3N_2$, and the substance is regarded as a compound of cyanide and nitride of Ti; Joly (*C. R.* 82, 1195) regards it as a compound of carbide and nitride of Ti, and writes the formula TiC.4TiN (or 2TiC.8TiN).

Titanium, chlorides of. Ti and Cl combine to form $TiCl_4$; by the regulated action of H on $TiCl_4$ one-fourth of the Cl can be removed and $TiCl_3$ produced; and by the further action of H on $TiCl_3$ one-third of the Cl can be removed and $TiCl_2$ produced. The V.D. of the tetrachloride has been determined, and the formula $TiCl_4$ is molecular; from the analogy of C_2Cl_6 and Si_2Cl_6 it is probable that the molecular formula of the trichloride is Ti_2Cl_6; from the analogy of $PbCl_2$ and $SnCl_2$ the formula $TiCl_2$ may be supposed to be molecular, but if the analogy of C_2Cl_4 is to be followed, the molecular formula must be Ti_2Cl_4.

TITANIC CHLORIDE $TiCl_4$. (*Titanium tetrachloride.*) Mol. w. 189·38. Melts at −25° (Haase, *B.* 26, 1052). Boils at 136·41° at 760 mm. (Thorpe, *C. J.* 37, 329). S.G. $\frac{0^{\circ}}{4^{\circ}}$ 1·76041; S.G. at b.p. 1·52223 (Thorpe, *l.c.*). V.D. 98·8 at 143° (Dumas, *A. Ch.* [2] 33, 388). S.V. 121·47 (Thorpe, *l.c.*).

Preparation.—1. TiO_2 is intimately mixed with c. half its weight of lampblack previously heated to redness in a stream of Cl, and the mixture is heated to full redness in a tube of hard glass connected with a receiver, while a stream of dry Cl is passed over it. The $TiCl_4$ which collects in the receiver is freed from Cl by shaking with Cu, Hg, or Na amalgam (Merz, *Bl.* [2] 7, 401), or by boiling for some time (Thorpe, *C. J.* 47, 119), and is then distilled. Thorpe (*l.c.*) conducted the final distillation in dry N.—2. Vapour of CCl_4, or a mixture of equal volumes of Cl and CO, is passed over TiO_2 in small lumps, heated to bright redness in a tube of hard glass connected with a receiver. The $TiCl_4$ is purified as described above (Watts a. Bell, *C. J.* 33, 443).

Properties.—A colourless liquid, solidifying at −25° (Haase, *B.* 26, 1052). Does not conduct electricity (O. v. d. Pfordten, *A.* 237, 201). Fumes in the air, rapidly absorbing moisture and solidifying to the hydrate $TiCl_4.5H_2O$ (Demoly, *A.* 72, 213). (For an apparatus for collecting $TiCl_4$ for analysis, *v.* Thorpe, *l.c.*) $TiCl_4$ is violently decomposed by water, forming HClAq, and $TiO_2.xH_2O$ some of which ppts. (*v. Reactions*, No. 8).

Reactions.—1. *Hydrogen* reduces $TiCl_4$, at a high temperature, to Ti_2Cl_6 and then to $TiCl_2$ (*v. trichloride* and *dichloride*). — 2. Mixed with *oxygen* and passed through a red-hot porcelain tube, $Ti_4O_2Cl_8$ is formed (*v. Oxychlorides*, p. 748). 3. Heated to 130° in a sealed tube with *sodium*, the chief product is $TiCl_2$, according to O. v. d. Pfordten (*A.* 237, 201); Robinson a. Hutchings (*Am.* 6, 74) say that Ti is produced in this reaction. Nilson a. Pettersson (*W.* 4, 554) obtained Ti by reducing $TiCl_4$ by Na at a very high temperature.—4. *Sodium-amalgam* produces Ti_2Cl_6 and $TiCl_2$ (O. v. d. P., *l.c.*).—5. Reduced *silver* gives Ti_2Cl_6 and Ti when heated with $TiCl_4$ to 180° (Friedel a. Guérin, *A. Ch.* [5] 7, 24).—6. By passing vapour of $TiCl_4$ over *silicon, boron,* or several *metals*, heated to bright redness, Lévy (*C. R.* 110, 1368) obtained hard, steel-white, cubical crystals which he supposed to be nearly pure Ti.—7. Pure, dry, *hydrogen sulphide* reacts at the ordinary temperature, forming Ti_2Cl_6; at a higher temperature a pp. is produced which is probably a thiochloride of Ti (O. v. d. P., *A.* 234, 257).—8. Cold *water* reacts violently with $TiCl_4$, with production of much heat and formation of a turbid liquid containing HCl and holding in suspension $2TiO_2.H_2O$ (*v. Metatitanic acid* under TITANIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 747); after 30 or 40 hours the liquid becomes clear, but ppn. occurs again on heating to c. 85° when about 7 pts. water are present to 1 pt. $TiCl_4$ used (*v.* Thorpe, *C. J.* 47, 120; and *cf.* TITANIUM OXYACIDS, p. 746). According to Merz (*Bl.* [2] 7, 401), an oxychloride, approximately $TiCl_4.3TiO_2.16H_2O$, is obtained by evaporating $TiCl_4Aq$, or $TiCl_4$ that has deliquesced in air, over H_2SO_4 and CaO (*v. Oxychlorides*, p. 748). TiO_2, in the form of *brookite*, is obtained by passing vapour of $TiCl_4$ and *water*, mixed with CO_2, through a red-hot porcelain tube (Daubrée, *C. R.* 29, 227; 39, 153).—9. With *hydrochloric acid* the compounds $TiCl_3.OH$ and $TiCl_2(OH)_2$ are formed (*v.* TITANIUM HYDROXYL CHLORIDES, p. 743).—10. *Chlorosulphonic acid* ($SO_2.OH.Cl$) reacts with $TiCl_4$ at the ordinary temperature to form a yellow, amorphous, deliquescent powder, having the composition $TiCl_4.SO_3$ ($= TiCl_3.OSO_2.Cl$) (Clausnizer, *B.* 11, 2011).—11. By passing vapour of $TiCl_4$, mixed with H, through a white-hot tube containing *titanium dioxide* the oxychloride $Ti_2O_2Cl_2$ is obtained (*v. Oxychlorides*, p. 748).

Combinations.—1. With *water* to form a pentahydrate and a dihydrate. Demoly (*A.* 72, 213) obtained $TiCl_4.5H_2O$, as deliquescent crystals, by allowing $TiCl_4$ to absorb moisture from the air, then adding a little more water, and evaporating under reduced pressure. By drying the pentahydrate over H_2SO_4 *in vacuo*, D. obtained $TiCl_4.2H_2O$.—2. With *ammonia*, to form $TiCl_4.4NH_3$ according to H. Rose (*P.* 16, 57), $TiCl_4.6NH_3$ according to Persoz (*A. Ch.* [2] 46, 315); easily decomposed in air; heated in a tube gives off NH_3, then NH_3 and HCl, and a yellowish sublimate of $TiCl_4.3NH_4Cl$, and leaves Ti; heated in NH_3 gives Ti_3N_4 (*v.* TITANIUM NITRIDES, p. 743). 3. With *hydrogen phosphide*, to form a brown powder, which when heated gives a sublimate of $3TiCl_4.2PH_4Cl$ according to H. Rose (*P.* 42, 527). 4. With *hydrogen cyanide* to form $TiCl_4.2HCN$ (Wöhler, *A.* 73, 226); by vaporising this compound through a red-hot tube Ti_3N_4 and C are formed (W., *l.c.*).—5. With *cyanogen chloride*, to form yellow crystals of $TiCl_4.CNCl$; sublimable at 100° (W., *A.* 73, 219).—6. With *phosphorus* *pentachloride* to form $TiCl_4.PCl_5$; obtained by heating $TiCl_4$ and PCl_5 to 150° in a sealed tube (Bertrand, *Bl.* [2] 33, 565); also by heating TiO_2 and PCl_5 in the ratio $TiO_2:3PCl_5$, or by saturating a mixture of $TiCl_4$ and PCl_3 with Cl (Tüttscheff, *A.* 141, 111), and removing excess of $TiCl_4$ by heating in a stream of Cl (Weber, *P.* 132, 452). A citron-yellow, loose, semi-crystalline solid; sublimes without melting; deliquescent in air.—7. With *phosphorus trichloride* to form yellow crystals of $TiCl_4.PCl_3$, melting at 85·5° (Bertrand, *l.c.*).—8. With *sulphur tetrachloride*, to form $2TiCl_4.SCl_4$; obtained by saturating a mixture of $TiCl_4$ and S_2Cl_2 with Cl, and warming in a stream of Cl (Weber, *P.* 132, 454).—9. By mixing $TiCl_4$ and *sulphurous chloride* H. Rose obtained large yellow crystals, probably a compound of the two chlorides (*P.* 42, 527).—10. With *ammonium chloride*, to form $TiCl_4.3NH_4Cl$ (*v. supra, Combinations*, No. 2).—11. With *phosphoryl chloride* to form $TiCl_4.POCl_3$; obtained by gradually adding $POCl_3$ to $TiCl_4$, and gently warming (Weber, *P.* 132, 453); colourless, deliquescent crystals, melting at 110°, and boiling at 140° (Wehrlin a. Giraud, *C. R.* 85, 288).—12. With *selenion oxychloride* to form a yellow powder, decomposed by heat, having the composition $TiCl_4.2SeOCl_2$; obtained by adding $SeOCl_2$ to $TiCl_4$, and drying the solid that separates on cooling on a tile over H_2SO_4 (Weber, *B. B.* 1865. 154).—13. With *nitrosyl chloride*; obtained by saturating $TiCl_4$ with NO_2, and subliming (Hampe, *A.* 126, 47), also by passing the vapours from *aqua regia* into $TiCl_4$ (Weber, *P.* 118, 476). Hampe (*l.c.*) gives the composition $3TiCl_4.4NOCl$, Weber (*l.c.*) the composition $TiCl_4.2NOCl$. A deep citron-yellow, crystalline mass; decomposes in air; sublimable out of air; with water gives off NO.—14. With *sulphur trioxide* to form $TiCl_4.SO_3$ (or $TiCl_3.OSO_2.Cl$), formed by the interaction of $TiCl_4$ and $SO_2.OH.Cl$ at the ordinary temperature; a yellow, amorphous, deliquescent powder (Clausnizer, *B.* 11, 2011).—15. Demarçay (*Bl.* [2] 20, 127) obtained a great many compounds of $TiCl_4$ with *esters*, *mercaptans*, and *ethyl sulphide* (*cf.* Bedson, *C. J.* 29, 309).

TITANIUM TRICHLORIDE Ti_2Cl_6. (*Titanium sesquichloride. Titanous chloride.*) Mol. w. not determined; but from analogy of C_2Cl_6 and Si_2Cl_6 the formula Ti_2Cl_6 is probably molecular.

Formation.—1. By reducing $TiCl_4$ by H (*v. Preparation*).—2. By reducing $TiCl_4$ by sodium-amalgam (O. v. d. Pfordten, *A.* 237, 201); or by pure, dry H_2S (O. v. d. P., *A.* 234, 257).—3. By heating $TiCl_4$ with reduced Ag to 180°; Ti is also formed, and probably $TiCl_2$ also (Friedel a. Guérin, *A. Ch.* [5] 8, 24).—4. A solution of Ti_2Cl_6 is obtained by digesting a solution of $TiO_2.xH_2O$ in HClAq with Cu at 40°-50° (Fuchs, *A.* 56, 319); or with Ag ppd. by zinc from AgCl (von Kobell, *P.* 62, 599). Ti_2Cl_6 is also probably present in the greenish liquid obtained by adding Na amalgam to K_2TiF_6 in HClAq (O. v. d. P., *A.* 237, 201).

Preparation.—$TiCl_4$ is placed in a retort connected with a tube of porcelain or hard glass (if a glass tube is used it should be wrapped in copper-foil) which is placed horizontally in a furnace; the other end of the tube projects considerably out of the furnace and is connected with a receiver to collect undecomposed $TiCl_4$. The delivery tube from an apparatus evolving pure and dry H passes into the retort beneath the surface of the $TiCl_4$. H is passed through the apparatus until it is entirely filled with the gas; the tube is then heated to redness, and the retort is gently warmed. Ti_2Cl_6 is formed and condenses as dark-violet scales on the part of the tube that projects out of the furnace. When all the $TiCl_4$ has been driven out of the retort, the Ti_2Cl_6 in the cooler part of the tube is gently warmed, while the passage of H is continued, to remove any adhering $TiCl_4$; the Ti_2Cl_6 is allowed to cool in the stream of H (Ebelmen, *A. Ch.* [3] 20, 385).

Properties.—A dark-violet, very lustrous solid, deliquescing in air, and dissolving in water to form a violet liquid, which gradually decolourises with ppn. of $TiO_2.xH_2O$. Ti_2Cl_6 is easily soluble in alcohol, forming a violet or green liquid; it is insoluble in ether, and sparingly soluble in HClAq (O. v. d. P., *A.* 237, 201).

Reactions.—1. Heated in *hydrogen* to c. 440°, $TiCl_4$ distils over and $TiCl_2$ remains (Friedel a. Guérin, *A. Ch.* [5] 8, 24).—2. Heated in *air*, $TiCl_4$ vaporises and TiO_2 remains.—3. Dissolves in *water*, forming a violet, or green-violet, liquid which slowly becomes colourless with ppn. of $TiO_2.xH_2O$.—4. *Alkalis*, or *alkali carbonates*, in solution ppt. $Ti_2O_3.xH_2O$ from Ti_2Cl_6Aq; *ammonium sulphide* forms the same pp.; *hydrogen sulphide* gives no pp. (Ebelmen, *l.c.*).—5. Ti_2Cl_6Aq reduces *solutions of gold, silver, or platinum salts* with ppn. of the metals; *ferric* and *cupric salts* are reduced to ferrous and cuprous salts; *sulphurous acid solution* is reduced by heating with Ti_2Cl_6Aq with ppn. of S (E., *l.c.*).—6. Ti_2Cl_6 reacts with *bromine* to form a liquid boiling at 154°, probably $TiBrCl_3$ (F. a. G., *l.c.*).

Combinations.—With *water* to form $Ti_2Cl_6.8H_2O$; obtained by Glatzel (*B.* 9, 1829) by evaporating a solution of Ti in HClAq to the crystallising point, filtering off ppd. $TiO_2.xH_2O$ from time to time. The hydrate is a green solid; it dissolves in water, forming an opalescent violet solution containing a little suspended $TiO_2.xH_2O$; the solution becomes colourless on standing, and then gives the reactions of titanic acid.

TITANIUM DICHLORIDE $TiCl_2$. (Sometimes called *titanous chloride.*) Mol. w. is not known. From the analogy of $SnCl_2$ and $PbCl_2$, the formula $TiCl_2$ would be molecular; but from the analogy of C_2Cl_4 the molecular formula would be Ti_2Cl_4.

Formation.—1. By reducing Ti_2Cl_6 by H (*v. Preparation*).—2. $TiCl_2$ is probably formed, along with Ti_2Cl_6, by heating $TiCl_4$ with reduced Ag (Friedel a. Guérin, *A. Ch.* [5] 8, 24).—3. Along with Ti_2Cl_6, by the action of Na amalgam on $TiCl_4$; also by heating $TiCl_4$ with Na to 130° in a sealed tube (O. v. d. Pfordten, *A.* 237, 201).

Preparation.—Ti_2Cl_6 reacts with H at a red heat to give $TiCl_2$ and $TiCl_4$. Friedel a. Guérin (*l.c.*) proceed as follows. The tube containing Ti_2Cl_6, prepared from $TiCl_4$ (*v. supra*), while still filled with H, is connected with an apparatus evolving pure, dry CO_2, and the whole of the H in the apparatus is driven out by CO_2. The Ti_2Cl_6 is then shaken into a small tubulated retort, placed on a sand-tray, and previously filled with CO_2; the CO_2 is displaced by pure, dry H; the retort is then heated to dull red.

ness, while a stream of H is passed through it, until $TiCl_4$ ceases to distil off; the retort is allowed to cool in the stream of H, and CO_2 is then passed in until all the H is removed (if this is omitted the $TiCl_2$ takes fire in the air), and the black $TiCl_2$ in the retort is quickly shaken into small dry tubes filled with CO_2, which are at once sealed off.

Properties.—A black, light powder; very rapidly absorbs water, forming a kind of mud; insoluble in CS_2, $CHCl_3$, or Et_2O. Volatilised without melting by heating to full redness in H. Shaken with Et_2O and KCNSAq, the Et_2O becomes dark brown; this is a delicate test for $TiCl_2$ (O. v. d. Pfordten, *A.* 237, 201).

Reactions.—1. Takes fire when touched with a drop of *water* (? with formation of $Ti_2O_2Cl_2$; *v.* F. a. G., *l.c.*); thrown into water, it hisses like red-hot iron, decomposing the water with evolution of H and formation of a yellowish liquid.—2. Decomposes absolute *alcohol*, giving off H and forming a yellowish liquid.—3. Heated in *air*, $TiCl_2$ burns like tinder, giving off $TiCl_4$ and leaving TiO_2.—4. With *bromine* it forms a liquid boiling at 176°, probably $TiCl_2Br_2$ (F. a. G., *l.c.*).

Titanium, chlorobromides of, *v.* TITANIUM BROMOCHLORIDES, p. 739.

Titanium, cyanonitride of, *v.* TITANIUM CARBONITRIDE, p. 739.

Titanium, ferrocyanides of, *v.* vol. ii. p. 337.

Titanium, fluorides of. The only compound that has been isolated with certainty is TiF_4. There are indications of the existence of Ti_2F_6, and compounds of this fluoride with alkali fluorides are known.

TITANIC FLUORIDE TiF_4. (*Titanium tetrafluoride.*) Formula probably molecular, from analogy of $TiCl_4$ and TiI_4. By heating a mixture of TiO_2 and CaF_2 with H_2SO_4, Unverdorben (*P.* 7, 320) obtained a colourless distillate, which he supposed to contain a compound of Ti and F. Berzelius (*P.* 4, 1) obtained crystals (? TiF_4) by dissolving $TiO_2.xH_2O$ in HFAq. The crystals were decomposed by water, giving an acid solution (? H_2TiF_6Aq), and an insoluble, 'so to say *basic*,' compound. TiO_2 is obtained by passing vapour of TiF_4, mixed with H_2O, through a tube heated to c. 800° or 1000° (Hautefeuille, *A. Ch.* [4] 4, 131; *cf.* TITANIUM DIOXIDE, p. 741). Heated to redness in H, perhaps gives Ti_2F_6 (H., *l.c.*).

Combinations.—1. TiF_4 probably combines with *hydrogen fluoride* to form H_2TiF_6. By dissolving $TiO_2.xH_2O$ in HFAq, evaporating, adding water to the crystals (? TiF_4) thus formed, and filtering from an insoluble solid (? oxyfluoride), Berzelius (*P.* 4, 1) obtained an acid solution from which, by neutralisation with KOHAq and evaporation, he obtained the salt K_2TiF_6. The acid solution probably contained H_2TiF_6. This compound (if it exists) is best called *titanifluorhydric acid*. It is analogous to H_2SiF_6, H_2SnF_6, and other acids of the type H_2MX_6, where M = an element of Group IV. (except C), and X = a halogen.—2. With various *metallic fluorides* to form $TiF_4.2MF = M_2TiF_6$. These salts were obtained from the K salt, which was got by neutralising the acid solution prepared as described under 1. Salts of NH_4, Ca, Cu, Fe, Pb, Mg, and Ni are described (B., *l.c.*; Weber, *P.* 120, 291). These salts are best called *titanifluorides*; they are similar to stannifluorides.—3. TiF_4 also combines with *ammonium fluoride* to form $TiF_4.3NH_4F$ (besides $TiF_4.2NH_4F$) (Baker, *C. J.* 35, 763).

By adding NH_3Aq, drop by drop, to warm $(NH_4)_2TiF_6Aq$, Piccini (*G.* 17, 479) obtained a compound of the form $TiO_2F_2.xNH_4F$; from this he prepared $TiO_2F_2.BaF_2$, and by carefully decomposing this salt by H_2SO_4Aq he obtained a solution of the acid $TiO_2F_2.2HF$. P. regards this acid as a F derivative of the hypothetical *pertitanic acid* H_2TiO_4 (the acid of TiO_3); he calls the acid *fluoroxypertitanic acid*, and the salts *fluoroxypertitanates*. Following the plan adopted in this *Dictionary*, the acid will be called *titanoxyfluorhydric acid* $H_2TiO_2F_4$, and the salts, $M^I_2TiO_2F_4$, will be called *titanoxyfluorides*. $H_2TiO_2F_4Aq$ is a yellow liquid, not ppd. by Ba salts, giving a pp. of TiO_3 with alkali carbonates.

TITANIUM TRIFLUORIDE Ti_2F_6. This compound is said to be formed by strongly heating K_2TiF_6 in a stream of H with a little HCl, according to Hautefeuille (*C. R.* 59, 189; *cf.* 57, 151). According to H., the compound is a purple-red solid, soluble in water. By treating Ti_2Cl_6Aq with KHF_2 or NH_4F, Piccini (*G.* 16, 104) obtained violet pps. of $Ti_2F_6.2MF$, where M = NH_4 or K; he also obtained $Ti_2F_6.3NH_4F$. The K salt is slightly soluble in water; soluble in dilute acids, forming green liquids, from which alkalis throw down azure-blue pps. that gradually oxidise to $TiO_2.xH_2O$ on exposure to air. The salt $TiF_4.3NH_4F$, when exposed to air, gradually oxidises to $TiO_2F_2.3NH_4F$.

Titanium, haloid compounds of. Ti combines with the halogens directly to form compounds TiX_4; these tetrahalides are generally prepared by passing the halogen as gas over a red-hot mixture of TiO_2 and C. TiI_4 is best prepared by heating $TiCl_4$ in HI gas, and $TiBr_4$ is very conveniently prepared by heating $TiCl_4$ in HBr gas; TiF_4 is prepared by dissolving $TiO_2.xH_2O$ in HFAq and evaporating. The two tetrahalides $TiCl_4$ and TiI_4 have been gasified. These formulæ are molecular, hence the formulæ TiF_4 and $TiBr_4$ probably also represent the compositions of the gaseous molecules of these compounds. By the action of H, or certain other reducing agents, on $TiCl_4$, two chlorides are obtained, Ti_xCl_{3x} and Ti_xCl_{2x}. The V.D. of neither has been determined, but from the analogy of C_2Cl_6 and Si_2Cl_6, the value of x in Ti_xCl_{3x} is probably 2; from the analogy of C_2Cl_4 the molecular formula of the lowest chloride is probably Ti_2Cl_4, but from the analogy of $SnCl_2$ and $PbCl_2$ the formula $TiCl_2$ would be given to it. Ti_2F_6 or TiF_3 probably exists. No bromide or iodide of either type Ti_2X_6 or Ti_2X_4 has been isolated. Two bromochlorides of the types TiX_4 and Ti_2X_4 probably exist. $TiCl_4$ and $TiBr_4$ dissolve in cold water; the solutions contain HXAq and $TiO_2.xH_2O$; dilution, and more quickly heating, ppts. insoluble $TiO_2.xH_2O$ from the solution of $TiCl_4$. TiF_4 is decomposed by water, giving H_2TiF_6Aq (and ? an oxyfluoride). TiI_4 is also decomposed by water; on heating insoluble $TiO_2.xH_2O$ separates. $TiCl_4$ combines with many non-metallic chlorides and oxychlorides. TiF_4 combines with metallic fluorides, forming salts M_2TiF_6, and also some more complex salts $xTiF_4.yMF$. A few *oxyhaloid compounds* have been isolated, but a great number can doubtless be formed. The acid $H_2TiO_2F_4$ and salts of this acid have been isolated. Ti_2Cl_6 dissolves in water, and after a time $TiO_2.xH_2O$ separates; the solution is an energetic reducing agent; alkalis ppt. $Ti_2O_3.xH_3O$. $TiCl_2$ reacts violently with water, giving off H, and probably forming an oxychloride.

Titanium, hydroxyl chlorides of. By the reaction of the proper quantity of 36 p.c. HClAq with $TiCl_4$, the compound $Ti(OH)Cl_3$ was obtained by Koenig a. O. v. d. Pfordten (*B.* 21, 1708); using the calculated quantity of 36 p.c. HClAq, the compound $Ti(OH)_2Cl_2$ was produced; and the prolonged action of ordinary air on either of the preceding compounds resulted in the formation of $Ti(OH)_3Cl$. These compounds are regarded by K. a. O. v. d. P. as derived from $Ti(OH)_4$ by replacement of OH by Cl; the compounds may be called *orthotitanic chlorhydrins.* The compounds are yellow or white deliquescent solids; they dissolve in water; $Ti(OH)Cl_3$ very rapidly with a hissing noise, $Ti(OH)_2Cl_2$ less violently, and $Ti(OH)_3Cl$ with some difficulty. The aqueous solutions give pps. of $TiO_2.xH_2O$ on boiling. When the compounds are heated they give (1) $TiCl_4$ and $TiO_2.xH_2O$, (2) $TiO_2.xH_2O$ and HCl, and (3) $TiO_2.xH_2O$, HCl, and H_2O. By reducing $Ti(OH)Cl_3$ by Na amalgam, in H, Ti_2O_3 is produced (K. a. O. v. d. P., *B.* 22, 2070; *cf.* *B.* 22, 1485).

Titanium, hydroxyl fluoride of. This name may be given to the compound $Ti(OH)_2F_4$; it is described as *titanoxyfluorhydric acid,* under TITANIC FLUORIDE (p. 742).

Titanium, iodides of. Only one compound has been isolated, TiI_4.

TITANIC IODIDE TiI_4. (*Titanium tetraiodide.*) Mol. w. 554·02. V.D. at 440° = 261·2 (Hautefeuille, *Bl.* [2] 7, 201).

Formation.—1. Vapour of I is passed over Ti heated to redness (Weber, *P.* 120, 287).—2. A mixture of $TiCl_4$ vapour, I vapour, and H is passed through a tube heated to dull redness; TiI_4, mixed with free I, condenses on the colder part of the tube (Hautefeuille, *Bl.* [2] 7, 201).—3. By decomposing $TiCl_4$ by HI.

Preparation.—Dry HI gas is passed into $TiCl_4$, which is gradually heated to its b.p. and kept at that temperature until the reaction is completed; the TiI_4 is freed from traces of I, which give it a violet tinge, by a few distillations in H (H., *l.c.*).

Properties and Reactions.—A reddish-brown, lustrous, brittle solid; when melted and cooled, crystallises in octahedra, changing after some days to tufts of silky, prismatic crystals. Melts at 150°, and boils a little above 360°; can be distilled without decomposition; melted TiI_4 remains liquid till cooled below 100°. Fumes strongly in the air. Dissolves easily in water; solution turns brown on exposure to air and ppts. $TiO_2.xH_2O$. When vapour of TiI_4 is heated in air it burns to TiO_2 and I_2O_5 (H., *l.c.*).

Titanium, nitrides of. Four compounds of Ti and N have been described; but according to later experiments only two seem to exist.

TRITITANIUM TETRANITRIDE Ti_3N_4. Mol. w. unknown. This compound is obtained by heating $TiCl_4.4NH_3$ (*v.* TITANIC CHLORIDE, *Combinations,* No. 2, p. 740), loosely packed in a tube of hard glass, in a stream of dry NH_3, until the glass begins to melt, and allowing to cool in NH_3 (Wöhler, *A.* 73, 43; Friedel a. Guérin, *A. Ch.* [5] 8, 24). Indigo-blue powder, or golden-yellow (? rhombohedral) crystals; strongly heated in H gives Ti_2N_2 (F. a. G., *l.c.*).

DITITANIUM DINITRIDE Ti_2N_2. Mol. w. unknown. Prepared by placing two porcelain boats, one containing Na and the other K_2TiF_6, in a hard-glass tube previously filled with N, passing a stream of dry N through the tube, heating the K_2TiF_6 to full redness while the Na is volatilised over it, and allowing to cool in N after all the Na has been volatilised; boiling with HClAq, washing, and drying (Wöhler a. Deville, *A.* 102, 234). Also obtained by heating K_2TiF_6 with K, KCl, NaCl, and Al in N; also by passing $TiCl_4$ vapour and H over heated Al, in N; also by passing vapour of $TiCl_4$ over heated NH_4Cl (W. a. D., *l.c.*). F. a. G. (*l.c.*) obtained the same compound by strongly heating TiO_2 in a stream of dry NH_3 for some hours; W. (*A.* 73, 43) said that TiN_2 was formed by this reaction. F. a. G. also obtained Ti_2N_2 by strongly heating Ti_3N_4 in H; W. said that Ti_5N_6 was formed by this reaction. An amorphous, brown-yellow, very hard powder; S.G. 5·28 at 18° (F. a. G., *l.c.*).

The nitrides of Ti are not decomposed by heating, out of air, to c. 950°-1,000°; fused with KOH, or strongly heated in steam (F. a. G., *l.c.*), they give off NH_3; heated in Cl, $TiCl_4$ is produced (F. a. G., *l.c.*); heated with CuO, PbO, or HgO, the nitrides burn, and Cu, Pb, or Hg is produced (W., *A.* 123, 34).

TITANIUM DINITRIDE TiN_2. This compound is formed, according to Wöhler (*A.* 73, 43), by heating TiO_2 in NH_3 for some time. Friedel a. Guérin (*A. Ch.* [5] 8. 24) say that the substance obtained by W. contained Ti_2O_3, and that if the heating is continued until a definite nitride is formed the compound so produced is Ti_2N_2.

PENTATITANIUM HEXANITRIDE Ti_5N_6. Formed, according to W. (*l.c.*), by heating Ti_3N_4 to full redness in H; or, mixed with C, by heating TiO_2 in CN or HCN gas. F. a. G. (*l.c.*) say that the product of either reaction is Ti_2N_2, in the latter reaction mixed with C.

Titanium, nitrocyanide of, *v.* TITANIUM CARBONITRIDE (p. 739).

Titanium, oxides and hydrated oxides of (*cf.* TITANIUM OXYACIDS AND SALTS AND DERIVATIVES THEREOF, p. 746). Ti burns when heated in O, forming TiO_2; by the reaction of reducing agents on $TiCl_4Aq$, and addition of alkalis, Ti_2O_3 is obtained; when the reduction is carried further it is probable that $TiO.xH_2O$ is formed. By the reaction of H_2O_2Aq in presence of alkali on salts of TiO_2, a pp. of TiO_3 is obtained. Oxides intermediate between TiO_2 and Ti_2O_3 probably exist. TiO_2 is a basic oxide, forming salts TiX_4, where $X = NO_3$, $\frac{1}{2}SO_4$, &c.; many of the salts are basic. A few salts corresponding with Ti_2O_3 have been isolated; no salt corresponding with TiO and derived from an oxyacid has yet been obtained. Some of the hydrates of TiO_2 react as feeble acids.

TITANIUM DIOXIDE TiO_2. (*Titanic oxide. Titanic anhydride.*) Mol. w. unknown.

Occurrence.—As *rutile*, *anatase*, and *brookite*; *rutile* occurs in dimetric prisms, isomorphous with *tinstone*; *anatase* in dimetric octahedra; and *brookite* in trimetric octahedra.

Formation.—1. By burning Ti in air or O.—2. By ppg. $TiCl_4Aq$ by alkali, and washing, drying, and strongly heating the ppd. $TiO_2.xH_2O$.—3. By ppg. K_2TiF_6Aq by NH_3Aq, and strongly heating the pp. after washing and drying.—4. Vapour of $TiCl_4$, or TiF_4, mixed with steam is passed through a red-hot tube.—5. TiS_2 is heated in dry CO_2 ($TiS_2 + 2CO_2 = TiO_2 + 2CO + 2S$; O. v. d. Pfordten, *B.* 22, 2070).

Preparation.—A. Amorphous titanic oxide.—1. Pure $TiCl_4$ is added, little by little, to water; sufficient NH_3Aq to neutralise the HCl produced is added, the solution is evaporated to dryness, and the residue is heated to somewhat above 700° until it ceases to lose weight. $TiCl_4$ may be obtained from *rutile* by mixing the finely-powdered mineral with c. half its weight of dry charcoal-powder, making into little pellets with starch-paste, drying the pellets, heating them to full redness in a covered crucible, then heating in a tube of hard glass (to get quite dry), and then passing dry Cl over the pellets while they are heated to bright redness, and a dry receiver is connected with the end of the hard glass tube. The $TiCl_4$ may be purified (from $SiCl_4$, $FeCl_3$, &c.) by repeatedly distilling, best in a stream of N (*v.* Merz, *J. pr.* 99, 161).—2. K_2TiF_6 is dissolved in water, NH_3Aq is added, the pp. of $TiO_2.xH_2O$ is thoroughly washed, dried, and heated to somewhat above 700°. (For a method of getting K_2TiF_6 from *rutile v. Preparation of titanium*, p. 738.) For other methods of preparing TiO_2 from Ti ores *v.* Lévy (*A. Ch.* [6] 25, 511), Austen a. Wilber (*Am.* 4, 211), Hempel (*Zeit. f. anorg. Chemie*, 3, 193), Jones (*Fr.* 9, 41, 330). B. Crystalline titanic oxide.—3. By long-continued heating to whiteness TiO_2 is said to become crystalline (*v.* Rammelsberg, *B.* 5, 1006).—4. Amorphous $TiO_2.xH_2O$ is heated to incipient redness in HCl gas, at a pressure of three atmospheres; the crystals have the form of *anatase* (Hautefeuille a. Perrey, *C. R.* 110, 1038).—5. Crystalline TiO_2 is also formed, according to Hautefeuille (*A. Ch.* [4] 4, 127), by passing the mixed vapours of TiF_4, HF, and HCl—obtained by decomposing molten K_2TiF_6 by HCl gas—through a Pt tube into which a stream of moist H is also passed; at c. 860° (boiling-point of Cd) crystals of *anatase* are produced, and at temperatures between 860° and 1,000° *brookite* is formed.—6. Heating amorphous TiO_2 in an atmosphere of HF causes crystallisation; at an incipient red heat *anatase* forms, at a higher temperature *brookite*, and at a very high temperature *rutile* (H., *l.c.*).—7. Crystals of *rutile* are formed by heating amorphous TiO_2 with microcosmic salt (Ebelmen, *A. Ch.* [3] 33, 34), or with borax (G. Rose, *B. B.* 1867. 129; Knop, *A.* 157, 365), in a porcelain oven. For other methods of producing crystals of TiO_2 *v.* Deville (*C. R.* 53, 161, 163), Senarmont (*A. Ch.* [3] 30, 129), Michel (*C. R.* 115, 1020), Wöhler (*A.* 73, 35), Daubrée (*C. R.* 29, 227; 39, 153), H. Rose (*A.* 56, 127; 68, 163).

Properties.—TiO_2 obtained by strongly heating $TiO_2.xH_2O$ forms reddish-brown lumps, more nearly resembling rutile in colour and lustre the higher the temperature to which it is heated. The dehydration by heat of $TiO_2.xH_2O$ is accompanied by the appearance of shades of colour from white, though grey and greenish, to black, according to Wagner (*B.* 21, 960); these colours are similar to those shown by *anatase*, *brookite*, and *rutile*. Nilson a. Pettersson (*Z. P. C.* 1, 33 *note*) prepared TiO_2 as a white powder with faintest yellow tinge, by decomposing $TiCl_4$ by NH_3Aq, evaporating, and heating to whiteness. When melted by the O-H flame the colour is blue to black. S.G. TiO_2 increases as the oxide is heated; heated to c. 700° S.G. is c. 3·95 (Karsten, *S.* 65, 394), after being very strongly heated S.G. rises to 4·25 (Ebelmen, *J.* 4, 15; 12, 14). S.G. of *anatase* is 3·75 to 3·9 (Breithaupt, *J.* 2, 730; Damour, *J.* 10, 666); S.G. of *brookite* is 4 to 4·2 (Rammelsberg, *J.* 2, 730; Beck, *J.* 3, 704); S.G. of *rutile* is c. 4·3 (Scheerer, *P.* 65, 296; Müller, *J.* 5, 847). After fusion in the O-H flame and cooling S.G. is 4·1, according to Hautefeuille (*A. Ch.* [4] 40, 140). S.H. 0° to 100° = ·1785, 0°-211° = ·1791, 0°-301° = ·1843, 0°-440° = ·1919° (Nilson a. Pettersson, *Z. P. C.* 1, 27; TiO_2 prepared by decomposing $TiCl_4$ by NH_3Aq, evaporating to dryness, and heating to white heat). TiO_2 crystallises in dimetric prisms (*rutile*), dimetric octahedra (*anatase*), and trimetric octahedra (*brookite*); it is isotrimorphous with SnO_2 (Wunder, *J. pr.* [2] 2, 206). TiO_2 is somewhat hygroscopic, even after prolonged and intense heating (Thorpe, *C. J.* 47, 125). It is insoluble in water, and in all acids except conc. H_2SO_4; when powdered TiO_2 is heated with conc. H_2SO_4 until the excess of acid is removed, the solid thus produced dissolves in water. TiO_2 melts in the O-H flame. According to Moissan (*C. R.* 115, 1034), when heated in an electric furnace to c. 2500° TiO_2 forms black crystals of TiO.

Reactions.—1. According to Ebelmen (*A. Ch.* [3] 20, 394), TiO_2 is reduced to Ti_2O_3 by heating to redness in *hydrogen*; but O. v. d. Pfordten (*A.* 237, 201) says the product has the composition Ti_7O_{12}.—2. A mixture of TiO_2 and *magnesium* powder heated to redness in H gives $MgTiO_3$, and a brown powder which is probably TiO (Winkler, *B.* 23, 2657).—3. A mixture of TiO_2 and *carbon* strongly heated in *chlorine* gives $TiCl_4$.—4. By long-continued heating in dry *ammonia* Ti_2N_2 is formed (Friedel a. Guérin, *A. Ch.* [5] 8, 24).—5. The compound $TiCl_4.PCl_5$ is obtained by heating an intimate mixture of TiO_2 and *phosphorus pentachloride*, in the ratio $TiO_2:3PCl_5$, in a retort until the $POCl_3$ formed is driven off (Weber, *P.* 132, 452).—6. Heated to redness in *carbon tetrachloride* vapour, $TiCl_4$ is formed (Watts a. Bell, *C. J.* 33, 443). Demarçay (*C. R.* 104, 111) says that the first product is $TiOCl_2$.—7. $TiCl_4$ is formed by heating TiO_2 to redness in a mixture of equal volumes of *chlorine and carbon monoxide* (W. a. B., *l.c.*).—8. Ti_2N_2 mixed with C is formed by heating TiO_2 in *cyanogen* or in *hydrogen cyanide* (Friedel a. Guérin, *A. Ch.* [5] 8, 24).—9. Heating in a mixture of *hydrogen sulphide and carbon disulphide* forms Ti_2S_3 or TiS_2, according to the temperature (Thorpe, *C. J.* 47, 491).—10. When TiO_2 is fused with *sodium* or *potassium carbonate* the weight of CO_2 expelled corresponds with the formation of M_2TiO_3; on treating the fused mass

with water MOHAq is formed, and an acid Na or K titanate which is insoluble in water (*v.* Hermann, *J. pr.* 38, 92).—11. Fusion with *potassium hydrogen sulphate* forms a substance soluble in water; by evaporating the fused mass with conc. H_2SO_4, and then treating with water, the double salt $Ti(SO_4)_2.K_2SO_4.3H_2O$ is obtained (Warren, *P.* 102, 449; Glatzel, *B.* 9, 1833; Hermann, *l.c.*).—12. Heating powdered TiO_2 with *conc. sulphuric acid* produces a substance that dissolves wholly in water (? forming $Ti(SO_4)_2.xH_2O$ or $TiO.SO_4$; *v.* Merz, *J. pr.* 99, 157). For reactions of $TiO_2.xH_2O$ *v. infra, hydrated titanic oxide*; and *v.* also *titanic acid* under Titanium oxyacids and salts and derivatives thereof, p. 746).

Hydrated titanic oxide. Hydrates of TiO_2 are obtained by gradually adding $TiCl_4$ or $TiBr_4$ to cold NH_3Aq; by fusing TiO_2 with $KHSO_4$, dissolving in water, diluting, and boiling for some time; by adding water to $TiCl_4$ and boiling; by fusing TiO_2 with K_2CO_3, washing the fused mass with small quantities of water till all KOH is removed, adding a little conc. HClAq, filtering cold, and allowing the liquid to stand, when it gradually deposits gelatinous $TiO_2.xH_2O_6$ (O. v. d. Pfordten, *B.* 17, 727); by decomposing $Ti(OEt)_4$ by H_2O (Demarçay, *C. R.* 80, 51); and by other reactions. The isolation of a great many definite hydrates of TiO_2 has been announced from time to time. By decomposing $TiCl_4.PCl_5$ (*v.* Titanic chloride, *Combinations*, No. 6, p. 740) by the action of moist air, and drying over H_2SO_4, Tüttscheff (*A.* 141, 111) said that the *dihydrate* $TiO_2.2H_2O$ was formed, and by drying this at 110°–120° he said that the *monohydrate* $TiO_2.H_2O$ was obtained. According to Carnelley a. Walker (*C. J.* 53, 66, 81), dehydration of $TiO_2.xH_2O$ (obtained by adding $TiCl_4$ to cold NH_3Aq), air-dried for 14 days, proceeds continuously from 15° to 710° whereat the whole of the water is removed. A very large number of hydrates probably exists, and these pass one into the other as temperature rises without any of them remaining unchanged through more than a few degrees.

Two classes of hydrates of TiO_2 exist; one obtained by ppg. $TiCl_4$ by NH_3Aq, or warming TiO_2 with conc. H_2SO_4, dissolving in water, diluting, and ppg. by alkali; the other obtained by dissolving hydrates of the former class in dilute acid, and boiling. Hydrates of the former class dissolve easily in dilute acids, while those of the latter class are insoluble in dilute acids (for more details *v.* Titanium oxyacids, p. 746).

Hydrated TiO_2, obtained by ppn. by alkali in the cold, dissolves in dilute acids, forming salts TiX_4, where $X = NO_3$, $\frac{1}{2}SO_4$, &c.; not many salts of this form have been isolated, and most of those that are known are basic salts. $TiO_2.xH_2O$ dissolves in molten H_3PO_4; on cooling crystals of $TiO_2.P_2O_5$ ($=TiP_2O_7$) are obtained (Hautefeuille a. Margottet, *C. R.* 102, 1017). By heating $TiO_2.xH_2O$ with a little cold conc. HClAq, pouring off the solution after a few days, and evaporating it in *vacuo*, Koenig a. O. v. d. Pfordten obtained crystals approximating to $Ti(OH)_2Cl_2$, but differing from $Ti(OH)_2Cl_2$ prepared by the interaction of $TiCl_4$ and HClAq (*B.* 22, 1485; *cf.* Titanium hydroxyl chlorides, p. 743).

Titanium sesquioxide Ti_2O_3. (*Titanous oxide.*) Mol. w. unknown. By digesting a solution of $TiO_2.xH_2O$ in HClAq with Cu at 40° to 50°, Fuchs (*A.* 56, 319) obtained a violet solution which gave a brownish black pp. with NH_3Aq; the pp. quickly reacted with water, giving off H and forming $TiO_2.xH_2O$. Von Kobell (*P.* 62, 599) obtained similar reactions by using reduced Ag in place of Cu. Ebelmen (*J. pr.* 42, 73) obtained a nearly black pp. by adding alkali to Ti_2Cl_6Aq. According to Ebelmen (*J. pr.* 42, 76) Ti_2O_3 can be prepared by heating TiO_2 to redness in perfectly dry H. Ti_2O_3 thus prepared is described as a black solid; unacted on by HNO_3 or HClAq; oxidised to TiO_2 only by heating to a very high temperature; soluble in H_2SO_4Aq, forming a violet solution. According to O. v. d. Pfordten (*A.* 237, 201), the product of reducing TiO_2 in H is not Ti_2O_3 but has the composition Ti_7O_{12}. Friedel a. Guérin (*A. Ch.* [5] 8, 38) obtained Ti_2O_3, but not free from other compounds, by passing $TiCl_4$ vapour mixed with H over TiO_2 at a red heat. They describe Ti_2O_3 as a copper-red, metal-like, microscopically crystalline powder; not acted on by boiling HNO_3Aq, but oxidised to $TiO_2.xH_2O$ by boiling H_2SO_4Aq; soluble in HFAq or warm *aqua regia*; giving off NH_3 and H with hot alkali solutions; oxidised to TiO_2 by heating to redness in air. Koenig a. O. v. d. Pfordten (*B.* 22, 2070) failed to obtain Ti_2O_3 by the method of F. a. G.

When Ti is dissolved in hot HClAq, in an atmosphere of H, the solution contains Ti_2Cl_6 (Rammelsberg, *J. pr.* 99, 176); a solution of $TiO_2.xH_2O$ in HClAq reduced by zinc also contains Ti_2Cl_6 (K. a. O. v. d. P., *l.c.*); in these solutions alkalis give black pps., probably $Ti_2O_3.xH_2O$; the pps. soon change in contact with H_2O to $TiO_2.xH_2O$, H being given off. According to O. v. d. P. (*A.* 237, 201), a solution of K_2TiF_6 in a *little* HClAq gives a pp. of $Ti_2O_3.xH_2O$ on treatment with Na-amalgam.

Sabatier a. Senderens (*C. R.* 114, 1429; 115, 236) say that Ti_2O_3 is oxidised to TiO_2 by heating to c. 500° in NO, or to c. 300° in NO_2.

Titanium monoxide TiO. This oxide has not been isolated with certainty. According to Moissan (*C. R.* 115, 1034) black prisms, which he took to be TiO, are formed by heating TiO_2 to c. 2500° in an electric furnace, and at a higher temperature the (?) TiO melts and then volatilises. By heating a mixture of TiO_2 and Mg powder to redness, in H, Winkler (*B.* 23, 2657) obtained a brown powder which probably contained some TiO, mixed with $MgTiO_3$. According to Berthier (*A. Ch.* [2] 54, 374) TiO_2 lost 6 p.c. O when heated strongly in a carbon crucible, 13 to 16 p.c. O when heated with 12 p.c. C, and 20 p.c. O when heated with 24 p.c. C (TiO_2 loses 20 p.c. O in becoming TiO); the product may have contained TiO, or it may have been a mixture of TiO_2, Ti_2O_3, and Ti.

Hydrated titanium monoxide $TiO.H_2O = TiO_2H_2$. O. v. d. Pfordten (*A.* 237, 201) obtained a black pp., said by him to be TiO_2H_2, by the continued action of Na-amalgam on a solution of K_2TiF_6 in a fair amount of HClAq (if there is little HClAq, Ti_2O_3 is ppd.); the solution became green, then colourless, and then the black pp. was formed. The black pp. formed by NH_3Aq, alkali carbonates, or $(NH_4)_2SAq$, in solutions of $TiCl_2$ (*q. v.*, p. 741) is TiO_2H_2, according

to O. v. d. P. (*l.c.*). With Na_2HPO_4Aq, and $NaC_2H_3O_2Aq$, $TiCl_2$ is said to give bluish-black and greenish-black pps., which may be salts of TiO (O. v. d. P., *l.c.*).

TITANIUM PEROXIDE. TiO_3. (*Titanium trioxide* or *superoxide.*) In 1882 (*Atti dei Lincei*, 1882. 1) Piccini dropped H_2O_2Aq into solution of $TiO_2.xH_2O$; from the quantity of H_2O_2 that reacted he concluded that an oxide TiO_3 was produced. In the same year (*B.* 15, 2599) Weller obtained a yellow pp., which reacted with HClAq, giving off Cl, by the interaction of H_2O_2Aq and freshly ppd. $TiO_2.xH_2O$ or a solution of $TiO_2.xH_2O$. In 1888, Classen (*B.* 21, 370) added $TiCl_4$, drop by drop, to dilute alcohol, then added to this solution a very large excess of H_2O_2Aq, and then KOHAq, NH_3Aq, or $(NH_4)_2CO_3Aq$; in each case he obtained a yellow liquid from which a yellow pp. separated after some time; after syphoning off the liquid, washing the pp. by decantation, and drying it on a tile, he obtained a yellow solid approximating to the composition $TiO_3.3H_2O$. In 1889, Lévy (*C. R.* 108, 294) approximately determined the composition of the pp. obtained by adding H_2O_2Aq to $TiO_2.xH_2O$ in H_2SO_4Aq, by dropping in H_2O_2Aq of known concentration, and determining the quantity of H_2O_2 used in the reaction; L. concluded that the results could be accounted for by supposing the yellow pp. to be TiO_3, $TiO_2.H_2O_2$, or $Ti_2O_5.H_2O_2$, but that probably the pp. was TiO_3. In 1893 Bailey a. Dawson (*Studies from the Phys. and Chem. Laboratories of the Owens College*, vol. i. p. 216) obtained yellow to orange solids, agreeing fairly in composition with the formula TiO_3. B. a. D. added (1) H_2O_2Aq, (2) freshly ppd. BaO_2, to $TiO_2.xH_2O$ in dilute H_2SO_4Aq, diluted the deep-red liquids thus obtained with twice their volumes of alcohol, added conc. alcoholic solution of KOH, washed the pps. with alcohol (to remove H_2O and H_2O_2), and then with ether, and, in some cases, dried in the air. According to B. a. D., TiO_3 dissolves in water, forming a deep-red liquid; this solution decolourises $KMnO_4Aq$; TiO_3 dissolves in HClAq, giving off Cl. By allowing ppd. TiO_3 to stand for some time, B. a. D. say that a modification is formed insoluble in water.

OXIDES OF TITANIUM INTERMEDIATE BETWEEN TiO_2 AND Ti_2O_3.

I. By heating TiO_2 with HCl gas in a reducing atmosphere, Deville (*C. R.* 53, 163) obtained a blue, crystalline solid, to which he gave the formula Ti_3O_5. A similar solid (? same composition) was obtained by Friedel a. Guérin (*A. Ch.* [5] 8, 44) by passing H and HCl over TiO_2 strongly heated in a porcelain tube. This blue solid is said to decompose water, in presence of strong bases, giving off H and forming TiO_2.

II. By very strongly heating TiO_2 in H, O. v. d. Pfordten (*A.* 237, 228) obtained a dark indigo-blue solid, to which he gave the formula Ti_7O_{12}; according to Ebelmen (*J. pr.* 42, 76), Ti_2O_3 is formed by this reaction. Heated in air the compound burns to TiO_2.

III. By adding alcoholic solution of KOH to a solution of $TiO_2.xH_2O$ in dilute H_2SO_4Aq, after treating the solution with BaO_2, Piccini (*Atti dei Lincei*, 1882. 1) obtained yellow pps. with compositions varying from Ti_5O_{11} to Ti_2O_5.

Titanium oxyacids and salts and derivatives thereof. The hydrates of TiO_2 react as feeble acids, besides reacting with the stronger acids as feeble bases. The salts wherein Ti forms part of the acidic radicles are generally obtained by fusing TiO_2 with salts of the metals which are to be converted into titanates. Only a very few titanates are soluble in water; several dissolve in HClAq, but on diluting and boiling most, if not all, of the $TiO_2.xH_2O$ is ppd.

TITANIC ACIDS. Hydrates of TiO_2 are obtained by various reactions (*v.* HYDRATED TITANIC OXIDE, p. 745). By drying under different conditions solids are obtained approximately corresponding with the formula $xTiO_2.yH_2O$, where $x = 1$, 2, or 3, and $y = 1, 2, 3, 4$, or 5. (For a list of the hydrates obtained by different experimenters *v.* Tüttscheff, *A.* 141, 111.) There seems to be a series of hydrates of TiO_2, all of which may be classed together under the name *titanic acids*, none of them being stable through more than a few degrees of temperature (*v.* Carnelley a. Walker, *C. J.* 53, 66, 81); the relations of composition of these acids may be expressed by such a general equation as $n\text{TiH}_4\text{O}_4 - m\text{H}_2\text{O} = \text{Ti}_n\text{H}_{4n-2m}\text{O}_{4n-m}$.

The titanic acids belong to two classes: those which are formed by decomposing $TiCl_4$ or $TiBr_4$ by dilute cold alkali solutions, or by warming TiO_2 with conc. H_2SO_4, dissolving the product in water, and ppg. by dilute cold alkali solutions; and those which are formed by decomposing $TiCl_4$ or $TiBr_4$ by water and boiling, or by dissolving titanic acids of the former class in dilute acid and boiling, or by fusing TiO_2 with $KHSO_4$, dissolving in much water and boiling. The acids of the former class are generally called *titanic acids* or *ortho-titanic acids*, and those of the latter class *meta-titanic acids*. *Orthotitanic acids* dissolve easily in dilute acids; *metatitanic acids* are insol. dilute acids; by prolonged heating with conc. H_2SO_4 compounds are produced which dissolve on adding water. *Meta-acids* are also formed by heating *ortho- acids* to c. 100°. Experiments made by Merz (*J. pr.* 99, 166) show that the *meta- acids* lose water, on heating, more easily than the *ortho- acids*.

ORTHOTITANIC ACIDS. According to Wagner (*B.* 21, 960), a clear solution of an orthotitanic acid is obtained by adding water, a drop at a time, to $TiCl_4$, with constant shaking; HCl and $TiCl_4$ are given off (by the heat of the reaction), a solid is produced, then a greenish-yellow liquid, and finally a clear solution. By adding 1 pt. $TiCl_4$ to c. 6 to 7 pts. water, Thorpe (*C. J.* 47, 120) obtained an opalescent liquid which became clear after standing for 40 hours, and then contained orthotitanic acid; when this solution was heated ppn. of metatitanic acids began at c. 87°, and at c. 90° most of the Ti was ppd. A solution of $TiBr_4$ in water forms a perfectly clear liquid containing ortho-acid (T., *l.c.*, p. 126). The white flocculent solid obtained by adding $TiCl_4$ to dilute HClAq, ppg. by NH_3Aq when cold, washing with cold water, and drying in the air is $TiO_2.2H_2O$ ($= TiO_4H_4$), according to Merz (*J. pr.* 99, 166); **this composition is also assigned to the solid formed by keeping $TiCl_4.PCl_5$ under a bell-jar, with water and CaO, for some days, and then drying over H_2SO_4 (Tüttscheff, *A.* 141, 111). When TiO_4H_4 is dried *in vacuo* (Tüttscheff, *l.c.*), or over H_2SO_4**

(Merz, *l.c.*), the product is said to be $TiO_2.H_2O$ ($=H_2TiO_3 = TiO.O_2H_2$). The composition $2TiO_2.H_2O$ ($=H_2Ti_2O_5 = Ti_2O_3.O_2H_2$) is given to the product dried at 100° (Merz, *l.c.*; Demoly, *C. R.* 1849. 325), dried at 140° (Tüttscheff, *l.c.*), or dried *in vacuo* over H_2SO_4 (H. Rose, *A.* 52, 268); after drying at 100° or upwards, *meta-acids* are probably produced.

Orthotitanic acids are insoluble in water or alcohol; but dissolve easily in dilute acids; said also to dissolve in alkali carbonate solutions. The solutions in acids probably contain salts of the type TiX_4, $X = Cl, NO_3, \frac{1}{2}SO_4$, &c.; but compounds of the form $Ti(OH)_xX_y$, where X is a monovalent acidic radicle, and x is not greater than 3, may be formed, similar to the compounds $Ti(OH)_3Cl$, $Ti(OH)_2Cl_2$, and $Ti(OH)Cl_3$, obtained by O. v. d. Pfordten by the interaction of HClAq and $TiCl_4$ (*B.* 21, 1708; *v.* TITANIUM HYDROXYL CHLORIDES, p. 753). By adding a little conc. cold HClAq to orthotitanic acid, allowing to stand for some days, pouring off the clear liquid from undissolved acid, and evaporating *in vacuo*, Koenig a. O. v. d. P. (*B.* 22, 1485) obtained a white solid containing Ti and Cl in the ratio 1:1·47; they regarded this as consisting chiefly either of $TiCl_2(OH)_2$ but different in some properties from $TiCl_2(OH)_2$ obtained from $TiCl_4$—or chiefly of $TiCl(OH)_3.HCl$. White pps. are obtained by adding H_3PO_4Aq, H_3AsO_4Aq, or $H_2C_2O_4Aq$ to solutions of orthotitanic acids in dilute HClAq, HNO_3Aq, or H_2SO_4Aq, after making nearly neutral by NH_3Aq. When acid solutions of orthotitanic acids are diluted considerably and boiled for some time the whole of the Ti is ppd. as meta- acids. Ortho- acids are also partly changed to meta- acids by keeping under water for a long time (Wagner, *B.* 21, 960), or by washing with hot water. When an orthotitanic acid is heated strongly TiO_2 is produced, with vivid incandescence; the change from a meta- acid to TiO_2 is not accompanied by incandescence. According to Wagner (*l.c.*), the dehydration of moist ortho- acids by gently warming is accompanied by changes of colour from white to grey, green, and black.

METATITANIC ACIDS. Formed, as white powders, by dissolving ortho- acids in dilute acid and boiling for some time; also by fusing TiO_2 with $KHSO_4$ and boiling with much water; also by adding water to $TiCl_4$ or $TiBr_4$ and boiling; also by oxidising Ti by HNO_3 S.G. 1·25 (Weber, *P.* 120, 287). According to Weber (*l.c.*), freshly prepared dilute $TiCl_4Aq$ is not rendered turbid by HClAq, HNO_3Aq, or H_2SO_4Aq, but these acids at once ppt. metatitanic acids when added to dilute $TiCl_4Aq$ that has been boiled even for a few seconds. The pp. obtained by boiling a diluted solution of an orthotitanic acid in dilute H_2SO_4 is said to have the composition $TiO_2.2H_2O$ ($=TiO_4H_4$) when dried over H_2SO_4, the composition $3TiO_2.4H_2O$ ($=Ti_3O_{10}H_8 = Ti_3O_2.O_8H_8$) when dried at 120°, and the composition $3TiO_2.2H_2O$ ($=Ti_3O_8H_4 = Ti_3O_4.O_4H_4$) when dried at 140° (Tüttscheff, *A.* 141, 111); Merz (*J. pr.* 99, 166) gives the composition $TiO_2.H_2O$ ($=TiO_3H_2 = TiO.O_2H_2$) to the air-dried pp., and the composition $2TiO_2.H_2O$ ($=Ti_2O_5H_2 = Ti_2O_3.O_2H_2$) to the pp. dried over H_2SO_4, or at 60°.

Metatitanic acids are white powders, insoluble in water or dilute acids; after heating with conc. H_2SO_4 the products dissolve in water; when strongly *heated TiO_2 is formed without* incandescence.

COLLOIDAL TITANIC ACIDS. Graham (*T.* 1861. 213) obtained a gelatinous, probably orthotitanic, acid, insoluble in water, by dialysing a solution of $TiO_2.xH_2O$ in HClAq; by dissolving this gelatinous acid in such a quantity of cold dilute HClAq that not more than 1 p.c. titanic acid was present in the solution, and dialysing for several days, G. (*C. J.* 17, 325) obtained a dilute aqueous solution of colloidal titanic acid. Colloidal, insoluble, titanic acids have also been prepared by Knop (*A.* 123, 351), Rose (*G. A.* 73, 76 [1823]), and O. v. d. Pfordten (*B.* 17, 727).

TITANATES. These salts have not been thoroughly investigated. Those which have been best examined are either derivatives of H_2TiO_3 or H_4TiO_4, or are basic salts of the type $xMO.TiO_2$, where $x>1$. Some acid salts $MO.xTiO_2$, where $x>1$, are also known. The older investigations were made chiefly by H. Rose (*P.* 61, 507) and by Hautefeuille (*A. Ch.* [2] 4, 129).

Barium titanates. An *acid salt* $2BaO.3TiO_2$ ($=2BaTiO_3.TiO_2$ or $Ba_2TiO_4.2TiO_2$) was obtained by Bourgeois (*C. R.* 103, 141) in lustrous microscopic crystals, by heating to full redness a mixture of equivalent parts of TiO_2 and $BaCO_3$ with excess of $BaCl_2$, and washing with very dilute HClAq.

Calcium titanates. The *normal salt* $CaTiO_3$ occurs native as *perowskite*. The same salt was formed by heating to bright redness a mixture of equivalent parts of TiO_2 and $CaCO_3$ with excess of $CaCl_2$, and washing with very dilute HClAq (Bourgeois, *l.c.*).

Iron titanates. The mineral *titaniferous iron* or *ilmenite* is more or less pure $xFe_2O_3.yTiO_2$. By fusing a mixture of 2 pts. TiO_2 and 5 pts. FeF_2 with a large excess of NaCl, washing with water, and then with very dilute acid, Hautefeuille (*C. R.* 59, 733) obtained dark purple-violet, lustrous crystals of *ferrous titanate* Fe_2TiO_4 ($=2FeO.TiO_2$); but according to Koenig a. O. v. d. Pfordten (*B.* 22, 1485) the salt produced is *ferric titanate* $Fe_4(TiO_4)_3$ ($=2Fe_2O_3.3TiO_2$). K. a. O. v. d. P. say that the salt dissolves in water after warming with conc. H_2SO_4, forming a green solution containing $Fe_2(SO_4)_3$ and titanic acid.

Magnesium titanates. The *normal salt* $MgTiO_3$ ($=MgO.TiO_2$) was obtained (by Hautefeuille, *l.c.*) by heating to whiteness, for a short time in a closed crucible, a mixture of 1 pt. TiO_2 and 10 pts. $MgCl_2$ with a little NH_4Cl, washing with extremely dilute acetic acid, and then with water; lustrous, six-sided (probably trimetric) crystals, S.G. 3·91. The same salt is formed, according to Winkler (*B.* 23, 2657), by heating a mixture of TiO_2 and Mg powder. By heating a mixture of 2 pts. TiO_2, 1 pt. MgO, and 40 pts. $MgCl_2$, and washing with very dilute acetic acid, the salt Mg_2TiO_4 ($=2MgO.TiO_2$) is said to be formed in hard, lustrous, regular octahedra, S.G. 3·42 (H.).

Potassium titanates. When TiO_2 is fused with excess of K_2CO_3 the quantity of CO_2 given off corresponds with the formation of the *normal salt* K_2TiO_3; after fusion two layers are obtained, the lower of which is said to consist of K_2TiO_3, while the upper contains the undecomposed K_2CO_3. K_2TiO_3 is described as a yellowish, fibrous, easily fused solid (H. Rose, *P.* 61, 507). Water resolves it (according to Rose) into an insoluble *acid salt*, and a soluble *basic salt*; but according to Hermann (*J. pr.* 38, 92) no trace of titanic acid goes into solution in water, but all remains in the insoluble acid salt.

Sodium titanates. The *normal salt* Na_2TiO_3 was obtained by H. Rose (*l.c.*) similarly to the K salt; water resolves it into an insoluble *acid salt* and NaOHAq. By heating Na_2WO_4, and in some cases also WO_3, with mixtures of TiO_2 and Na_2CO_3 previously fused, Cormimbœuf (*C. R.* 115, 823) obtained three *acid salts*:
(1) $2Na_2O.3TiO_2$ ($=2Na_2TiO_3.TiO_2$, or $Na_4TiO_4.2TiO_2$), (2) $Na_2O.2TiO_2$($Na_2TiO_3.TiO_2$, or $Na_2Ti_2O_5$), (3) $Na_2O.3TiO_2$ ($=Na_2TiO_3.2TiO_2$, or $Na_2Ti_3O_7$).

Strontium titanates. An *acid salt* $2SrO.3TiO_2$ ($=2SrTiO_3.TiO_2$ or $Sr_2TiO_4.2TiO_2$) was obtained, in pale-greenish yellow cubes, S.G. 5·1, by Bourgeois (*C. R.* 103, 141), by heating equivalent parts of TiO_2 and $SrCO_3$ with excess of $SrCl_2$, and washing with very dilute HClAq.

Zinc titanates. The *normal salt* $ZnTiO_3$ was obtained by Lévy (*C. R.* 107, 421), by heating to redness a mixture of 2 pts. TiO_2, 8 pts. $ZnSO_4$, and 3 pts. K_2SO_4, and washing with dilute HClAq; pale-violet, silky needles, S.G. 3·17, scarcely acted on by boiling conc. acids or conc. KOHAq. By varying the proportion of TiO_2, $ZnSO_4$, and K_2SO_4 used, L. (*l.c.*) obtained the *normal salt* Zn_2TiO_4, which may also be regarded as a *basic salt* $ZnTiO_3.ZnO$; the *basic salt* $3ZnO.2TiO_2$ ($=2ZnTiO_3.ZnO$); and the *acid salt* $4ZnO.5TiO_2$ ($=4ZnTiO_3.TiO_2$).

FLUOTITANATES; *v. Titanifluorides*, under TITANIC FLUORIDE, *Combinations*, No. 2 (p. 742).

FLUOROXYTITANATES; *v. Titanoxyfluorides*, under TITANIC FLUORIDE (p. 742).

MOLYBDOTITANATES. A few compounds of the form $TiO_2.12MoO_3.2M_2O.x$aq, where $M=NH_4$ and K, are described by Péchard (*C. R.* 117, 788). By shaking with ether a solution of the NH_4 salt, acidified by HClAq, and allowing the ethereal liquid to evaporate, P. (*l.c.*) obtained *molybdotitanic acid* $TiO_2.12MoO_3.22$aq, in golden yellow octahedra, melting at c. 60°, very soluble in water.

OXALOTITANATES. By dissolving $TiO_2.xH_2O$ in hot KHC_2O_4Aq and cooling, Péchard (*C. R.* 116, 1513) obtained triclinic crystals of $2KHC_2O_4.TiO_2.H_2O$. By treating a solution of this salt with $BaCl_2$Aq, crystals of $Ba(HC_2O_4)_2.TiO_2.H_2O$ were obtained; and by decomposing this by an equivalent quantity of dilute H_2SO_4Aq, filtering, and evaporating *in vacuo*, long needles of *oxalotitanic acid* $2H_2C_2O_4.TiO_2.2H_2O$ were obtained.

SILICOTITANATES; *v.* this heading, p. 464.

Titanium, oxychlorides of. Several oxychlorides are known. (1) $TiOCl_2$. According to Demarçay (*C. R.* 104, 111), this is the first product of heating TiO_2 and CCl_4 in a sealed tube; it is described as a yellow crystalline solid. Heated with CCl_4 it gives $TiCl_4$ and $COCl_2$. (2) TiOCl. Obtained by passing a mixture of $TiCl_4$ vapour and dry H over TiO_2 in a tube heated white hot; Ti_2O_3 and Ti_2Cl_6 are also produced in the reaction (Friedel a. Guérin, *Bl.* [2] 22, 481). Brown, orthorhombic leaflets; heated in air burns to TiO_2 and $TiCl_4$. (3) $Ti_4O_2Cl_8$. Formed by passing $TiCl_4$ vapour through a red-hot tube containing fragments of porcelain (Troost a. Hautefeuille, *C. R.* 73, 563). (4) By allowing $TiCl_4$ to deliquesce in air, and then evaporating over H_2SO_4 and CaO, Merz (*Bl.* [2] 7, 401) obtained a solid approximating in composition to $Ti_4O_6Cl_4.16H_2O$. In connection with oxychlorides *cf.* TITANIUM HYDROXYL CHLORIDES (p. 743).

Titanium, oxyfluoride of. By decomposing by water the crystals formed by dissolving $TiO_2.xH_2O$ in HFAq and evaporating, Berzelius (*P.* 4, 1) obtained a white solid, of which he said it was an insoluble, 'so to say, *basic*,' compound.

The *titanoxyfluorides* $TiO_2F_2.2MF$ may be regarded as compounds of the oxyfluoride TiO_2F_2 (*v.* TITANIC FLUORIDE, p. 742).

Titanium, oxythiochloride of. The compound $TiCl_3.OSO_2.Cl$ formed by the reaction of $TiCl_4$ with $SO_2.OH.Cl$ may be regarded as TiO_3SCl_4 (*v.* TITANIC CHLORIDE, *Reactions*, No. 10, p. 740).

Titanium, salts of. Not many salts have been prepared by replacing H of oxyacids by Ti; most of those that have been isolated are basic salts derived from the oxide TiO_2. One salt, $Ti_2(SO_4)_3$, corresponding with the oxide Ti_2O_3 has been isolated. For the individual salts *v.* NITRATES, vol. iii. p. 517; PHOSPHATES, this vol. p. 112, TiP_2O_7, prepared by dissolving $TiO_2.xH_2O$ in molten H_3PO_4 (Hautefeuille a. Margottet, *C. R.* 102, 1017) should be added; and SULPHATES, this vol. p. 580.

Titanium, sulphides of. Three compounds of Ti and S have been isolated: TiS_2, Ti_2S_3, and TiS, corresponding with the three oxides TiO_2, Ti_2O_3, and TiO.

TITANIUM DISULPHIDE TiS_2. (*Titanic sulphide.*) Mol. w. unknown. H. Rose (*P.* 8, 177) said that this compound was obtained by passing vapour of CS_2 over very strongly heated TiO_2; but O. v. d. Pfordten (*B.* 17, 727) and Thorpe (*C. J.* 47, 491) have found that it is not possible by this method to obtain TiS_2 free from Ti oxides. TiS_2 is prepared by passing perfectly dry H_2S into $TiCl_4$ kept somewhat below its b.p., and sending the mixed vapours through a glass tube heated to incipient redness; TiS_2 deposits in the tube, and HCl is given off (Ebelmen, *A. Ch.* [3] 20, 285; confirmed by O. v. d. Pfordten, *B.* 17, 727). According to O. v. d. P. (*A.* 234, 257), the H_2S should be passed through $CrCl_2$Aq, to remove traces of O, and dried by means of P_2O_5; and the tube should be filled with H_2S before the mixed vapours are passed into it.

TiS_2 forms large, brass-yellow, lustrous, metal-like scales.

TiS_2 is decomposed to Ti_2S_3 and S by heating in *hydrogen* or *nitrogen*; it is not changed by heating in *hydrogen in presence of excess of hydrogen sulphide*; heated to redness in *carbon dioxide* it is completely oxidised to TiO_2 (O. v. d. P., *A.* 234, 257). Ebelmen (*l.c.*) gives the following reactions: with dry *chlorine* gives $TiCl_4$ and S_2Cl_2; *heated in air*, TiS_2 is burnt to

TiO_2 and SO_2; exposure to *moist air* decomposes **TiS_2 gradually, with evolution of H_2S;** heated to redness with *steam* gives $TiO_2.xH_2O$, H_2S, and H; *nitric acid* produces $TiO_2.xH_2O$, S, and NO; *aqua regia* oxidises it to $TiO_2.xH_2O$ and H_2SO_4Aq; not acted on by *hydrochloric acid* (H. Rose said that TiS_2 dissolved slowly in HClAq, giving off H_2S); insoluble in *potassium sulphide* solution; digestion with *potash solution* produces K titanate and KHSAq (Rose).

Titanium sesquisulphide Ti_2S_3. Mol. w. unknown. Thorpe (*C. J.* 47, 491) obtained this compound by passing the vapours of moist H_2S and CS_2 over powdered TiO_2 heated to very bright redness in a porcelain tube; dry H_2S and CS_2 had no action on TiO_2. T. describes Ti_2S_3 as a greenish-black powder; he did not obtain it quite free from TiS_2, as by heating at a lower temperature than full redness in H_2S and CS_2 it is slowly changed to TiS_2. O. v. d. Pfordten (*A.* 234, 257) obtained Ti_2S_3 by heating TiS_2 to full redness in dry H or N (S being set free); he describes it as a grey, metal-like solid; insoluble in NaOHAq; soluble in HNO_3Aq or conc. H_2SO_4 forming green solutions.

Titanium monosulphide TiS. Mol. w. unknown. Formed by very strongly heating TiS_2 in perfectly dry H quite free from O (T., *l.c.*; O. v. d. P., *l.c.*). A black powder (T., *l.c.*); forms dark-red crystals (O. v. d. P., *l.c.*). Slowly acted on by HNO_3Aq or *aqua regia*; insoluble in NaOHAq.

Titanium, sulphochloride of, *v.* Titanium thiochloride, *infra*.

Titanium, thiochloride of. The pp. formed by passing pure dry H_2S into hot $TiCl_4$ is probably a thiochloride, according to O. v. d. Pfordten (*A.* 234, 257). M. M. P. M.

TITANIUM GROUP OF ELEMENTS. The four elements, *titanium*, *zirconium*, *cerium*, and *thorium* form, with *carbon*, the *even-series* family of Group IV. in the periodic classification of the elements. There is yet an element to be discovered between Ce and Th; this unknown element will come in series 10 of Group IV. The titanium family of elements is closely allied to the tin family—Ge, Sn, Pb—which, with Si, form the odd-series members of Group IV. Carbon is the first even-series member, and silicon the first odd-series member, of the group; these two elements are more like one another than they are like the rest of the group.

For the properties and relations of C and Si *v.* Carbon group of elements, vol. i. p. 682; and for the tin family *v.* Tin group of elements, this vol. p. 735.

The presence of an element, before unknown, in a Cornish mineral was recognised by Gregor in 1791, and by Klaproth a few years later; the element—called titanium by Klaproth—was isolated by Berzelius in 1824. Klaproth, in 1789, recognised the presence of a new earth in *zirconite* from Ceylon; the metal zirconium was isolated by Berzelius in 1824. In 1803 the presence of a new earth in a Swedish mineral was announced by Klaproth, who gave the name of cerium to the metal of the earth he had discovered; Mosander isolated the element in 1826. Berzelius discovered a new earth, in a Norwegian mineral, in 1828, and isolated the metal of the earth, which he called thorium, in the same year.

None of the four elements Ti, Zr, Ce, or Th occurs native; the compounds of these elements are comparatively rare, especially those of Ce and Th.

The most frequently found compounds are the oxides MO_2, generally in combination with SiO_2 and with alkaline earths. The metals are obtained by reducing their double fluorides by Al, K, or Na; also in some cases by reducing the chlorides by K or Na; Ce has also been isolated by electrolysing molten $CeCl_3$. The table on the following page presents some of the physical and chemical properties of the elements.

General formulæ and characters of compounds.—Oxides.—MO_3, probably for all (? Th_2O_7); MO_2, for all; M_2O_3, when M = Ti or Ce; perhaps TiO. Hydrates of MO_2 exist.

Sulphides.—MS_2, when M = Ti or Th, ? Zr; M_2S_3, when M = Ti or Ce; TiS.

Haloid compounds.—MX_4, when X = Br, Cl, F or I (only CeF_4 prepared); MX_3, when M = Ti, and X = Cl, also when M = Ce and X = Br, Cl, F or I; $TiCl_2$. Salts.—MR_4, R = NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; most are basic when M = Ti or Zr, but when M = Ce many are normal, and when M = Th most are normal; several salts Ce_2R_6 are known, and a few Ti_2R_6; the Ce_2R_6 salts are more stable than the CeR_4 salts. Salts containing M in the acidic radicle.—M_2TiO_3 and others of general form $xMO.yTiO_2$; M_2ZrO_3, M_4ZrO_4, and others of general form $xMO.yZrO_2$. No cerates or thorates isolated. Salts X_2MF_6 known when M = Ti, Zr, or Th; $3CeF_4.3KF$ known. Acids. H_2TiO_3, $H_2Ti_2O_5$, H_4TiO_4, H_2TiF_6; various hydrates $ZrO_2.yH_2O$ act as feeble acids; H_4ThO_4 and $H_2Th_4O_9$ are perhaps feeble acids, but it is said that ThO_2 does not decompose alkali carbonates when fused therewith.

The *oxides* MO_2 are basic, and also feebly acidic when M is Ti or Zr; they interact with some acids to form corresponding salts, and, when M = Ti or Zr, with alkalis to form salts wherein M forms part of the acidic radicle; no salts of oxyacids with Ce or Th in the negative radicles have yet been isolated. Several hydrates of MO_2 exist, they easily pass one into the other with small changes of temperature; some of these hydrates react as feeble acids towards strong bases, forming salts of the types X'_2MO_3, X'_4MO_4, and, generally, $xX'_2O.yMO_2$; these salts are not referable to such definite forms as the stannates or silicates are, but they resemble these classes of salts fairly closely.

The *salts* which are derived from the oxides MO_2, by the interactions of these oxides with acids, are of the form MX_4, where X = NO_3, $\frac{1}{2}SO_4$, $\frac{1}{3}PO_4$, &c.; when M = Ti most of the salts that are known are basic; when M = Zr, many are basic, but a fair number of normal salts is also known; when M = Ce or Th, most of the salts that have been isolated are normal. Little is known of the oxides MO_3; as they are obtained by adding H_2O_2Aq and an alkali to solutions of salts MX_4, they are probably superoxides; the formula Th_2O_7 that is assigned to the oxide of Th formed in this way cannot be accepted as final. The oxides Ti_2O_3 and Ce_2O_3 are basic; the most definite and stable salts of

—	TITANIUM.	ZIRCONIUM.	CERIUM.	THORIUM.
Atomic weights.	48	90	139·9	232
	Molecular weights unknown. Mol. weights of one or more compounds of each element, except Ce, have been determined by Avogadro's law; spec. heats determined directly.			
Melting-points.	Has not been fused	c. 1200°	c. 800°	Has not been fused
Spec. gravities (approx.)	3·6	4·2	6·7	11·0
Spec. heats.	·13	·066	·0448	·0276
$\frac{\textit{Atomic weight.}}{\textit{Spec. gravities}\text{ (approx.)}}$	13·4	21·4	21·1	21·1
Physical properties.	Obtained only as a powder; black, lustrous, apparently amorphous. The powder has not been fused.	A black amorphous powder; resembling lampblack, but much heavier. Also obtained as a very lustrous, hard, brittle solid, resembling Sb. Said to melt above m.p. of Si.	Steel-grey, very lustrous metal; malleable, and ductile. Melts much more easily than any other member of the family.	Dark-grey, lustrous powder; also obtained in microscopic octahedral crystals. Has not been fused.
Occurrence and Preparation.	The four metals occur chiefly as silicates, Ti and Zr in moderate quantities and the others only in a few rare minerals. The metals are prepared by reducing the chlorides, or alkali salts of the form K_2(or Na_2)MF_6, by heating with K or Na; Ce also prepared by electrolysing molten $CeCl_3$.			
Chemical properties.	Burns brilliantly when heated in air, or in O, forming TiO_2. Decomposes H_2O at 100°, giving off H. Combines readily with Cl, less readily with Br, and with I only when vapour of I is passed over heated Ti. Dissolves in warm dilute HClAq, H_2SO_4Aq, HNO_3Aq, or HFAq. Forms two classes of salts TiX_2 and TiX_4, $X = NO_3$, $\frac{1}{2}SO_4$, &c.; very few TiX_2 salts isolated, and not many TiX_4; all salts easily decomposed. Salts derived from the acidic hydrates $xTiO_2.yH_2O$ also known. The acids H_2TiF_6 and $H_2TiO_2F_4$, and salts derived therefrom, are known. TiO_3, probably a superoxide, exists. Combines fairly readily with N, and with N and C. Atom of Ti is tetravalent in gaseous molecules $TiCl_4$ and TiI_4.	Amorphous Zr burns brilliantly when heated in air, or O, forming ZrO_2; the crystalline metal is superficially oxidised at a white heat; it burns in O-H flame. Combines with Cl, probably also with Br and I; compounds ZrX_4 are formed by heating ZrO_2 and C in X. Combines directly with S. Dissolves slowly in hot H_2SO_4, HClAq, HNO_3Aq; rapidly in HFAq. Decomposes molten KOH; crystalline Zr is said not to be oxidised by molten KNO_3 or $KClO_4$. Forms salts ZrX_4, $X = NO_3$, $\frac{1}{2}SO_4$, &c.; most salts isolated are basic, $xZrO_2.yR$. Salts derived from acid H_2ZrF_6 are known. Also forms zirconates $yMO.zZrO_2$ where Zr enters into negative radicle of salts. Oxide higher than ZrO_2, probably ZrO_3, (? superoxide) exists. ZrH_2 perhaps exists. Atom of Zr is tetravalent in gaseous molecule $ZrCl_4$.	Burns when heated in air, or O, to CeO_2. Decomposes cold water, giving off H. Combines directly with Cl, Br, I vapour, S vapour, and P vapour. Dissolves easily in HClAq, HNO_3Aq, H_2SO_4Aq, or HFAq. Forms two classes of salts, Ce_2X_6 and CeX_4, $X = NO_3$, $\frac{1}{2}SO_4$, &c.; salts Ce_2X_6 are more stable than CeX_4, the latter are easily reduced to Ce_2X_6. No cerates, where Ce forms part of negative radicle, have been isolated. Salts of form M_2CeF_6 not isolated. CeO_3, probably a superoxide, seems to exist.	Burns, when heated in air or O below redness, to ThO_2. Combines with Cl, Br, or I when heated; also with S vapour when heated therein. Easily dissolved by HClAq or HFAq; slowly by hot H_2SO_4Aq; HNO_3Aq has only a slight action. Forms salts ThX_4, $X = NO_3$, $\frac{1}{2}SO_4$, &c.; fair number of basic salts known. Hydrates of ThO_2, $ThO_2.2H_2O$ and $4ThO_2.H_2O$, are probably weak acids, but thorates have not been isolated. Oxide higher than ThO_2, probably Th_2O_7, isolated (? superoxide). ThH_2 perhaps exists. Atom of Th is tetravalent in gaseous molecule $ThCl_4$.

Ce are derived from this oxide. Several of the *haloid compounds* MX_4 have been gasified without decomposition, viz. $TiCl_4$, TiI_4, $ZrCl_4$, and $ThCl_4$. The haloid compounds MX_4 form many double compounds with other halides; some of these are certainly best regarded as salts of hypothetical acids containing M and X in their acidic radicles; the salts of this class R_2MF_6 are characteristic of the elements of Group IV.; all the elements of the group, except C and Ce, give these salts R_2MF_6, Ce is said to form $K_3Ce_2F_{11}(=2CeF_4.3KF)$, but further examination will most probably lead to the isolation of salts R_2CeF_6. Ti and Ce form chlorides MX_3, or more probably M_2X_6 from the analogy of C_2Cl_6 and Si_2Cl_6; Ce also forms Ce_2Br_6, Ce_2F_6, and Ce_2I_6, indeed the only haloid compound of Ce belonging to the form MX_4 that has yet been isolated is CeF_4. The *sulphides* have not been thoroughly examined; Ti is the only member of Group IV. which is known to form three sulphides corresponding with the oxides, TiS, Ti_2S_3, and TiS_2; one sulphide of Zr is known, probably ZrS_2; ThS_2 is the only sulphide of Th that has been isolated; and the only known sulphide of Ce is Ce_2S_3. So far as investigation has gone, the sulphides of Ti, Zr, Ce, and Th are basic.

A comparison of the titanium family with the tin family, which comprises the odd-series members of Group IV. (C and Si being omitted), shows that Ti, Zr, Ce, and Th are more metallic, on the whole, than Ge, Sn, and Pb. Th is certainly the most markedly positive element of Group IV., and Ti is at least not more negative than Ge; Zr is more metallic than Ge, and Ce more metallic than tin. The following formulæ show that, so far as composition goes, there is about an equal similarity between C and Si and the Ti elements, as between C and Si and the tin elements:

Oxides				*Sulphides*			*Chlorides, &c.*		
CO	? C_2O_3	CO_2		CS	? C_2S_3	CS_2		C_2Cl_6	CCl_4
? SiO		SiO_2		? SiS		SiS_2	? $SiCl_2$	Si_2Cl_6	$SiCl_4$
? TiO	Ti_2O_3	TiO_2	TiO_3	TiS	Ti_2S_3	TiS_2	$TiCl_2$	Ti_2Cl_6	$TiCl_4$
		ZrO_2	ZrO_3			ZrS_2 (?)			$ZrCl_4$
	Ce_2O_3	CeO_2	CeO_3		Ce_2S_3			Ce_2Cl_6	CeF_4
		ThO_2	? ThO_3			ThS_2			$ThCl_4$
GeO		GeO_2		GeS		GeS_2	? $GeCl_2$		$GeCl_4$
SnO	? Sn_2O_3	SnO_2		SnS	? ? Sn_2S_3	SnS_2	$SnCl_2$		$SnCl_4$
PbO	Pb_2O_3	PbO_2		PbS		? PbS_2	$PbCl_2$		$PbCl_4$ (?)

A comparison of the odd-series families of the different groups with the even-series families (omitting series 2 and 3) shows that, speaking broadly, the members of the even-series families are more metallic in their chemical properties than the members of the odd-series families, and that the general difference between even and odd families becomes more marked in the higher than in the lower groups (*v.* Table in vol. iii. p. 811). For instance, the even family of Group VI.—Cr, Mo, W, and U—is decidedly more metallic than the odd family of the same group—S, Se, and Te; but although the even family of Group II.—Ca, Sr and Ba—is more metallic than the odd family of the same group—Mg, Zn, Cd and Hg—there is not nearly so great a difference between these two families as there is between the two families of Group VI. Considering that the titanium and the tin elements belong to even and odd series, respectively, of Group IV., which group comes midway in the general periodic scheme of classification, we should expect the titanium (even-series) family to be rather more metallic than the tin (odd-series) family, but at the same time we should expect these two families to be very like one another; this is exactly what a study of the two families shows to be the case.

In connection with this article *v.* TIN GROUP OF ELEMENTS, this vol. p. 735, and CARBON GROUP OF ELEMENTS, vol. i. p. 682).

M. M. P. M.

TITANOFLUORHYDRIC ACID H_2TiF_6 *v.* *Titanifluorhydric acid*, under TITANIC FLUORIDE, *Combinations*, No. 1, p. 742.

TITANOFLUORIDES M_2TiF_6 *v.* *Titanifluorides*, under TITANIC FLUORIDE, *Combinations*, No. 2, p. 742.

TITANOXYFLUORHYDRIC ACID $H_2TiO_2F_4$ *v.* TITANIC FLUORIDE, p. 742.

TITANOXYFLUORIDES $M_2TiO_2F_4$ *v.* TITANIC FLUORIDE, p. 742.

TOLALLYL SULPHIDE C[illegible]H[illegible]S_2. [174°]. (350°–360° i.V.). A product of distillation of benzyl sulphide (Märcker, *A.* 136, 75; Forst, *A.* 178, 370; Baumann a. Klett, *B.* 24, 3313). Plates (from ether).

TOLANE *v.* DI-PHENYL-ACETYLENE.

Tolane dibromide *v.* DI-BROMO-PHENYL-ETHYLENE.

Tolane chlorides *v.* CHLORO-PHENYL-ETHANE and CHLORO-PHENYL-ETHYLENE.

TOLENE *v.* TOLU BALSAM.

p-**TOLENYL-AMIDINE** $C_8H_{10}N_2$ *i.e.* $C_6H_4Me.C(NH)(NH_2)$. [102°]. Formed by the action of alcoholic NH_3 on the hydrochloride of *p*-tolenyl-imido-ethyl-ether (Glock, *B.* 21, 2653). Pearly plates, sol. alcohol and ether.

Reactions.—1. $CO.Cl_2$ in toluene and NaOH give $(C_6H_7.C(NH).NH)_2CO$ and $C_7H_7.C\begin{matrix}\diagup N.C(C_7H_7)\diagdown\\ \diagdown N:C(OH)\diagup\end{matrix}N$ [over 300°] (Pinner, *B.* 25, 1425).—2. *Oxalacetic ether* and NaOH form $C_7H_7.C(NH).NH.CO.CH_2.CO.CO_2Et$ [190°] and $C_7H_7.C\begin{matrix}\diagup N.C(CO_2H)\diagdown\\ \diagdown N:C(OH)\diagup\end{matrix}CH$ [252°] (Pinner, *B.* 25, 1422).

Salts.—$B'HCl\frac{1}{2}aq.$ [218°].—$B'_2H_2PtCl_6$ [225°].—$B'HNO_2$. [133°]. Needles, v. sol. water (Kirschnick, *A.* 265, 187).—$B'HNO_3 2aq.$ [95°].—$B'_2H_2SO_4 2aq.$ [240°], v. sol. water.

o-**TOLENYL-AMIDOXIM** $C_8H_{10}N_2O$ *i.e.* $C_7H_7.C(NOH).NH_2$. [149·5°]. Formed by heating *o*-toluic nitrile with hydroxylamine hydrochloride, alcohol, and Na_2CO_3 (Schubart, *B.* 22, 2438). Needles (from hot water), v. sol. alcohol and ether.

Ethyl ether $C_7H_7.C(NOEt).NH_2$. [140°]. Prisms, v. sol. alcohol.

Benzoyl derivative $C_7H_7.C(NOBz).NH_2$. [145°]. Needles, sol. alcohol. Conc. H_2SO_4 forms $C_7H_7.C{<}\substack{N.O\\N}{>}CPh$ [80°].

o-Toluyl derivative $C_7H_7.C(NO.CO.C_7H_7).NH_2$. [168°]. Converted at 180° into $C_7H_7.C{<}\substack{N.O\\N}{>}C.C_7H_7$ [59°] (Stieglitz, *B.* 22, 3156). Sodium diazobenzene sulphonate forms $C_7H_7.C{<}\substack{N.O\\NH}{>}C(NH_2).C_7H_7$ [110°].

p-**Tolenyl-amidoxim** $C_8H_{10}N_2O$ *i.e.* $C_6H_4Me.C(NOH).NH_2$. *Toluamidoxim.* [146°]. Formed by combination of toluic nitrile with hydroxylamine (Schubart, *B.* 19, 1487). White plates, sol. alcohol, ether and hot water. Yields NaA′, a hygroscopic mass, and HA′HCl [187°], crystallising in prisms.

Reactions.—1. *Benzene sulphonic chloride* forms $C_7H_7.C{<}\substack{N.O\\N}{>}SO.C_6H_5$ [89°] (Pinner, *B.* 24, 4173).—2. *Aceto-acetic ether* gives rise to $C_7H_7.C{<}\substack{N.O\\N}{>}C.CH_2Ac$ [97°] (Schubart, *B.* 22, 2438).—3. *Acetic aldehyde* forms the compound $C_7H_7.C{<}\substack{N.O\\NH}{>}CHMe$ [127·5°].—4. Hot HOAc forms $C_7H_7.C{<}\substack{N.O\\N}{>}C.C_7H_7$ [135°].—5. $COCl_2$ produces $C_7H_7.C{<}\substack{N.O\\NH}{>}CO$ [220°].—6. $ClCO_2Et$ yields $C_7H_7.C(NH_2){:}NO.CO_2Et$ [130°].—7. *Phenyl cyanate* gives $C_7H_7.C(NOH).NH.CO.NHPh$ [155°].—8. *Phenyl thio-carbimide* reacts forming $C_7H_7.C(NOH).NH.CS.NHPh$.—9. *Potassium cyanate* acting on the hydrocloride gives rise to $C_7H_7.C(NOH).NH.CO.NH_2$ [170°].—10. Ac_2O and NaOAc acting on the hydrochloride form $NH(C(NH).C_7H_7)_2$ [153°] (Glock, *B.* 21, 2657).—11. *Succinic anhydride* forms the compound $C_7H_7.C{<}\substack{N.O\\N}{>}C.CH_2.CH_2.CO_2H$ [138·5°].—12. Boiling Ac_2O forms $C_7H_7.C{<}\substack{N.O\\N}{>}CMe$ [80°]. 13. CS_2 and alcohol form, on long boiling, $C_7H_7.C(NSH)NH.CS.SHH_2N.C(NSH).C_7H_7$ (Crayen, *B.* 24, 390).—14. CS_2 and alcoholic potash yield $C_7H_7.C{<}\substack{N.S\\NH}{>}CS$ [165°].

Methyl ether $C_7H_7.C(NOMe).NH_2$. [85°].

Ethyl ether EtA′. [64°]. Needles. Converted by HBr and $NaNO_2$ into $C_7H_7.CBr{:}NOEt$, an oil, decomposed at 155° (Schubart, *B.* 22, 2434), while hydrogen chloride and $NaNO_2$ form $C_7H_7.CCl{:}NOEt$ (200°).

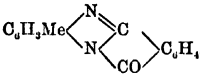
Benzoyl derivative $C_7H_7.C(NOBz).NH_2$. [178°]. Converted by heat into $C_7H_7.C{<}\substack{N.O\\N}{>}CPh$.

References.—Nitro- and Oxy-toluamidoxim.

p-**TOLENYL-IMIDO-ETHYL ETHER** $C_7H_7.C(NH).OEt$. The hydrochloride B′HCl [161°] formed by the action of dry HCl on *p*-toluic nitrile dissolved in ether-alcohol forms prisms, yielding $B'_2H_2PtCl_6\,2aq$, converted at 200° into *p*-toluic amide, by NH_3 into *p*-tolenyl-amidine, by aniline into di-phenyl-tolenyl-amidine [168°], and by Ac_2O into the compound $C_6H_4Me.C(NH).OAc$ [147°] (Glock, *B.* 21, 2650). The free base is liquid and changes on keeping into a polymeride [260°].

TOLENYL-PHENYLENE-DIAMINE $C_6H_4{<}\substack{NH\\N}{>}C.C_7H_7$. [268°]. Formed by reduction of tolyl-*o*-nitro-aniline and also from *p*-toluyl chloride and *o*-phenylene-diamine in benzene (Hübner a. Hanemann, *A.* 210, 328). Prisms, sl. sol. water, sol. alcohol.

TOLENYL-PHTHALAMIDONE $C_{15}H_{10}N_2O$ *i.e.*



[188°]. Got from tolenyl-benzenyl-amidine *o*-carboxylic acid (Bistrzycki, *B.* 25, 1984).

TOLENYL-XYLYLENE-DIAMINE $C_{15}H_{16}N$ *i.e.* [1:4] $C_6H_4Me{<}\substack{N\\NH}{>}C_6H_2Me_2$ $\left[\substack{5\\6}:1:3\right]$ [217°]. Formed by reducing the *p*-toluyl derivative of nitro-xylidine (Brückner, *A.* 205, 125; Hübner, *A.* 210, 333). Long crystals (from dilute alcohol).—B′HCl.—$B'HNO_3$.—$B'_2H_2SO_4$.

TOLIDINE *v.* Di-amido-ditolyl.

TOLIL *v.* Di-tolyl-diketone.

TOLIL-BENZOÏN *v.* Benzoïn, *Reaction* 9.

TOLINDOLE *v.* Methyl-indole.

TOLISATIN *v.* *Methyl*-isatin.

TOLU-ACET-ALDEHYDINE $C_{11}H_{14}N_2$ *i.e.* $C_7H_6(N{:}CHMe)_2$ or $C_7H_6{<}\substack{N\\NEt}{>}CMe$ (?) [91° uncor.]. Formed together with a small quantity of ethenyl-tolylene-diamine, by mixing tolylene *o*-diamine (1 mol.) with aldehyde (2 mols.) in cold HOAc (Hinsberg, *B.* 20, 1588).

TOLU-AMIDOXIM *v.* Tolenyl-amidoxim.

TOLU BALSAM. Obtained from incisions in the stem of *Myroxylum toluiferum* growing in Columbia, South America. It contains a terpene, tolene $C_{10}H_{16}$ (154°–170°), benzoic and cinnamic acids, benzyl cinnamate and two resins: $C_{18}H_{18}O_4$ [60°] v. sol. alcohol and ether and $C_{18}H_{20}O_5$ [above 100°], insol. alcohol and ether (Deville, *A.* 44, 304; Scharling, *A.* 97, 71; E. Kopp, *A.* 64, 372; Busse, *B.* 9, 830; Baillon, *Ph.* [3] 4, 385).

TOLUBENZYLAMINE *v.* Methyl-benzyl-amine.

TOLUENE C_7H_8 *i.e.* $C_6H_5.CH_3$. *Methyl-benzene. Retinaphtha. Phenyl-methane.* Mol. w. 92. V.D. 3·20 (calc. 3·29). (109°) (R. Schiff, *A.* 220, 91); (111°) (Wilbrand a. Beilstein, *A.* 128, 259; Tollens a. Fittig, *A.* 131, 304). S.G. $\frac{20}{4}$ ·8656 (Brühl); ^{24} ·8566 (Gladstone, *C. J.* 59, 290); $\frac{13}{4}$ ·8708 (S.). C.E. (13°–109°) ·001242. S.V. 118 (S.). μ_D = 1·4893 (G.). μ_β = 1·507 (B.). R_∞ = 50·06. H.F.p. −3520. H.F.v. −5260 (Thomsen, *Th.*). H.C. 933,762 (Stohmann, *J. pr.* [2] 35, 41). *Critical temperature* 321° (Pawlewski, *B.* 16, 2634). Occurs in coal tar (Mansfield). Obtained by dry distillation from balsam of tolu (Deville, *A. Ch.* [3] 3, 168; Muspratt a. Hofmann, *A.* 54, 9), from dragon's blood (Glénard a. Boudault, *C. R.* 19, 505), from the resin of *Pinus maritima* (Pelletier a. Walter, *A. Ch.* [2] 67, 278), and from wood (Völckel, *A.* 86, 334).

Formation.—1. By distilling vulpic acid with KOH (Möller a. Strecker, *A.* 113, 69).—2. By the action of sodium on a mixture of bromobenzene and MeI (Fittig a. Tollens, *A.* 131, 303).—3. By passing petroleum vapour over red-hot charcoal (Letny, *B.* 11, 1210).—4. By heating petroleum with $AlCl_3$ in presence of PbO and air (Friedel a. Crafts, *Z.* 1878, 1166).—5. By passing MeCl or CH_2Cl_2 into benzene containing $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 460; 11, 264).—6. Together with CH_4 by heating benzene with MeI and I (Rayman a. Preis, *A.* 223, 317).—7. By distilling cresol with P_2S_5 (Geuther, *A.* 221, 58).—8. By distilling toluic acid with baryta (Noad, *A.* 63, 305).

Properties.—Oil, smelling like benzene.

Reactions.—1. When passed through a *red-hot tube* it yields benzene, styrene, naphthalene, diphenyl, anthracene, phenanthrene, and other products (Ferko, *B.* 20, 661; *cf.* Berthelot, *Bl.* 7, 218; Graebe, *B.* 7, 48).—2. Distillation over red-hot PbO gives benzene, di-phenyl-ethylene, diphenyl, phenanthrene, and anthracene (Lorenz, *B.* 7, 1097; Vincent, *C. R.* 100, 908).—3. By *electrolysis* of toluene to which alcohol and H_2SO_4 have been added benzoic aldehyde and phenose are formed (Rénard, *C. R.* 92, 965).—4.—When electric sparks are passed through toluene, acetylene and hydrogen are given off (Destrem, *Bl.* [2] 42, 267).—5. $AlCl_3$ at 200° in sealed tubes forms benzene, and *m*- and *p*-xylene (Friedel a. Crafts, *C. R.* 100, 692; Anschütz, *A.* 235, 178).—6. *Oxygen* passed through toluene containing $AlCl_3$ forms cresol (Friedel a. Crafts, *C. R.* 86, 884).—7. A mixture of toluene and ethylene passed through a red-hot tube yields benzene, styrene, and anthracene (Ferko).—8. CH_2Cl_2 and $AlCl_3$ yield di-tolyl-methane (280°-290°), di-methyl-anthracene [232°], and *m*-, and *p*-xylenes (Friedel a. Crafts, *Bl.* [2] 41, 322).—9. *Bromine* acts upon toluene in the dark as readily as in diffused daylight, with production of *o*- and *p*-bromo-toluene. The addition of iodine greatly hastens the reaction, but the same products are formed. In direct sunlight the substitution takes place entirely in the side-chain, with production of benzyl bromide. But if iodine (even 2 p.c.) is present the effect of the sunshine is entirely counteracted, and the substitution takes place wholly in the nucleus (Schramm, *B.* 18, 606; *cf.* Zakrzewski, *M.* 8, 304).—10. *Chlorine*, in presence of I, acting even on boiling toluene, forms chloro-toluene and benzyl chloride (Beilstein a. Geitner, *A.* 231, 170; *cf.* Aronheim, *B.* 8, 1401).—11. CrO_2Cl_2 added slowly to a solution of toluene in CS_2 ppts. $C_7H_8 2CrO_2Cl_2$, which slowly absorbs moisture, being converted into benzoic aldehyde (Étard, *A. Ch.* [5] 22, 223).—12. H_2SO_4 yields the *o*- and *p*-sulphonic acids, converted by potash-fusion into *o*- and *p*-cresol (Wurtz, *A. Ch.* [4] 25, 108).—13. Bz_2O_2 forms $C_{14}H_{12}$ (c. 260°) isomeric with the di-phenyl-ethylenes, and yielding benzoic acid on oxidation (Lippmann, *M.* 7, 521).—14. HNO_3 forms *o*- and *p*-nitro-toluene.—15. *Paraldehyde* and conc. H_2SO_4 form ditolylethane and $C_{23}H_{24}$ (350°-360°) (O. Fischer, *B.* 7, 1194).

Compounds $(C_7H_8)_3AlCl_6$. S.G. ^{2} 1·08 (Gustavson, *B.* 11, 2151). Oil.—$(C_7H_8)_3AlBr_3$. S.G. 1·37.

Dihydride C_7H_{10}. (105°-108°). Formed by heating toluene with PH_4I at 350° (Baeyer, *A.* 155, 271; *Z.* [2] 4, 445).

Tetrahydride C_7H_{12}. (104°). S.G. ^{15} ·797. Occurs in the product of distillation of colophony (Rénard, *A. Ch.* [6] 1, 231). Oil, sol. alcohol and ether. Rapidly absorbs oxygen. In contact with water it forms crystalline $C_7H_{16}O_2$. H_2SO_4 forms two polymerides (230°-235°), one only being oxidisable by air.

Hexahydride C_7H_{14}. (97°). S.G. $\frac{0}{0}$ ·7741. C.E. (0°-20°) ·00119. S.V. 142 (Lossen, *A.* 225, 109). H.C. 1,092,800 (Longuinine, *C. R.* 93, 275). Formed by heating toluene with conc. HIAq at 280° (Wreden, *A.* 187, 161; *cf.* Berthelot, *Bl.* [2] 7, 124; 26, 146). Occurs in oil of resin. Completely oxidised by a hot mixture of HNO_3 and H_2SO_4.

References.—TRI-AMIDO-, BROMO-, BROMO-IODO-, BROMO-IODO-NITRO-, BROMO-NITRO-, CHLORO-, CHLORO-IODO-, CHLORO-NITRO-, IODO-, IODO-NITRO-, NITROSO-, NITRO-, and OXY- TOLUENE.

TOLUENE ARSONIC ACID *v.* ARSENIC.

TOLUENE-AZIMIDO-TOLUENE *v.* AZIMIDO-COMPOUNDS.

TOLUENE-AZO- compounds *v.* AZO- COMPOUNDS and DISAZO- COMPOUNDS.

TOLUENE-AZOXY- compounds *v.* AZOXY-COMPOUNDS.

TOLUENE CARBOXYLIC ACID *v.* TOLUIC ACID.

Toluene dicarboxylic acid $C_9H_8O_4$ *i.e.* $C_6H_3Me(CO_2H)_2$ [4:2:1]. *Methyl-phthalic acid.* Mol. w. 180. [152°]. Formed from (*a*)-amido-*p*-toluic nitrile by Sandmeyer's reaction, the resulting nitrile being saponified (Niementowski, *M.* 12, 623). V. e. sol. water and alcohol. With *o*-amido-phenol it forms $C_6H_3Me(CO)_2N.C_6H_4OH$ [205°], whence boiling aqueous sodium carbonate gives rise to $C_6H_3Me(CO_2H).CO.NH.C_6H_4.OH$ [200°].

Amide $C_6H_3Me(CONH_2)_2$. [188°]. Formed from the imide and NH_3Aq.

Anhydride. [92°]. Needles.

Imide $C_6H_3Me.C_2O_2.NH$. [196°]. Got by fusing the anhydride with urea. Needles.

Nitrile $C_6H_3Me(CN)_2$. [120°] (N.); [117°] (Glock, *B.* 21, 2663). Needles. Converted by alcohol and HCl into $C_7H_6Cy.C(NH_2Cl).OEt$ [199°].

Toluene dicarboxylic acid $C_6H_3Me(CO_2H)_2$ [4:3:1]. (*β*)-*Xylidic acid. Methyl-isophthalic acid.* [320°-330°]. Formed by oxidation of *m*-xylene carboxylic acid (Jacobsen, *B.* 14, 2112) and of $C_6H_3Me(CH_2.OH)_2$ (Hjelt a. Gadd, *B.* 19, 868). Formed also by fusing potassium toluene *m*-disulphonate or the salt $C_6H_3Me(SO_2NH_2).CO_2K$ with sodium formate (Hakansson, *B.* 5, 1088; Remsen a. Iles, *Am.* 1, 119). The same acid (?) is got by oxidation of $C_6H_3Me_2CO_2H$ [1:4:2] by HNO_3 (S.G. 1·12) at 150° (Claus a. Wollner, *B.* 18, 1858). Small crystals, sl. sol. hot water. May be sublimed.—Ag_2A'': crystals, v. sol. hot water.

Toluene dicarboxylic acid $C_6H_3Me(CO_2H)_2$ [2:4:1]. *Methyl-terephthalic acid.* (*a*)-*Xylidic acid.* [c. 282°]. Formed by boiling pseudocumene with dilute HNO_3 (Fittig a. Laubinger, *A.* 151, 276). Got also by fusing

$C_6H_3Me(SO_2NH_2)CO_2K$ with sodium formate (Remsen a. Iles, *Am.* 1, 114). Needles (by sublimation). Sl. sol. Aq. Oxidised by $KMnO_4$ to trimellitic and isophthalic acids (Krinos, *B.* 10, 1494).—ZnA''. S. 36 at 0°; ·735 at 100°, ·5 at 130° (Jacobsen, *B.* 10, 859).

Toluene dicarboxylic acid $C_6H_3Me(CO_2H)_2$. [310°-315°]. Formed by fusing potassium toluene (γ)-disulphonate with sodium formate (Senhofer, *A.* 164, 134). Minute needles, v. sl. sol. cold water, v. sol. alcohol and ether. May be sublimed.—$BaA''2aq$.—Ag_2A'': amorphous pp.

Toluene ω o-dicarboxylic acid $CO_2H.CH_2.C_6H_4.CO_2H$. [2:1]. *Homophthalic acid v. o-Carboxy-phenyl-acetic acid.*

Nitrile v. o-CYANO-BENZYL CYANIDE.

Toluene ω m-dicarboxylic acid $CO_2H.CH_2.C_6H_4.CO_2H$ [3:1]. Formed by oxidation of *m*-di-ethyl-benzene (Allen a. Underwood, *Bl.* [2] 40, 100). Needles (from alcohol). Sublimes without melting at 200°-210°.—Ag_2A''.

Toluene ω p-dicarboxylic acid $CO_2H.CH_2.C_6H_4.CO_2H$. [285°-288°]. S. 1 at 50°. S. (alcohol) 14·3 at 30°. Formed by the action of dilute (25 p.c.) HCl on the amide (Mellinghoff, *B.* 22, 3215). V. sl. sol. ether and benzene.—Ag_2A'': crystalline pp. The same (?) acid formed by oxidation of C_6H_4PrPr [1:4] yields $BaA''1\frac{1}{2}aq$ (Paterno a. Spica, *B.* 10, 1746).

Amide $CO(NH_2).CH_2.C_6H_4.CO.NH_2$. [235°]. Formed from $CH_2Cy.C_6H_4.Cy$ and H_2SO_4. Small hard nodules.

Amic acid $CO(NH_2).CH_2.C_6H_4.CO_2H$. [261°]. Formed from $CH_2Cy.C_6H_4.CO_2H$ and H_2SO_4. Sl. sol. ether, hot water and alcohol.—AgA': crystalline.

Iso-amic acid $CO_2H.CH_2.C_6H_4.CO.NH_2$. [229°]. Formed from *p*-cyano-phenyl-acetic acid. Crystalline, v. sol. alcohol and hot water.—AgA'. Crystalline.

Nitrile $CH_2Cy.C_6H_4.Cy$. *p-Cyano-benzyl cyanide.* [100°]. (above 360°). Formed from $CH_2Cl.C_6H_4Cy$ and KCy (Mellinghoff, *B.* 22, 3209). Needles, v. sl. sol. hot water, sol. alcohol and ether.

Semi-nitrile $CH_2Cy.C_6H_4.CO_2H$. [201°]. Formed from ω-chloro-*p*-toluic acid by treatment with KOHAq and alcoholic KCy (Mellinghoff, *B.* 22, 3213). Crystalline, v. sol. alcohol and ether.—AgA'.

Semi-nitrile $CO_2H.CH_2.C_6H_4.Cy$. [152°]. Formed from the nitrile and HCl at 105°. Prisms, v. sol. alcohol.—AgA'. Crystalline.

Nitrile-amide $CH_2Cy.C_6H_4.CO.NH_2$. [182°]. Formed from ω-chloro-*p*-toluic amide and KCy. Plates.

Amide-nitrile $CO(NH_2).CH_2.C_6H_4.Cy$. [196·5°]. Formed from the nitrile and HCl at 70°. Crystalline, v. sol. alcohol.

Toluene tri-carboxylic acid $C_6H_2(CO_2H)_2.CH_2.CO_2H$. Formed in small quantity by oxidation of *s*-tri-ethyl-benzene (Friedel a. Balsohn, *Bl.* [2] 34, 635). Needles. Sublimes before melting.—Ag_3A'''. Tables (from hot water).

TOLUENE o-PHOSPHINIC ACID $C_6H_4Me.P(OH)_2$. Obtained by decomposing its chloride with water (Michaelis a. Paneck, *A.* 212, 223). Oil. Monobasic acid.—CaA'_2aq.

Chloride $C_6H_4Me.PCl_2$. (244°). Formed by the action of PCl_3 on mercury ditolyl [107°] and by warming toluene with $AlCl_3$ and PCl_3. Liquid.

Toluene p-phosphinic acid $C_6H_4Me.P(OH)_2$. [105°]. Formed in like manner. Plates, v. sl. sol. water. Oxidised by HNO_3 to the phosphonic acid. Decomposed on heating into tolyl-phosphine and toluene phosphonic acid.—KA'.—NH_4A'.—BaA'_2aq.—PbA'_2.—CuA'_24aq.

Ether $C_6H_4Me.P(OEt)_2$. [280°]. Formed from the chloride and dry NaOEt.

Chloride $C_6H_4Me.PCl_2$. [25°]. (245°). Formed, together with the *o*-isomeride, from toluene, PCl_3, and $AlCl_3$ (Michaelis a. Paneck, *A.* 212, 203). Formed also from $Hg(C_7H_7)_2$ [235°] and PCl_3. Needles, v. sol. ether and benzene.

References.—NITRO- and OXY-TOLUENE PHOSPHINIC ACID.

TOLUENE PHOSPHINIC ANHYDRIDE *v.* PHOSPHINO-TOLUENE.

TOLUENE o-PHOSPHONIC ACID $C_6H_4Me.PO(OH)_2$. [141°]. Formed by the action of water on its chloride (Michaelis a. Paneck, *A.* 212, 231). Crystals, v. sol. water.—Ag_2A''.

Chloride $C_7H_7.PCl_4$. This is formed from $C_7H_7.PCl_2$ and chlorine. Yellow solid.

Toluene p-phosphonic acid $C_6H_4Me.PO(OH)_2$. [189°]. Formed from $C_7H_7.PCl_4$ and cold water. Woolly needles. Oxidised by alkaline $KMnO_4$ to $CO_2H.C_6H_4.PO(OH)_2$. Bromine forms bromo-toluene.—$KH_3A''_2$: needles.—$BaH_2A''_2$—$AgHA''$.—Ag_2A''.

Chloride $C_7H_7.PCl_4$. [42°]. Formed from $C_7H_7PCl_2$ and chlorine. Yellow mass, converted by dry SO_2 into liquid $C_7H_7.POCl_2$ (285°).

Toluene ω-phosphonic acid $C_6H_5.CH_2.PO(OH)_2$. [166°]. Formed, together with $(C_7H_7)_2PO(OH)$ [191°], from benzoic aldehyde and PH_4I (Litthauer, *B.* 22, 2145). Stellate groups of prisms (from HOAc).

Reference.—OXY-TOLUENE PHOSPHONIC ACID.

TOLUENE ω-SELINIC ACID $C_7H_8SeO_2$ *i.e.* $C_6H_5.CH_2.SeO.OH$. [85°]. Formed by oxidising benzyl diselenide with HNO_3 (Jackson, *A.* 179, 8). Needles, sl. sol. cold water, v. sol. alcohol, nearly insol. ether.—AgA': slender crystals (from hot water).

TOLUENE SULPHAMINE *v.* AMIDO-TOLUENE SULPHINIC ACID.

TOLUENE o-SULPHINIC ACID $C_7H_8SO_2$ *i.e.* $C_6H_4Me.SO.OH$. [80°]. Formed by boiling $C_7H_7.N_2H_2.SO_2.C_7H_7$ with baryta-water (Limpricht, *B.* 20, 1241). Long needles, v. sol. ether.—$BaA'_2 3aq$. Nodules, v. sol. water.

Toluene p-sulphinic acid $C_6H_4Me.SO_2H$. [85°]. Formed in like manner (Limpricht), and also from toluene *p*-sulphonic chloride and sodium-amalgam, zinc-dust, or Na_2SO_3 (Otto, *A.* 142, 92; 145, 19; *B.* 9, 1586; Blomstrand, *B.* 3, 965). Plates, v. sol. ether. Fuming HNO_3 forms crystals [190°]. The Na salt heated with $CH_3.CHCl_2$ and alcohol at 150° gives a small quantity of $CH_3.CHCl.SO_2.C_7H_7$ [48°] (Otto, *J. pr.* [2] 40, 519). The Na salt with $ClCO_2Et$ gives the ether (Otto, *B.* 26, 308).—BaA'_2: plates.—$CaA'_2 4aq$.—$ZnA'_2 2aq$.—AgA'.

Methyl ether. Formed from the Na salt and $ClCO_2Et$ in MeOH. Oil (Otto, *J. pr.* [2] 47, 166).

Ethyl ether **EtA′. Oil. Oxidised by $KMnO_4$ in HOAc to toluene *p*-sulphonic ether (Otto a. Rossing, *B.* 19, 1226).**

Toluene *exo*-sulphinic acid $C_6H_5.CH_2.SO_2H$. Prepared by reducing $C_6H_5.CH_2.SO_2Cl$ with sodium-amalgam (Otto a. Lüders, *B.* 13, 1288). Very unstable.—NaA′: leaflets, sol. hot alcohol.

Reference.—AMIDO-TOLUENE SULPHINIC ACID.

TOLUENE *o*-SULPHONIC ACID $C_7H_8SO_3$ *i.e.* $C_6H_4Me.SO_3H$ [1:2].

Formation.—1. In small quantity together with the *p*-isomeride, by dissolving toluene in hot fuming H_2SO_4 (Engelhardt a. Latschinoff, *Z.* [2] 5, 617; Anna Wolkoff, *Z.* [2] 6, 321).—2. Together with the *m*- and *p*- isomerides by the action of $Cl.SO_2.OH$ on toluene (Claesson a. Wallin, *B.* 12, 1848; Noyes, *Am.* 8, 176).—3. From *o*-toluidine by diazotisation followed by treatment with H_2SO_3 (Müller a. Wiesinger, *B.* 12, 1348).—4. By reducing *p*-bromo-toluene sulphonic acid with sodium-amalgam (Terry, *A.* 169, 27).—5. From (4,1,2)- nitro-toluene sulphonic acid by elimination of NO_2 (Jenssen, *A.* 172, 235).

Preparation.—By adding toluene (60 g.) to $ClSO_3H$ (150 g.) in the cold, and pouring the product into water (Noyes).

Properties.—Thin leaflets (containing 2aq), v. sol. water. Deliquescent.

Salts (C. a. W.; Hubner a. Post, *A.* 169, 1).—KA′aq.—NaA′aq: tables, sol. water.—NH_4A': thin leaflets.—CaA'_2: leaflets, sl. sol. water.—BaA'_2aq. S. 4 at 12°. $BaA'_2$4aq.—PbA'_2aq.—$PbA'_2$4aq.—$MgA'_2$7aq.—$ZnA'_2$7aq.—$CuA'_2$4aq.—$CdA'_2$2aq.—$MnA'_2$2aq.—AgA′: sl. sol. water.

Chloride $C_7H_7.SO_2Cl$. Oil.

Amide $C_7H_7.SO_2NH_2$. [154°]. S. ·1 at 9°; S. (alcohol) 3·5 at 5°. Octahedra, sl. sol. water. Yields a benzoyl derivative [112°], which forms $C_7H_7.SO_2.NKBz$ 1½aq and $(C_7H_7.SO_2.NBz)_2Ba$ aq. (Wolkoff, *Z.* [2] 6, 57). Oxidised by $KMnO_4$ in acid solution to *o*-sulpho-benzoic acid and in neutral solution to $C_6H_4\left\langle\begin{matrix}SO_2\\CO\end{matrix}\right\rangle NH$ (Fahlberg a. List, *B.* 21, 242).

Anilide $C_7H_7.SO_2NHPh$. [136°].

Toluide $C_7H_7.SO_2.NHC_7H_7$. [131°].

Toluene *m*-sulphonic acid $C_6H_4Me.SO_3H$ [1:3]. *Formation.*—1. By the action of H_2SO_3 on *m*-diazo-toluene salts (Müller a. Wiesinger, *B.* 12, 1349).—2. A product of the action of $ClSO_3H$ on toluene (Claesson a. Wallin, *B.* 12, 1848).—3. From *o*-bromo-toluene *m*-sulphonic acid and sodium-amalgam (Müller, *A.* 169, 47). 4. By the diazo-reaction from *p*-toluidine sulphonic acid and from *o*-toluidine sulphonic acid (Pechmann, *A.* 173, 202; Pagel, *A.* 176, 297; Nevile a. Winther, *C. J.* 37, 628; Klason, *B.* 19, 2887).

Properties.—Thin deliquescent scales (containing aq), v. sol. water.

Salts.—KA′aq.—NaA′aq.—NH_4A': scales, v. sol. water.—$CaA'_2$3aq: needles, v. sol. water.—$BaA'_2$2aq.—BaA'_2aq. S. 22·75 at 12° (C. a. W.); 15·5 at 15° (Vallin, *B.* 19, 2952).—PbA'_2aq.—$PbA'_2$2aq.—$PbA'_2$3aq.—$MgA'_2$8aq.—$ZnA'_2$6aq.—$ZnA'_2$7aq.—$CdA'_2$5aq.—$CdA'_2$6aq: crystals. $MnA'_2$7aq.—$CuA'_2$4aq.—AgA′: v. sol. water.

Chloride $C_7H_7.SO_2Cl$. Oil.

Amide $C_7H_7.SO_2NH_2$. [108°]. **S. ·4 at 9° (C. a. W.); ·265 at 14° (V.). S. (alcohol) 18 at 5° (C. a. W.); 17·4 at 14° (V.). Monoclinic tables and octahedra (from alcohol). Melts at** 91° according to Noyes. Oxidised by alkaline K_3FeCy_6 to $CO_2H.C_6H_4.SO_2NH_2$ (Noyes a. Walker, *Am.* 8, 187).

Anilide $C_7H_7.SO_2NHPh$. [72°].

m-Toluide $C_7H_7.SO_2.NHC_7H_7$. [103°].

Toluene *p*-sulphonic acid $C_6H_4Me.SO_3H$ [1:4.] The chief product of sulphonation of boiling toluene (Deville, *A. Ch.* [3] 3, 172; Fittig a. Tollens, *A.* 131, 310; Mürcker, *A.* 136, 85; Engelhardt a. Latschinoff, *Z.* [2] 5, 617; Jaworsky, *Z.* 1865, 221; Otto a. Gruber, *A.* 142, 92; 145, 10; Chrustshoff, *B.* 7, 1167; Fahlberg, *B.* 12, 1048).—2. From toluene and $ClSO_3H$ (Claesson a. Wallin, *B.* 12, 1848).—3. By the action of H_2SO_3 on *p*-diazo-toluene salts (M. a. W.).

Properties.—Thick leaflets or flat prisms (containing aq). Deliquescent. Melts at 92° (Norton a. Otten, *Am.* 10, 110). Fusion with sodium formate yields *p*-toluic acid (Remsen, *B.* 8, 1412). Potash-fusion gives *p*-cresol. Hydrolysis by steam begins at 150° (Armstrong a. Miller, *C. J.* 45, 148).

Salts. KA′aq. Trimetric crystals; *a*:*b*:*c* = ·864:1:3·237.—NaA′3aq. NaA′2aq.—NH_4A'.—$CaA'_2$4aq.—BaA'_2. BaA'_2aq. S. 21 at 12°.—$BaA'_2$3aq (Kelbe, *B.* 16, 621).—PbA'_2.—$MgA'_2$6aq. $ZnA'_2$6aq. $CdA'_2$6aq.—$MnA'_2$6aq.—$CuA'_2$6aq.—AgA′: long plates, v. sol. water.

Methylamine salt [125°].—NMe_2H_2A'. [78°].—NMe_3HA'. [92°]. Aniline salt [223°].—*o*-Toluidine salt [180°] (N. a. O.).

Chloride $C_7H_7.SO_2Cl$. [69°]. Triclinic crystals; *a*:*b*:*c* = ·768:1:1·114; α = 97° 24′; β = 117° 6′; γ = 84° 28′. Acetoxim and NaOH form $C_7H_7.SO_2.O.N{:}CMe_2$ [89°] (Wege, *B.* 24, 3538). In ethereal solution it is reduced by sodium-amalgam to toluene sulphinic acid and the compound $C_8H_{10}SO_2$ [76°]. In presence of isoamyl ether $(C_5H_{11})_2O$ the compound $C_{12}H_{18}S_2O_4$ [36°] is formed (Otto, *A.* 143, 216).

Bromide $C_7H_7.SO_2Br$. [96°].

Iodide $C_7H_7.SO_2I$. [85°]. Formed by adding an alcoholic solution of I to aqueous $C_7H_7.SO_2Na$ (Otto a. Tröger, *B.* 24, 479). Yellow crystalline powder, v. sol. ether, turning brown in air. Heated with water at 100° it forms $C_7H_7.S_2O_2.C_7H_7$. Reduced silver acts in like manner. $ZnEt_2$ forms zinc toluene sulphinate.

Methyl ether MeA′. [c. 30°].

Ethyl ether EtA′. [32°]. S.G. ^{32} **1·174.** Thick prisms (Kraft a. Roos, *B.* 25, 2259).

Phenyl ether $C_7H_7.SO.OPh$. [95°]. **Formed** by the action of NaOPh on the chloride **dissolved** in benzene (Otto, *B.* 19, 1832). Trimetric **crystals**; *a*:*b*:*c* = ·289: [illegible] ·476. Not affected by alcoholic NH_3, even at 200°.

Amide $C_7H_7.SO_2NH_2$. [136°]. **S. ·2 at 9°.** S. (alcohol) 7·4 at 5°. **Leaflets. Yields** $C_7H_7.SO_2NHK$ aq. BzCl forms $C_7H_7.SO_2.NHBz$ [147°-150°], which gives KA′, CaA'_2aq, BaA'_2, AgA′, and $AgA'NH_3$, and is converted by PCl_5 into $C_7H_7SO_2N{:}CCl.C_6H_5$ [100°], whence ammonium carbonate solution forms $C_{14}H_{14}N_2SO_2$ [114°] (Wolkoff, *B.* 5, 140). Succinyl chloride forms crystalline $C_7H_7.SO_2.NC_4H_4O_2$, converted by NH_3Aq into $C_7H_7.SO_2.N_2H_3(C_4H_4O_2)$ [180°] and

$(C_7H_7SO_2)_2N_2H_4(C_4H_4O_2)$, which crystallises from alcohol (Wolkoff. *Z.* 1870, 580).

Methylamide $C_7H_7.SO_2.NHMe$. [75°]. Rectangular plates, sl. sol. hot water. Yields $C_7H_7.SO_2.NBzMe$ [58°].

Ethylamide $C_7H_7.SO_2.NHEt$. [58°].

Anilide $C_7H_7.SO_2NHPh$. [103°]. BzCl forms $C_7H_7.SO_2NBzPh$ [149° cor.] (Remsen a. Palmer, *Am.* 8, 242).

Methylanilide $C_7H_7.SO_2.NMePh$ [95°]. Monoclinic crystals (Otto, *J. pr.* [2] 47, 371).

Ethyl-anilide [88°]. Prisms, insol. water.

p-Toluide $C_7H_7.SO_2NHC_7H_7$. [118°].

Toluene *exo*-**sulphonic acid** $C_6H_5.CH_2.SO_3H$. Formed by boiling benzyl chloride with aqueous K_2SO_3 (Böhler, *A.* 154, 50; 221, 215; Mohr, *A.* 221, 216; Otto a. Lüders, *B.* 13, 1286). Formed also by oxidising benzyl disulphide with HNO_3 (Barbaglia, *B.* 5, 270, 688), and also, together with acetic acid, by heating benzyl methyl ketone with H_2SO_4 (Krekeler, *B.* 19, 2625). Very hygroscopic crystals. The K salt heated with KCy yields $C_6H_5.CH_2.CN$.

Salts.—NH_4A'.—KA'aq. Trimetric prisms. —BaA'_2 2aq. Plates, sl. sol. water.—CaA'_2 2aq.— $PbA'(OH)$: crystals.—PbA'_2.—AgA': crystalline.

Chloride $C_6H_5.CH_2.SO_2Cl$. [93°]. Decomposed by heat into SO_2 and benzyl chloride.

Amide $C_6H_5.CH_2.SO_2NH_2$. [102°] (O. a. L.) [105°] (Pechmann, *B.* 6, 534). Needles, sol. water and alcohol.

Toluene (α)-**disulphonic acid** $C_6H_3Me(SO_3H)_2$ [1:2:4]. Formed by sulphonation of toluene and of toluene *o*- or *p*-sulphonic acid (Hakansson, *B.* 5, 1084; Senhofer, *A.* 164, 129; Gnehm a. Forrer, *B.* 10, 542; Claesson a. Berg, *B.* 13, 1170; Klason, *B.* 20, 354). Formed also by heating toluene *p*-sulphonic chloride with H_2SO_4 (Fahlberg, *B.* 12, 1052; *Am.* 1, 170; 2, 182). Thick liquid.—$(NH_4)_2A''$aq.—K_2A''aq.—BaA''aq. S. ·75 at 17°. Insol. alcohol.—Ag_2A'' 2aq.

Chloride $C_7H_6(SO_2Cl)_2$. [52°].

Amide $C_7H_6(SO_2NH_2)_2$. [186°].

Toluene (β)-**disulphonic acid** $C_6H_3Me(SO_3H)_2$ [1:2:5]. Formed by heating toluene *o*-sulphonic acid with fuming H_2SO_4 at 160° (H.), or toluene *m*-sulphonic acid with H_2SO_4 at 180° (Klason, *B.* 19, 2889; 20, 352).—K_2A'' aq.—BaA'' aq. S. 3·9 at 15° (K.).

Chloride $C_6H_3Me(SO_2Cl)_2$. [96°].

Amide $C_6H_3Me(SO_2NH_2)_2$. [224°].

Toluene disulphonic acid $C_6H_3Me(SO_3H)_2$ [1:2:3]. Formed by the action of sodium-amalgam on *p*-iodo-toluene disulphonic acid (Limpricht a. E. Richter, *B.* 18, 2179; *A.* 230, 326), and by heating toluene *m*-sulphonic acid with fuming H_2SO_4 at 180° (Klason). Slender needles, v. sol. water and alcohol.—K_2A'' aq.— BaA'' $3\frac{1}{2}$aq. Prisms, v. sol. water.

Chloride $C_6H_3Me(SO_2Cl)_2$. [95°].

Amide $C_6H_3Me(SO_2NH_2)_2$. [214°].

Toluene *o*-**disulphonic acid** $C_6H_3Me(SO_3H)_2$. [1:2:6]. Formed by reduction of *p*-bromo-toluene disulphonic acid with sodium-amalgam (Kornatzki, *A.* 221, 199).—K_2A''.—BaA'' 4aq. V. e. sol. water.

Chloride [86·5°]. Prisms (from ligroïn).

Amide [above 260°]. Needles, v. sol. Aq.

Toluene disulphonic acid $C_6H_3Me(SO_3H)_2$ [1:3:4]. Formed from *p*-toluidine sulphonic acid by conversion into $C_6H_3Me(SH).SO_3H$ and oxidation of the product (Klason, *B.* 20, 356).— K_2A'' aq.—BaA'' 2aq. S 15. Prisms.

Chloride. [111°]. V. sol. $CHCl_3$.

Amide. [235°–239°]. V. sol. water.

Toluene-*s*-disulphonic acid $C_6H_3Me(SO_3H)_2$ [1:3:5]. Formed from *o*-iodo- (or bromo-) toluene disulphonic acid or *o*-diazo-toluene disulphonic acid by long boiling with conc. HI (Limpricht a. Hasse, *B.* 18, 2177; *A.* 230, 295).—K_2A'' $2\frac{1}{2}$aq.—$(NH_4)_2A''$.

Chloride [132°]. Long prisms.

Amide [over 240°]. Small plates.

Toluene trisulphonic acid $C_6H_2Me(SO_3H)_3$. Formed by heating sodium toluene (α)-disulphonate with $ClSO_3H$ at 240° (Claësson, *B.* 14, 307). Slender needles (containing 6aq), v. sol. water. Salts.—K_3A''' $3\frac{1}{2}$aq.—$Pb_3A'''_2$ 8aq.— $Ba_3A'''_2$ 14aq. Crystals, v. sol. water.

Chloride $C_6H_2Me(SO_2Cl)_3$. [153°].

Amide $C_6H_2Me(SO_2NH_2)_3$. [above 300°]. Minute crystals, nearly insol. water.

References.—Amido-, Bromo-, Bromo-amido-, Bromo-nitro-, Chloro-, Iodo-, Iodo-amido-, Nitro-amido-, Nitro- and Oxy- toluene sulphonic acid.

TOLUENE *p*-THIOSULPHONIC ACID $C_6H_4Me.SO_2.SH$. Formed by heating a solution of a salt of toluene *p*-sulphinic acid with sulphur (Otto, *B.* 15, 129; 20, 2087) or by adding a mixture of Na_2S and $C_7H_7.SO_2Na$ to an alcoholic solution of iodine (Otto a. Tröger, *B.* 24, 1132). A solution of Na salt gives a white pp. of cuprous salt on adding $CuSO_4$.

Reactions.—1. *Iodine* added to an alcoholic solution of the K salt forms the three compounds $(C_7H_7SO_2)_2S$ [134°], $(C_7H_7SO_2)_2S_2$ [109°], and $(C_7H_7SO_2)_2S_3$ [182°]. The compound $(C_7H_7SO_2)_2S$ is also formed by the action of I on a mixture of $C_7H_7.SO_2SNa$ and $C_7H_7SO_2Na$, and crystallises from benzene in monoclinic forms $a:b:c = 2·829:1:3·221$; $\beta = 60°\ 7'$. The compound $(C_7H_7SO_2)_2S_2$ is split up by boiling HOAc into $(C_7H_7SO_2)_2S$ and $(C_7H_7SO_2)_2S_3$ (Otto a. Tröger, *B.* 24, 1126).—2. $Cl.CO_2Et$ acting on the Na salt forms the ethyl and tolyl ethers and the compound $(C_7H_7SO_2)_2S_3$ [182°] (Otto a. Rössing, *B.* 24, 1148).

Salts.—NaA' 2aq. Trimetric tables.— KA' 2aq.—AgA'aq: small tables, sl. sol. water.

Ethyl ether $C_7H_7.SO_2.SEt$. *Tolyl ethyl disulphoxide.* Got from NaA' and EtI. Oil.

Ethylene ether $C_2H_4A'_2$. [77°]. Needles. Decomposed by zinc-dust into the zinc salts of toluene sulphinic acid and ethylene mercaptan (Otto a. Heydecke, *B.* 25, 1478).

Tolyl ether $C_7H_7.SO_2.SC_7H_7$. *Tolyl disulphoxide.* [78°]. Formed by oxidation of *p*-tolyl mercaptan (Märcker, *A.* 136, 83). Formed also from toluene *p*-sulphonic acid and water at 100° (Otto a. Tröger, *B.* 24, 480). Monoclinic prisms (from alcohol). Decomposed on saponification by alkalis into toluene *p*-sulphonic acid and di-tolyl disulphide [41°] (Otto a. Rössing, *B.* 19, 1240). Reduced by zinc and dilute H_2SO_4 to tolyl mercaptan. Bromine forms $(C_{14}H_{14}S_2O_2)_2Br_2$ (Otto a. Grüber, *A.* 149, 105). Alcoholic H_2S forms, on warming, toluene *p*-sulphinic acid, di-tolyl disulphide, and tolyl tetrasulphide.

Reference.—Amido-toluene thiosulphonic acid.

TOLUENYL- *v.* Tolenyl-.

o-TOLUIC ACID $C_6H_4Me.CO_2H$ [1:2]. Mol. w. 136. [104°]. H.C.v. 928,800. H.C.p. 929,400. H.F. 98,600 (Stohmann, *J. pr.* [2] 40, 133).

Formation.—1. By oxidation of *o*-xylene with dilute HNO_3 (Bieber a. Fittig, *Z.* [2] 6, 496; *A.* 156, 242).—2. From toluene *o*-sulphonic acid *viâ* $C_7H_7.CN$ (Ramsay a. Fittig, *Z.* [2] 7, 584; *A.* 168, 246).—3. By the action of sodium-amalgam on a mixture of $ClCO_2Et$ and *o*-iodo-toluene and saponification of the resulting $C_7H_7.CO_2Et$ (Kekulé, *B.* 7, 1007).—4. By boiling phthalide (3 mols.) with HIAq (127°) and yellow P (2 at.), the yield being 97 p.c. (Hessert, *B.* 11, 238; Racine, *A.* 239, 72).—5. From *o*-toluidine *viâ* the nitrile (Cahn, *A.* 240, 280).

Properties.—Plates (containing 2aq), volatile with steam, sl. sol. cold water. Oxidised by alkaline $KMnO_4$ to phthalic acid (Weith, *B.* 7, 1057). Bromine-vapour above 100° forms phthalide; in the cold Br forms bromo-toluic acid $C_6H_3MeBr.CO_2H$ [167°].

Salts.—NaA′ 2aq. [228°]. Efflorescent plates.—CaA'_2 2aq.—BaA'_2 2aq.

Ethyl ether EtA′. (220°).

Amido-ethyl ether $C_7H_7.CO.O.CH_2.CH_2.NH_2$. Formed from *o*-tolyl-oxazoline and HClAq. Oil. Yields B′HBr [156°], $B'C_6H_3N_3O_7$ [188°].

Amido-propyl ether $C_7H_7.CO.O.CHMe.CH_2.NH_2$. Formed by evaporating tolyl-methyl-oxazoline with HClAq. Yields B′HBr [140°], $B'C_6H_3N_3O_7$ [192°], and a platinochloride [214°].

Benzyl ether C_7H_7A'. (315°). S.G. $\frac{17}{17}$ 1·12. Oil (Hodgkinson, *C. J. Proc.* No. 103, p. 167).

Chloride C_8H_7OCl. (211° at 733 mm.).

Anhydride $(C_7H_7.CO)_2O$. [c. 38°]. (above 325°). Formed from the Na salt (6 mols.) and $POCl_3$ (1 mol.). Insol. water, sol. ether and benzene.

Amide $C_7H_7.CONH_2$. [140°] (Hutchinson, *B.* 24, 174; *C. J.* 57, 957; *cf.* Weith, *B.* 6, 420). On reduction in acid solution it yields *o*-tolyl alcohol and a small quantity of the dihydride $C_7H_9.CO.NH_2$ [156°], which on boiling with water yields an acid [68°]. The dihydride is also formed by reducing the amide in alkaline solution.

Anilide $C_7H_7.CO.NHPh$. [125°]. Formed from *anti*-phenyl-*o*-tolyl ketoxim and PCl_5 followed by water (Smith, *B.* 24, 4017).

Xylide $C_7H_7.CO.NHC_6H_3Me_2$ [1:2:4]. [165°]. Formed by heating *o*-tolyl xylyl ketone with hydroxylamine at 120° (Smith).

Bromo-ethylamide $C_7H_7.CO.NH.CH_2.CH_2Br$. [71°] (Salomon, *B.* 26, 1322).

Chloro-ethylamide $C_7H_7.CO.NH.CH_2.CH_2Cl$. [73°]. White needles.

Bromo-propyl-amide $C_7H_7.CO.NH.CH_2.CHBr.CH_3$. [86°]. Needles (from benzene-ligroïn) (Salomon, *B.* 26, 1323).

Chloro-propyl-amide $C_7H_7.CO.NH.CH_2.CHMeCl$. [84°]. Formed by evaporating *o*-tolyl-methyl-oxazoline with excess of HClAq. Needles (from ligroïn).

o-Nitro-benzyl-amide $C_7H_7.CO.NH.CH_2.C_6H_4.NO_2$. [135°]. Needles (from alcohol). May be reduced to the *o*-amido-benzyl-amide [116°], which yields B′HCl [214°] (Wolff, *B.* 25, 3034).

Imide $(C_7H_7.CO)_2NH$. [148°].

Nitrile $C_7H_7.CN$. (204° cor.). V.D. 4·03 (obs.). H.F. −34,800 (Berthelot a. Petit, *A. Ch.* [6] 17, 123). Formed by heating KCy with potassium toluene *o*-sulphonate or with tri-*o*-tolyl phosphate (Heim, *B.* 16, 1776), by heating *o*-tolyl thiocarbimide with finely-divided copper (Weith, *B.* 6, 419), by boiling *o*-tolyl carbamine (Weith, *B.* 7, 722), by heating *o*-iodo-toluene with AgCy at 350° (Merz a. Weith, *B.* 10, 751), by boiling the formyl derivative of *o*-toluidine with zinc-dust (the yield being 18 p.c.) (Gasiorowski a. Merz, *B.* 17, 74; 18, 1004), and by Sandmeyer's reaction from *o*-toluidine (Cahn, *B.* 19, 756). Liquid. H_2SO_4 at 60° to 70° forms $C_7H_7.C(NH).NH.CO.C_7H_7$ [103°], which is converted, by warming its acid solution, into the imide $(C_7H_7.CO)_2NH$ (Krafft a. Kerstens, *B.* 25, 455). Conc. HIAq forms $C_7H_7.CI_2.NH_2$ [98°] (Biltz, *B.* 25, 2540).

Hexahydride *v.* Methyl-hexamethylene carboxylic acid.

m-**Toluic acid** $C_6H_4Me.CO_2H$ [1:3]. [110°] (Jacobsen, *B.* 14, 2347; Bornemann, *B.* 20, 1382). (263°). H.C.v. 928,500. H.C.p. 929,100. H.F. 98,900 (Stohmann, *J. pr.* [2] 40, 134). S. ·09 at 15°; 1·66 at 100°.

Formation. 1. By oxidising bromo-xylene and reducing the resulting bromo-toluic acid with sodium-amalgam (Ahrens, *Z.* [2] 5, 106; Richter, *B.* 5, 421; Böttinger a. Ramsay, *A.* 168, 255). 2. By distilling uvitic acid with lime (Fittig, *B.* 5, 268). 3. By oxidation of *m*-xylene with dilute HNO_3 (Tawildaroff, *B.* 4, 410; Bruckner, *B.* 9, 406; Reuter, *B.* 17, 2028).—4. By saponifying the nitrile.

Preparation.—1. By boiling ω-chloro-xylene with HNO_3 (1 vol. of S.G. 1·4) and water (3 vols.) (Senff, *A.* 220, 247).—2. By sulphonating crude xylene, then preparing $C_6H_3Me_2.SO_2NH_2$, oxidising by $KMnO_4$, heating the resulting $C_6H_3Me(SO_2NH_2).CO_2H$ with HCl at 230°, and distilling with steam (Jacobsen, *B.* 14, 2347).

Properties.—Long needles, volatile with steam, v. sol. alcohol and ether. Oxidised by chromic acid mixture to isophthalic acid.

Salts.—CaA'_2 3aq. S. 3·17 at 15°; 8·2 at 100°.—BaA'_2 2aq: trimetric plates or tables.—AgA′.

Ethyl ether EtA′. (226°).

Chloride (218° at 724 mm.) (Ador a. Rilliet, *B.* 12, 2300).

Nitrile $C_7H_7.CN$. (209°). Formed by heating *m*-tolyl thiocarbimide with Cu (Weith a. Landolt, *B.* 8, 720), and in other ways (Buchka a. Schachtebeck, *B.* 22, 841).

p-**Toluic acid** $C_6H_4Me.CO_2H$ [1:4]. [179°]. (275° cor.) (Fischli, *B.* 12, 615). H.C.v. 926,800. H.C.p. 927,400. H.F. 100,600 (Stohmann, *J. pr.* [2] 40, 134).

Formation.—1. By the action of dilute NHO_3 on cymene (Noad, *P. M.* [3] 32, 19; *A.* 63, 289) on *p*-xylene (Beilstein, *A.* 137, 302; Brückner, *A.* 205, 113), and on terpenes (Hirzel, *Z.* 1866, 205).—2. By saponification of the nitrile.—3. By heating *p*-bromo-toluene with $ClCO_2Et$ and sodium-amalgam and saponifying the product (Wurtz, *C. R.* 68, 1298).—4. From *p*-bromo-toluene, CO_2, and sodium (Kekulé, *A.*

187, 184).—5. By the action of $POCl_3$ (40 g.) on a mixture of toluene (40 g.), HOAc (80 g.) and $ZnCl_2$ (80 g.) at 110° (Frey, *J. pr.* [2] 43, 116).—6. By reducing bromo-*p*-toluic acid with sodium-amalgam (Remsen a. Morse, *Am.* 1, 138).—7. From the chloride which is formed by the action of $COCl_2$ on toluene in presence of $AlCl_3$ (Ador a. Crafts, *B.* 10, 2176).—8. From the amide which is formed by the action of $AlCl_3$ on a mixture of toluene, CS_2, and $NH_2.CO.Cl$ (Gattermann a. Schmidt, *B.* 20, 859).—9. By fusing $C_7H_7.CO.C_6H_4.CO_2H$ with potash (Friedel a. Crafts, *Bl.* [2] 35, 508), and also by passing gaseous cyanic acid and HCl into toluene at 100° containing $AlCl_3$ (Gattermann a. Rossolymo, *B.* 23, 1195).

Properties.—Needles, v. sol. hot water, v. e. sol. alcohol and ether. Volatile with steam. Oxidised by CrO_3 or $KMnO_4$ to terephthalic acid. Yields a di-nitro-derivative [158°].

Salts.—KA′.—BaA'_2 2aq: needles (Buchka a. Irish, *B.* 20, 1764).—CaA'_2 3aq.—MgA'_2 3aq.—CuA'_2.—AgA′.

Methyl ether MeA′. [32°]. (217°).

Ethyl ether EtA′. (228°). Oil.

Amido-ethyl ether $C_7H_7.CO.O.C_2H_4NH_2$. Yields B′HBr [167°] and $B'C_6H_3N_3O_7$ [180°].

p-Amido-propyl ether $C_7H_7.CO.O.C_3H_6.NH_2$. The hydrobromide B′HBr is formed by evaporating a solution of the bromo-propyl-amide. It yields $B'C_6H_3N_3O_7$ [186°] and $B'_2H_2PtCl_6$.

Phenyl ether PhA′. [72°].

Chloride (225° at 720 mm.).

Amide $C_7H_7.CO.NH_2$. [159°]. Formed by heating the NH_4 salt in sealed tubes at 230° (Hallemann, *R. T. C.* 6, 79).

Methylamide $C_7H_7.CO.NHMe$. [143°]. Formed by the action of NHMe.COCl on toluene in presence of $AlCl_3$ (Gattermann a. Schmidt, *B.* 20, 120; *A.* 244, 51). Tables.

Ethylamide $C_7H_7.CO.NHEt$. [96°].

Bromo-ethyl-amide $C_7H_7.CO.NH.CH_2.CH_2Br$. [129°] (Salomon, *B.* 26, 1325). Formed from *p*-toluic chloride and bromo-ethylamine. Plates. Converted by boiling water into the amido-ethyl ether.

Chloro-ethyl-amide $C_7H_7.CO.NH.CH_2.CH_2Cl$. [122°]. Needles (from ligroïn).

Bromo-propyl-amide $C_7H_7.CO.NH.CH_2.CHBr.CH_3$. Melts at 74°, becomes solid, and melts again at 158° (*B.* 26, 1326).

Chloro-propyl-amide $C_7H_7.CO.NH.CH_2.CHMeCl$. [78°].

Anilide $C_7H_7.CO.NHPh$. [145°]. Formed from toluene, phenyl cyanate, and $AlCl_3$ (Leuckart, *J. pr.* [2] 41, 306).

o-Nitro-anilide. [110°]. Yellow prisms.

p-Toluide $C_7H_7.CO.NHC_7H_7$. [160°]. Formed by the action of sodium-amalgam and HOAc at 60° on an alcoholic solution of di-*p*-tolyl ketoxim (Goldschmidt a. Stöcker, *B.* 23, 2747; 24, 2799). Needles.

Nitro-toluide $C_7H_7.CO.NHC_6H_3Me(NO_2)$ [4:1:3]. [166°].

Diphenylamide $C_7H_7.CO.NPh_2$. [155°]. Prisms (from alcohol) (Lellmann a. Bonhöffer, *B.* 20, 2118).

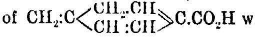
Xylide $C_7H_7.CO.NHC_6H_3Me_2$. [139°]. Yields $C_7H_7.CO.NH.C_6H_2Me_2(NO_2)$ [187°].

Phenyl-methyl-amide $C_7H_7.CO.NPhMe$. [70°] (Lellmann a. Benz, *B.* 24, 2114).

o-Nitro-benzyl-amide $C_7H_7.CO.NH.CH_2.C_6H_4.NO_2$. [142°] (Wolff, *B.* 25, 3036).

Nitrile $C_6H_4Me.CN$. [28·5°]. (218°). Formed by distilling potassium toluene *p*-sulphonate with KCy (Merz, *Z.* [2] 4, 33), by heating $C_7H_7.N.CS$ with Cu (Weith, *B.* 6, 421), by heating tri-*p*-tolyl phosphate with KCy (Heim, *B.* 16, 1775), and by passing $C_7H_7.NH.CHO$ over heated zinc-dust (G. a. M.). Obtained also from *p*-toluidine by Sandmeyer's reaction (Glock, *B.* 21, 2650). Sodium added to its boiling alcoholic solution forms a small quantity of ω-amido-*p*-xylene, the greater part being saponified (Bamberger a. Lodter, *B.* 20, 1710). H_2SO_4 gives $C_7H_7.C(NH).NH.CO.C_7H_7$ [145°]. Easily converted into the imide $(C_7H_7.CO)_2NH$ [155°] (Krafft a. Karstens, *B.* 25, 454). Conc. HIAq forms $C_7H_7.CI_2.NH_2$ [115°–120°], decomposed by fusion (Biltz, *B.* 25, 2539).

Tetrahydride $C_8H_{12}O_2$. (252°). Formed by reduction of $CH_2:C\!\left\langle\begin{smallmatrix}CH_2.CH\\ CH:CH\end{smallmatrix}\right\rangle\!C.CO_2H$ with sodium-amalgam (Einhorn a. Willstälter, *B.* 26, 2009). Needles, melting below 0°. Yields CaA'_2 4aq, CuA'_2 2aq, MeA′. (210°–220°), and an *amide* [158°]. Boiling NaOHAq converts the acid into a solid isomeride [47°] (254°–260°) which yields CaA'_2 4aq and an amide [135°].



Hexahydride (Serebojakoff, *B.* 25, 3355).

References.—AMIDO-, BROMO-, BROMO-NITRO-, CHLORO-, NITRO-, NITRO-AMIDO-, OXY-, OXY-AMIDO-, and SULPHO- TOLUIC ACID.

α-Toluic acid is PHENYL-ACETIC ACID.

o-TOLUIC ALDEHYDE $C_6H_4Me.CHO[1:2]$. *o-Toluylic aldehyde.* (200°). Prepared by boiling ω-chloro-*o*-xylene with lead nitrate solution (Lauth a. Grimaux, *Bl.* [2] 7, 233; Rayman, *Bl.* [2] 27, 498). Prepared also from *o*-xylene by the successive action of CrO_2Cl_2 and water (Bornemann, *B.* 17, 1467), and by oxidising $C_6H_4Me.CH_2OH$ with chromic acid mixture (Kröber, *B.* 23, 1029). Oil, smelling like bitter almonds. Yields a crystalline compound with $NaHSO_3$. Reduced by sodium-amalgam to *o*-tolyl-carbinol.

Oxim $C_6H_4Me.CH:NOH$. [49°]. Is an *anti-oxim.* White crystals (from ether), v. sol. alcohol. Yields a crystalline hydrochloride. Ac_2O yields an acetyl derivative [56°]. AcCl acts in like manner. The acetyl derivative is decomposed by alkalis with regeneration of the oxim, no nitrile being formed (Dollfus, *B.* 25, 1921). The oxim is converted in ethereal solution by PCl_5 into the nitrile (204°).

***m*-Toluic aldehyde** $C_6H_4Me.CHO[1:3]$. (199°). S.G. ⁰ 1·037. Formed by boiling ω-chloro-*m*-xylene or ω-bromo-*m*-xylene with lead nitrate solution (Gundelach, *Bl.* [2] 26, 44; Müller, *B.* 20, 1213), and also by the action of water on $C_7H_8CrO_2Cl_2$ obtained from *m*-xylene (Étard, *B.* 14, 848; Bornemann, *B.* 17, 1464). Oil, smelling like almonds. Combines with $NaHSO_3$. Aniline forms $C_7H_7.CH:NPh$. (314°).

Phenyl-hydrazide $C_6H_4Me.CH:N_2HPh$. [91°]. (B.); [88°] (Rudolph, *A.* 248, 100). Prisms (from ligroïn), v. sol. ether.

p-Toluic aldehyde $C_6H_4Me.CHO$[1:4]. (205°). Formed by distilling calcium p-toluate with calcium formate (Cannizzaro, *A.* 124, 254). Formed also by the action of water on the product of combination of p-xylene with CrO_2Cl_2 (Bornemann). Oil, with peppery smell. Oxidised by air to toluic acid. Alcoholic potash forms potassium toluate and tolyl-carbinol.

Reference.—NITRO- and OXY-TOLUIC ALDEHYDE.

TOLUIC CHLORIDE *v. Chloride* of TOLUIC ACID.

TOLUIDES. Compounds derived from toluidine by displacement of H in NH_2 by an acid radicle.

o-TOLUIDINE $C_6H_4Me.NH_2$ [1:2]. Mol. w. 107. (198°). S.G. $\frac{20}{4}$ ·9986 (Brühl, *A.* 200, 189). H.C.p. 964,700. H.C.v. 963,750. H.F. 3,800 (Petit, *C. R.* 107, 266). μ_β 1·5895. R_∞ 57·56. S.V. 126·6. Formed from o-cresol, $ZnBr_2$, NH_3, and NH_4Cl at 335° (Merz a. Müller, *B.* 20, 547). Prepared by reduction of o-nitro-toluene. May be separated from p-toluidine by means of the acid oxalates (Bindschedler, *B.* 6, 448; Ihle, *J. pr.* [2] 14, 449; Miniati, Booth a. Cohen, *S. C. I.* 6, 418), by freezing (Rosenstiehl, *Bl.* [2] 17, 7), by means of the nitrates (Schad, *B.* 6, 1361), hydrochlorides, sulphates, or phosphates (Lewy, *Fr.* 23, 269; *B.* 19, 1717, 2728; *cf.* Wülfing, *B.* 19, 2132). o-Toluidine can be prepared from $C_6MeHBr(NH_2)(NO_2)H$ *viâ* $C_6MeHBrI(NO_2)H$, $C_6MeHBrI(NH_2)H$, $C_6MeHBrIBrH$, followed by $C_6Me(NO_2)BrIBrH$, and $C_6Me(NH_2)BrIBrH$. It can also be got from $C_6Me(NH_2)BrIBrH$ *viâ* $C_6MeIBrIBrH$, followed by $C_6MeIBrIBr(NO_2)$ and $C_6MeIBrIBr(NH_2)$ thus proving that the toluidine $C_6H_4Me(NH_2)$ [1:2] is identical with $C_6H_4Me(NH_2)$ [1:6] (Wroblewsky, *A.* 192, 213).

Properties.—Oil. A solution in $H_2SO_4H_2O$ is coloured orange by HNO_3 and blue by CrO_3, the solution in the latter case becoming reddish-violet on dilution. Forms a crystalline compound with liquid CO_2 at 8° (Bitte, *C. R.* 105, 614). With PbO_2 and aqueous acetic acid gives a green colour, while PbO_2 and alcoholic acetic acid gives a reddish-violet colour (Lauth, *C. R.* 111, 975). Unlike p-toluidine, it forms a crystalline compound with alloxan (Pellizzari, *C. C.* 1887, 1288, 1396). If an ethereal solution of o-toluidine is shaken with very dilute bleaching-powder solution the aqueous layer becomes yellow or brown, and the ethereal layer, if decanted and shaken with dilute H_2SO_4, colours this reddish-violet. A solution of p-tolylene diamine hydrochloride mixed with a little o-toluidine gives a green colour on addition of $FeCl_3$ or $K_2Cr_2O_7$ (Nietzki, *B.* 10, 1157).

Reactions.—1. $POCl_3$ forms $PO(NHC_7H_7)_3$ [225°] (Michaelis a. Rudert, *B.* 26, 565), v. sol. water, whence Br forms $PO(NHC_6H_3BrMe)_3$ [253°]. Another product of the action of $POCl_3$ on o-toluidine is $POCl(NHC_6H_4Me)_2$, whence water forms $HO.PO(NHC_7H_7)_2$ [95°]. $PSCl_3$ forms $PS(NHC_7H_7)_3$ [135°].—2. $SiCl_4$ reacts forming $SiCl_2(NHC_7H_7)_2$, a white granular powder (Harden, *C. J.* 51, 40).—3. On heating with *malic acid* it yields the mono-toluide [178°], di-toluide [181°], and a tolyl-imide [116°] of malic acid (Bischoff, *B.* 23, 2043).—4. *Chloro-citryl chloride* forms

$C_7H_7.N{<}\begin{array}{l}CO.CH\\CO.\ddot{C}.CH_2.CO.NHC_7H_7\end{array}$ [214°] (Skinner a. Ruhemann, *C. J.* 55, 239).—5. SO_2, alcohol, and nitrous acid give rise to the 'sulphazide' $C_{14}H_{16}N_2SO_2$ [142°] (Limpricht, *B.* 20, 1241).—6. On *nitration* of o-toluidine or its acetyl derivative NO_2 enters the p- and o- positions, but in presence of H_2SO_4 (10 pts.) the compound $C_6H_3Me(NO_2)(NH_2)$ [1:4:6] [107°] is formed (Nölting a. Collin, *B.* 17, 265), together with the (1,2,6)-isomeride (Green a. Lawson, *C. J.* 59, 1013).—7. *Benzoic aldehyde* forms $C_6H_5CH:NC_7H_7$, an oil (316°) (Étard, *Bl.* [2] 39, 530; Pictet, *B.* 19, 1063). 8. *Hydrobenzamide* on warming forms the same body (310°) (Lachovitch, *M.* 9, 695).—9. Toluidine heated with toluidine hydrochloride and benzoic aldehyde in sealed tubes at 120° forms $C_6H_5.CH(C_6H_3Me.NH_2)_2$, a crystalline powder turning blue in the air (Ullmann, *J. pr.* [2] 36, 251).—10. The *methyl derivative* of *p-oxy-benzoic aldehyde* at 120° produces the compound $C_6H_4(OMe).CH:N.C_7H_7$ [32°] (Steinhart, *A.* 241, 340). 11. *Bromo-propionic acid* reacts, forming $C_{17}H_{18}N_2O_2$ [185°] (Mabery a. Krause, *B.* 22, 3308).—12. *αβ-Di-bromo-acrylic acid* produces pale-yellow needles [115°] (M. a. K.).—13. The hydrochloride heated with MeOH at 250°–300° gives rise to di-methyl-toluidine, xylidine $C_6H_3Me_2(NH_2)$ [4:3:1] and mesidine (Limpach, *B.* 21, 640).—14. *Cyanogen* passed into an alcoholic solution forms crystalline $C_{16}H_{16}N_4$, which yields $B''H_2Cl_2$ and $B''2HNO_3$ (Bladin, *Bl.* [2] 41, 128).—15. On heating with S it yields $C_{14}H_{12}N_2S$ [120°] crystallising from alcohol in yellow plates and yielding a dibromide $C_{14}H_{10}Br_2N_2S$ [190°] (Gattermann, *B.* 22, 425).—16. $ClSO_3H$ in $CHCl_3$ forms $C_7H_7NH.SO_3H$, which yields BaA'_2 2aq. Both the acid and its salts reproduce o-toluidine when treated with hot water (Traube, *B.* 23, 1656).

Salts (Beilstein a. Kuhlberg, *A.* 156, 66; Rosenstiehl).—B'HCl aq. S. 37·4 at 15·5°. S. (alcohol) 100.—$B'_2H_2PtCl_6$. Decomposed by boiling water (difference from p-toluidine) (De Coninck, *Bl.* [2] 45, 131).—$B'_2H_2ZnCl_4$. White tables (Bibanoff, *Monit. scient.* [3] 4, 925).—B'_2ZnCl_2 2aq (Lachovitch, *M.* 9, 513).—B'_2HgCl_2. [115°]. Prepared by shaking an alcoholic solution of the base with $HgCl_2$ (Klein, *B.* 11, 743). Crystalline powder, sol. alcohol and ether.—B'_2MnCl_2.—$B'_2H_2CuCl_4$. Yellow crystalline pp. got by adding $CuCl_2$ to a solution of the hydrochloride (Pomey, *C. R.* 104, 365).—B'HBr. Trimetric prisms.—B'_2HgBr_2. [101°]. Leaflets (Klein, *B.* 13, 835).—B'_2ZnBr_2 (Leeds, *J.* 1882, 503).—B'HI. Trimetric prisms (Städel, *B.* 16, 28).—B'_2HgI_2. White needles.—B'_2ZnI_2.—B'_2CdI_2.—B'_2HgCy_2.—$B'_4H_4FeCy_6$: crystals.—$B'_2H_2Cu_2(SO_3)_2$. Formed by adding aqueous cupric sulphate and $NaHSO_3$ to a solution of the base in acetic acid (Denigès, *C. R.* 112, 870).—$B'HgH_2(SO_3)_2$ aq.—$B'H_2SO_4$. Crystals (Wellington a. Tollens, *B.* 18, 3313).—$B'_2H_2SO_4$. S. 7·8 at 22°. S. (89 p.c. alcohol) 1·6 at 21·5°.—$B'HNO_3$. S. 10 at 19°. S. (89 p.c. alcohol) 23·5 at 16·5°.—$B'H_3PO_4$. Crystals, v. sol. water (Lewy, *B.* 19, 1717). The salts $B'_2H_3PO_4$ and $B'_3H_3PO_4$ could not be prepared. Aniline sets free o-toluidine from $B'H_3PO_4$. p-Toluidine also sets free o-toluidine from its phosphate.—$B'HSCyCr(SCy)_2 2NH_3$. Red plates, v. sol. hot water (Christensen, *J. pr.* [2] 45, 362).—**Oxalate**: small plates. S. 2·38 at 21°. S. (84 p.c.

alcohol) 2·68 at 21°. S. (ether) ·65 at 21°.—**Chloroacetate** $B'C_2H_3ClO_2$. [95°] (Bischoff, *B.* 21, 1257).—(β ?)-**naphtholate** [81°] (Dyson, *C. J.* 43, 470).

Formyl derivative $C_7H_7.NH.CHO$. [58°]. (288°). Plates (Ladenburg, *B.* 10, 1129; Tobias, *B.* 15, 2446). The crystalline polymeride [211°] is v. sol. hot HOAc, nearly insol. ether and cold alcohol.

Thioformyl derivative $C_7H_7.NH.CSH$: [96°]; yellow needles; bitter taste; sol. alcohol and ether, insol. water. Formed by heating the formyl derivative with P_2S_5. It dissolves unaltered in cold aqueous NaOH, and is reprecipitated by an acid. By distillation in vacuo it forms di-tolyl-formamidine $\begin{matrix}C_7H_7.NH\\ C_7H_7.N\end{matrix}\!\!>\!CH$ with evolution of H_2S and CS_2. By heating for 7 hours at 190° under pressure a crystalline compound $C_{16}H_{16}N_2S$ [160°] is formed with evolution of H_2S (Senier, *B.* 18, 2292; *C. J.* 47, 762).

Acetyl derivative $C_7H_7.NHAc$. [109°] (Bedson a. King, *C. J.* 37, 753). (296°). S. ·85 at 19°. Formed from the base and HOAc (Beilstein a. Kuhlberg, *A.* 156, 77; Alt, *A.* 252, 318), or by shaking it with water and Ac_2O (Hinsberg, *B.* 23, 2962). Converted by PCl_5 into the compound $C_7H_7N:CClMe$, which when carefully heated gives a base $C_7H_7N:CMe.CH_2.CCl:NC_7H_7$ [53°], and when treated with excess of *o*-toluidine gives di-tolyl-acetamidine [69°]. Br in HOAc forms $C_6H_3MeBr(NHAc)$ [1:6:2] [157°].

Chloro-acetyl derivative $C_7H_7NH.CO.CH_2Cl$. [112°]. Formed by the action of chloro-acetyl chloride on *o*-toluidine dissolved in benzene (Widman, *J. pr.* [2] 38, 299). Needles (from dilute alcohol). Converted by alcoholic potash into a pyrazine derivative [160°].

Di-chloro-acetyl derivative $C_7H_7NH.CO.CHCl_2$. Needles, volatile with steam (Rügheimer a. Hoffmann, *B.* 18, 2987).

Tri-chloro-acetyl derivative $C_7H_7NH.CO.CCl_3$. [67°]. Formed from hexachloro-acetone and *o*-toluidine (Cloez, *A. Ch.* [6] 9, 215). Needles, sl. sol. cold alcohol.

Bromo-acetyl derivative $C_7H_7.NH.CO.CH_2Br$. [113°]. Formed from *o*-toluidine and bromo-acetyl bromide (Widman, *J. pr.* [2] 38, 298). Needles. Converted by alcoholic potash into $C_{10}H_{18}N_2O_2$ [160°].

Thio-acetyl derivative $C_7H_7.NH.CS.CH_3$. [68°] (Wallach, *B.* 13, 529; 16, 147). Converted by NaOEt and EtBr into oily $C_7H_7N:CMe.SEt$ (262°).

Propionyl derivative $C_7H_7.NH.COEt$. [87°]. (299° at 730 mm.) Formed from *o*-toluidine and propionic acid (Pictet a. Duparc, *B.* 20, 3421). Needles, sl. sol. hot water. Oxidised by $KMnO_4$ to propionyl-*o*-amido-benzoic acid [117°].

a-Bromo-propionyl derivative $C_7H_7.NH.CO.CHBr.CH_3$. [131°]. Needles, insol. ligroïn (Tigerstedt, *B.* 25, 2920).

Benzoyl derivative $C_7H_7.NHBz$. [131°] (Gudeman, *B.* 21, 2553); [143°] (Brückner, *A.* 205, 130). Long broad needles. Yields benzoyl-*o*-amido-toluic acid on oxidation by $KMnO_4$. PCl_5 forms $C_7H_7.N:CCl.C_6H_5$ (Just, *B.* 19, 982).

Oxalyl derivative $C_2O_2(NH.C_7H_7)_2$. [181°]. Plates (from alcohol) (Bladin, *Bl.* [2] 41, 130).

Phthalyl derivative $C_7H_7N:C_2O_2:C_6H_4$. [182°]. (near 360°). Needles, sol. hot HOAc (Fröhlich, *B.* 17, 2679).

Phenacyl derivative $C_7H_7NH.CH_2.CO.C_6H_5$. [89°]. Formed from the base in alcohol and ω-bromo-acetophenone (Bischler, *B.* 25, 2865). Needles. Yields B'HCl and an acetyl derivative [92°].

m-**Toluidine** $C_6H_4Me.NH_2$ [1:3]. (197°) (Beilstein a. Kühlberg, *A.* 156, 83); (201°) (Buchka a. Schachtebeck, *B.* 22, 840); (205°) (Lorenz, *A.* 172, 180; Merz a. Müller, *B.* 20, 548). S.G. 25 ·998. S.N. 128·1. H.C.v. 964,600. H.C.p. 965,600. H.F. 2,900 (Petit, *A. Ch.* [6] 17, 155). Formed by reduction of *m*-nitro-toluene. Obtained also from *p*-toluidine by successive acetylation, nitration, saponification, diazotisation, boiling with alcohol, and reduction (Lorenz, *B.* 7, 448). Formed also by heating *m*-cresol with $ZnBr_2$, ammonia, and NH_4Br at 300° (M. a. M.). Prepared from benzoic aldehyde by nitration, conversion into *m*-nitro-benzylidene chloride and reduction of this body by zinc and HClAq in the cold (Vienne a. Steiner, *Bl.* [2] 35, 428; Widman, *B.* 13, 676; *Bl.* [2] 36, 216; Ehrlich, *B.* 15, 2011; Harz, *B.* 18, 3398). *m*-Toluidine can be shown to exist in commercial toluidine by means of the nitroso- derivative of di-methyl-*m*-toluidine, since *o*- and *p*- di-methyl-toluidines do not give nitroso- derivatives (Wurster a. Riedel, *B.* 12, 1796).

Properties.—Oil. Its solution in $H_2SO_4H_2O$ is coloured yellowish-brown by CrO_3 and blood-red by HNO_3. Its ethereal solution, shaken with water and a little bleaching-powder, is coloured reddish, the aqueous layer being brownish yellow. HNO_3 added to its solution in a mixture of H_2SO_4 and HOAc below 0° forms nitro-toluidine [134°] and some of its isomerides. Cyanogen passed into its alcoholic solution gives the compound $(C_7H_7.NH_2)_2C_2N_2$ [200°] which forms B'_2HCl, B'_22HNO_3, and $B'_22H_2SO_4$ (Clève a. Bladin, *Bl.* [2] 41, 129). Yields (4,2,1)- xylidine when its hydrochloride is heated with MeOH at 200°–300° (Limpach, *B.* 21, 616).

Salts.—B'HCl. S. 96·3 at 12°. S. (94 p.c. alcohol) 61·9 at 9°.—$B'_2H_2PtCl_6$.—$B'HNO_3$. S. 20·1 at 23·5°. S. (94 p.c. alcohol) 46 at 15°.—$B'HBiI_4$ (Kraut, *A.* 210, 323).—$B'_2H_2SO_4$. S. 6·25 at 14°. S. (94 p.c. alcohol) ·41 at 15°.—$B'_4H_4FeCy_6$ (Eisenberg, *A.* 205, 270).—$B'H_2C_2O_4$. Silky needles. S. 2·65 at 13°; S. (94 p.c. alcohol) 1·77 at 15°; S. (ether) ·13 at 15°.—$B'_32H_2C_2O_4$. White plates, S. 1·45 at 15°; S. (94 p.c. alcohol) ·96; S. (ether) ·128 at 15·5°.—$B'_2H_2C_2O_4$ aq. Very unstable.

Formyl derivative $C_7H_7.NH.CHO$. (278° at 724 mm.) (Niementowski, *B.* 20, 1892). Converted by long boiling into $C_7H_7N:CH.NHC_7H_7$ [123°].

Acetyl derivative $C_7H_7.NHAc$. [65°]. (303°). S. ·44 at 13°.

Di-chloro-acetyl derivative $C_7H_7.NH.CO.CHCl_2$. [106°]. Silky plates (Rügheimer a. Hoffmann, *B.* 18, 2988).

Benzoyl derivative $C_7H_7.NHBz$. [125°] (Just, *B.* 19, 983).

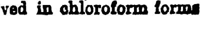
Phthalyl derivative $C_7H_7N:C_2O_2:C_6H_4$.

[153°]. Needles, v. sol. HOAc (Fröhlich, *B.* 17, 2679).

p-Toluidine $C_6H_4Me(NH_2)$[1:4]. [45°] (Städeler); [42·8°] (Mills). (198°) (M. a. H.); (206°) (Städeler, *J. pr.* 96, 65). S.G. 1·046. S. ·35 at 11·5°. H.C.p. 958,800. H.C.v. 957,860. H.F. 9,700 (Petit, *C. R.* 107, 266). S.V. 128,700. Formed by reduction of p-nitrotoluene (Muspratt a. Hofmann, *A.* 54, 1; 66, 144; Noad, *A.* 63, 305: Hugo Müller, *Z.* 1864, 161; Sell, *C. J.* 16, 186; *v.* also o-TOLUIDINE). Formed also by heating p-cresol with ammoniacal $ZnCl_2$ (Buch, *B.* 17, 2637; Merz a. Müller, *B.* 20, 545) and by treating methyl-aniline hydrochloride at 350° (Hofmann, *B.* 5, 720). On sulphonating a mixture of o- and p-toluidine the o-toluidine is first attacked and the p-toluidine can then be distilled off.

Properties.—Plates (from ligroïn or dilute alcohol). Its solution in $H_2SO_4H_2O$ is turned yellow by CrO_3 and blue by HNO_3, in the latter case changing to red and finally brown (Rosenstiehl, *Bl.* 10, 200). Bleaching-powder does not colour its solution in water or ether. PbO_2 and HOAc diluted with water or alcohol give a bright red colour (Lauth, *C. R.* 111, 975). When boiled with water, crystals of an efflorescent hydrate separate on cooling (Lewy, *B.* 19, 2728).

Reactions.—1. Oxidised by $KMnO_4$, alkaline K_3FeCy_6, or chromic acid to $C_{21}H_{21}N_3$ or $C_6H_2Me(NC_7H_7)_2(NH_2)$ [1:2:5:4], which may be readily reduced to $C_6H_2Me(NHC_7H_7)_2(NH_2)$ crystallising from alcohol in colourless plates [166°], readily re-oxidised to $C_{21}H_{21}N_3$ (Barsilowsky, *A.* 207, 102, 118; *J. R.* 1887, 132; Perkin, *C. J.* 35, 728; 37, 546; Klinger a. Pitschke, *B.* 17, 2439; Green, *C. J.* 63, 1395). The compound $C_{21}H_{21}N_3$ crystallises from xylene in dark-red plates [227°], dissolving in acids, forming maroon-red liquids, quickly decomposing with separation of p-toluidine. Conc. H_2SO_4 dissolves $C_{21}H_{21}N_3$, forming a greenish-blue liquid which on warming becomes wine-red with production of p-toluidine.—2. Oxidised by CrO_3 and HOAc to toluene-azo-toluene $C_7H_7.N_2.C_7H_7$. — 3. *Nitrous acid* forms $C_7H_7.N_2.NHC_7H_7$. When $NaNO_2$ is added to a solution of the hydrochlorides of o- and p-toluidine, the o-toluidine is first attacked, yielding $C_7H_7.N_2.C_7H_6NH_2$ and can thus be removed when mixed with p-toluidine (Wülfing, *D. P. J.* 263, 260).—4. Substituents usually enter positions 3 and 5 [Me = 1] but when p-toluidine or its acetyl derivative is dissolved in H_2SO_4 (20 pts.) and *nitrated* the compound $C_6H_3Me(NO_2)(NH_2)$ [1:2:4] is formed instead of the (1,3,4)- isomeride (Nölting a. Collin, *B.* 17, 263).—5. *Bromine* in conc. HClAq at 0° forms $C_6H_2Br_2Me(NH_2)$ [5:3:1:4]; but $C_6H_3BrMe(NH_2)$ [2:1:4] is formed in presence of conc. H_2SO_4 (Hafner, *B.* 22, 2538, 2902).—6. ICl forms $C_6H_2I_2Me(NH_2)$ [5:3:1:4] (Michael a. Norton, *B.* 11, 107).—7. *Chlorine* passed into p-toluidine dissolved in H_2SO_4 at 0° forms $C_6H_3MeCl(NH_2)$ [1:3:4] and larger quantities of its (1,2,4)- isomeride. In HClAq (40 p.c.) the chief product is $C_6H_2MeCl_2(NH_2)$ [1:3:5:4] (Hafner).—8. *Cyanogen* passed into an alcoholic solution forms $C_{16}H_{18}N_4$ or $(C_7H_8N)_2C_2N_2$ crystallising in pearly scales [222°-230°] and yielding the crystalline salts $B'_2 2HCl$, $B'_2 2HNO_3$, $B'_2H_2SO_4$ 6aq, and $B'_2H_2C_2O_4$ (Hofmann, *C. J.* 1, 170; *A.* 66, 144; Clève a. Bladin, *Bl.* [2] 41, 125). The mother-liquor contains $C_{24}H_{23}N_5$ [182°] which yields the salts B′HCl 3aq (a red powder) and $B'_2H_2PtCl_6$. The compound $C_{16}H_{18}N_4$ is also formed when p-toluidine is heated with oxalimido-ether at 100° (Vorländer, *B.* 24, 805).—9. *Cyanuric chloride* forms $C_3N_3(NHC_7H_7)_3$ [283°] (Klason, *J. pr.* [2] 33, 294).—10. *Chloro-acetic acid* (½ mol.) forms $C_7H_7NH.CH_2.CO_2H$, while chloro-acetamide forms $C_7H_7NH.CH_2.CO.NH_2$ (P. F Meyer, *B.* 8, 1158). An alcoholic solution of chloro-acetic acid and HCyS yields $C_{10}H_{12}N_2SO_2$ [176°-182°] (Nencki, *J. pr.* [2] 16, 1).—11. *Di-chloro-acetic acid* forms tolylamido-methyl-oxindole.—12. *Chloral* reacts, with formation of $CCl_3.CH(NHC_7H_7)_2$ [115°] (Wallach, *A.* 173, 278). When chloral is warmed with an alcoholic solution of p-toluidine there is also formed $CCl_3.CH(OEt).NHC_7H_7$ [77°].—13. *Aldehyde* forms crystalline $CH_3.CH(NHC_7H_7)_2$ [c. 60°].—14. *Furfuraldehyde* added to a hot alcoholic solution of p-toluidine and its hydrochloride forms brown amorphous $C_{19}H_{22}N_2O_2$, which yields B′HCl and $B'HNO_3$ both crystallising in purple needles (Stenhouse, *A.* 156, 203). 15. Nascent *formic aldehyde* produces a base $C_{17}H_{18}N_2$ [134°] which is converted by nitrous acid with evolution of CO_2 into $C_{16}H_{18}N_4O_2$ [260°-264°] (Tollens, *J. pr.* [2] 36, 225).—16. *Benzoic aldehyde* at 100° reacts, forming $C_6H_5.CH(NHC_7H_7)_2$ [100°] (326° i.V. at 723 mm.), which changes at 160° into an isomeride [120°-125°] and is converted by Br in CS_2 into $C_{14}H_{11}Br_2N$ [160°-165°] (Schiff, *Z.* 1865, 400; Mazzara, *J.* 1880, 566; Pictet, *B.* 19, 1063). In the action of p-toluidine and its hydrochloride on benzoic aldehyde at 120° there is produced $C_{21}H_{16}N_2$ [178°] and $C_6H_5.CH(C_6H_3Me.NH_2)_2$ [186°] (c. 430°), which yield a di-acetyl derivative [218°] and a di-benzoyl derivative [196°] (Ullmann, *J. pr.* [2] 36, 267).—17. *p-Methoxy-benzoic aldehyde* forms $C_6H_4(OMe).CH:(NC_7H_7)$ [92°] (Steinhart, *A.* 241, 332).—18. *p-Methoxy-benzophenone chloride* yields the compound $C_6H_4(OMe).CPh:NC_7H_7$ [96°] Hantzsch a. Kraft, *B.* 21, 3520).—19. An ethereal solution of $C_6H_5.CCl:NSO_2Ph$, obtained from benzene sulphonic anilide and PCl_5, forms the compound $C_6H_5.C(NHC_7H_7):N.SO_2Ph$, which separates in monoclinic crystals; $a:b:c$ = ·650:1:·533; β = 69° 16′, insol. water (Wallach a. Gossmann, *A.* 214, 216).—20. Alcohol, SO_2 and nitrous acid form the sulphazide $C_{14}H_{16}N_2SO_2$ [140°] (Limpricht, *B.* 20, 1241).—21. Heated with persulphocyanic acid it gives p-tolyl-thiobiuret (*B.* 17, 584).—22. On heating with *sulphur* it yields dehydrothiotoluidine and primuline; *v.* PRIMULINE.—23. *Diazobenzene chloride* yields $C_6H_5.N_2.NHC_7H_7$ [85°] which is identical with the product of the action of p-diazotoluene chloride on aniline (Nölting a. Binder, *B.* 20, 3005).—24. *Bromo-propiolic acid* forms di-tolyl-acetamidine $C_{16}H_{18}N_2$ [120°] (Mabery a. Krause, *B.* 22, 3307), which is also formed by the action of HOAc and PCl_3 on p-toluidine (Hofmann, *Pr.* 15, 55).—25. *Itaconic acid* in boiling aqueous solution forms



$C_7H_7.N{<}\genfrac{}{}{0pt}{}{CH_2.CH.CO_2H}{CO\,.\,CH_2}$

[185°] (Scharfenberg, *A.* 254, 150).—26. *Acetyl-citric anhydride* dissolved in chloroform forms

$C_3H_5O(CO_2H)(CO.NHC_7H_7)_2$ [189°] Klingemann, *B.* 22, 987).—27. *Malic acid* at 160° yields $C_2H_4O(CO.NHC_7H_7)_2$ [208°] (Bischoff, *B.* 23, 2045).—28. The hydrochloride heated with MeOH yields $C_6H_3Me_2(NH_2)$ [1:3:4] (Limpach, *B.* 21, 640).—29. *Ethylene oxide* forms oxy-ethyl-*p*-toluidine (Demole, *B.* 7, 635). —30. $SOCl_2$ forms thionyl-toluidine (*q. v.*).—31. $POCl_3$ forms $PO(NHC_7H_7)_3$ [192°], which yields $PO(NHC_7H_6Br)_3$ [180°] and $PO(NH.C_7H_6.NO_2)_3$ [247°] (Rudert, *B.* 26, 569). Another product of the action of $POCl_3$ is $POCl(NHC_7H_7)_2$, whence water forms $HO.PO(NHC_7H_7)_2$ [124°]. — 32. $PSCl_3$ forms $PS(NHC_7H_7)_3$ [135°].

Salts.—$B'HCl$. S. 22·9 at 11°; S. (89 p.c. (alcohol) 25 at 17°.—$B'HAuCl_4$.—$B'_2H_2PtCl_6$. Not decomposed by boiling water (De Coninck, *Bl.* [2] 45, 131).—B'_2PtCl_2 (Gordon, *B.* 3, 177; Cochin, *Bl.* [2] 31, 499).—$B'_2H_2PtCy_4$ (Scholz, *M.* 1, 905).—$B'PtCl_2Et_3PO_3$ (Saillard, *Bl.* [2] 18, 111). — $B'_2PtCl_2Me_3PO_3$. — $B'PtCl_22Et_3PO_3$ (Cochin, *J.* 1878, 315).—$B'_2ZnCl_2$3aq (Lachovitch, *M.* 9, 513).—$B'_2H_2ZnCl_4$ (Gräfinghoff, *Z.* 1865, 599).—B'_2HgCl_2. [125°]. Thick needles, sol. alcohol and ether (Klein, *B.* 11, 743).—B'_2NiCl_22EtOH. Green pp. (Lippmann a. Vortmann, *B.* 12, 81).—B'_2CoCl_2. Blue needles.—$B'_2H_2SnCl_6$. Monoclinic crystals (Hjortdahl, *J.* 1882, 535).—$B'_2H_2CuCl_4$ (Pomey, *C. R.* 104, [illegible]00).—B'_2MnCl_2 (Leeds, *J.* 1882, 503).—$B'_2UrO_2Cl_2$.—$B'HBr$. Plates (Städel, *B.* 16, 28).—B'_2HgBr_2. [121°]. Plates (Klein, *B.* 13, 835). — B'_2ZnBr_2. — B'_2CdBr_2.—$B'HI$.—B'_2HgI_2. [81°]. — $B'HBiI_4$ (Kraut, *A.* 210, 324). — $B'_6(H_2SO_4)_3HI_5$ (Jörgensen, *J. pr.* [2] 14, 386).—B'_2ZnI_2.—B'_2CdI_2.—$B'HNO_3$. S. 17·7 at 23·5°; S. (89 p.c. alcohol) 42 at 20°. B'_2AgNO_3. [101°] (Mixter, *Am.* 1, 239).—$B'_2Cd(NO_3)_2$.—$B'_2Hg_2(NO_3)_2$.—$B'_2H_2SO_4$. S. 5·06 at 22°; S. (84 p.c. alcohol) 1·3 at 23°.—$B'H_2SO_4$. Crystals, converted into $B'_2H_2SO_4$ by water (Tollens, *B.* 18, 3312).—$B'_4Ag_2SO_4$ 2aq (Mixter).—$B'H_3PO_4$. Thick needles, v. sl. sol. cold water (Lewy, *B.* 19, 1717).—$B'_2(NH_2Ph)H_4CoCy_6$ 1½aq (Weselsky, *J.* 1869, 314).—$B'_3H_3CoCy_6$ 2aq. B'_2HgCy_2.—$B'HCr(SCy)_42NH_3$. Plates (Christensen, *J. pr.* [2] 45, 362).—$B'_2Cu_2H_2(SO_3)_2$. Yellowish-white hexagonal plates.—$B'HgH_2(SO_4)_2$aq (Denigès, *C. R.* 112, 870).—**Oxalate** $B'H_2C_2O_4$ ½aq (Bornemann, *B.* 22, 2710). S. ·87 at 14°; S. (84 p.c. alcohol) ·48 at 22°. Insol. ether.—**Chloroacetates** $B'C_2H_3ClO_2$ [102°] (Baralis, *J.* 1884, 698).—$B'C_2H_2Cl_2O_2$. [141°]. (B.) [136°] (Duisberg, *B.* 18, 194).—$B'C_2HCl_3O_2$. [137°].—**Tri-chloro-lactate** $B'C_3H_3Cl_3O_3$. [135°].—**Mucate** $B'_2C_6H_{10}O_8$. Yellowish crystals, sol. hot water. —**Picrate** $B'C_6H_3N_3O_7$. [169°] (Smolka, *M.* 6, 923). S. ·54 at 18·5°; S. (95 p.c. alcohol) 4·29 at 18°.—**Phenate** [31·1°]. Got by heating *p*-toluidine with phenol (Dyson, *C. J.* 43, 468). Needles (from ligroïn).—**Compound with picramide** $B'C_6H_2(NO_2)_3NH_2$. Black needles with green reflex (Mertens, *B.* 11, 843).

Formyl derivative $C_7H_7.NH.CHO$. [45°] (Hübner a. Rudolph, *A.* 209, 371); [52°] (Tobias, *B.* 15, 2446); [53°] (Bamberger a. Wulz, *B.* 24, 2080). Formed by boiling *p*-toluidine with formic acid or, together with the **oxalyl derivative** $C_2O_2(NHC_7H_7)_2$ [263°], by heating *p*-toluidine oxalate. Prisms. Converted by heating with P_2S_5 into $C_7H_7.NH.CHS$ [174°] (Senier, *B.* 18, 2294; *C. J.* 47, 766). Yields $C_7H_7.NNa.CHO$ aq.

Acetyl derivative $C_7H_7.NHAc$. [147°] (Hübner a. Wallach, *A.* 154, 302; Kelbe, *C. J.* 44, 915). (307°) (Beilstein a. Kuhlberg, *A.* 156, 74). S. ·089 at 22°. Dimorphous, crystallising in monoclinic forms; $a:b:c = 1·216:1:·788$; $\beta = 106° 7'$, and also in trimetric crystals; $a:b:c = ·651:1:·329$ (Panebianco, *G.* 9, 362). Oxidised by $KMnO_4$ to acetyl-*p*-amido-benzoic acid (Hofmann, *B.* 9, 1299). Oxidised in like manner in the animal body (Jaffe a. Hilbert, *H.* 12, 295). PCl_5 forms a liquid product which solidifies when strongly cooled, the crystals doubtless being $C_7H_7NH.CCl_2.CH_3$. This readily splits up into HCl and $C_7H_7.N:CCl.CH_3$. This is a colourless solid which is converted by Aq into acetyl-*p*-toluidine; by toluidine into di-tolyl-acetamidine. The chloro-imide $C_7H_7.N:CCl.CH_3$ at 100° forms a base $C_{18}H_{19}N_2Cl$ [72°], which may be crystallised from alcohol. It is probably $C_7H_7N:CMe.CH_2.CCl:NC_7H_7$. It is decomposed by moist air or water with production of $MeC(NC_7H_7)NC_7H_7H$, HOAc and $MeCONHC_7H_7$, and by heat with production of an amorphous base $C_{18}H_{18}N_2$ (Wallach a. Fassbender, *A.* 214, 202). Nitrous acid converts acetyl-*p*-toluidine into $C_7H_7.NAc.NO$ [80°] (O. Fischer, *B.* 10, 959).

Chloro-acetyl derivative $C_7H_7NH.CO.CH_2Cl$. [162°]. Needles (Tommasi, *Bl.* [2] 19, 400; Meyer, *B.* 8, 1154).

Di-chloro-acetyl derivative $C_7H_7NH.CO.CHCl_2$. [153°] (Rügheimer a. Hoffmann, *B.* 18, 2980).

Tri-chloro-acetyl derivative $C_7H_7NH.CO.CCl_3$. [80°] (C.); [102°] (J.). S. (alcohol) 12·5 at 14°. Formed from *p*-toluidine and $(CCl_3)_2CO$ (Cloez, *A. Ch.* [6] 9, 145), and also from *p*-toluidine and $CCl_3.COCl$ (Judson, *B.* 3, 784).

Bromo-acetyl derivative $C_7H_7NH.CO.CH_2Br$. [164°]. Needles (Abenius, *J. pr.* [2] 40, 433) converted by alcoholic potash into an azine and $C_7H_7NH.CO.CH_2.OEt$ [32°] which is v. e. sol. alcohol.

Thio-acetyl derivative $C_7H_7.NH.CS.CH_3$. [131°]. Formed from the acetyl derivative and P_2S_5 (Jacobsen a. Ney, *B.* 22, 906). Got also by heating tolyl-acetamidine with CS_2 at 100°, or di-tolyl-acetamidine with H_2S (Bernthsen a. Trompetter, *B.* 11, 1759; Wallach a. Pannes, *B.* 13, 529). Converted by NaOEt and EtBr into oily $C_7H_7N:CMe.SEt$ (272°) (Wallach a. Wüsten, *B.* 16, 147).

a-Bromo-propionyl derivative $C_7H_7NH.CO.CHBr.CH_3$. [125°] (Tigerstedt, *B.* 25, 2921). Plates, v. sol. $CHCl_3$.

Benzoyl derivative C_7H_7NHBz. [158°]. (232°). Formed from *p*-toluidine and BzCl (Jaillard, *Z.* 1865, 440; Kelbe, *B.* 8, 875; Hübner, *A.* 208, 310; Wallach, *A.* 214, 217; Gudeman, *B.* 21, 2553; Müller, *B.* 22, 2404). Needles, v. sol. alcohol. Converted by PCl_5 into $C_7H_7N:CCl.C_6H_5$ [52°] (Just, *B.* 19, 980) crystallising from ligroïn in prisms.

p-Nitro-benzoyl derivative $C_6H_4(NO_2).CO.NHC_7H_7$. [197°]. Formed from *p*-toluidine and *p*-nitro-benzoyl chloride. Yellow needles (Gattermann, *B.* 25, 1082). Converted by PCl_5 into $C_6H_4(NO_2).CCl_2.NHC_7H_7$ [119°] crystallising in golden prisms.

Phenacyl derivative $C_7H_7NH.CH_2.CO.C_6H_5$. [127°]. Formed from ω-bromo-acetophenone and *p*-toluidine in alcohol (Bischler, *B.* 25, 2866). Yellow prisms, yielding B'HCl and an acetyl derivative [89°] crystallising in white needles (from alcohol).

Phthalyl derivative $C_7H_7N{:}C_2O_2{:}C_6H_4$. [205°] (Fröhlich, *B.* 17, 2679).

References.—BROMO-, DIBROMO-IODO-, BROMO-NITRO-, CHLORO-, TRI-CHLORO-NITRO-, IODO-, NITRO-, and NITROSO- TOLUIDINES.

TOLUIDINE SULPHONIC ACID *v.* AMIDO-TOLUENE SULPHONIC ACID and also NITRO- and IODO- TOLUIDINE SULPHONIC ACID.

TOLUIDINE THIOSULPHONIC ACID *v.* AMIDO-TOLUENE THIOSULPHONIC ACID.

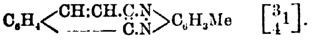
TOLUIDO- *v.* TOLYL-AMIDO-.

TOLUIDYL-CYANURAMIDE *v.* CYANIC ACIDS.

TOLUIDYL-MELAMINE *v.* CYANIC ACIDS.

TOLUISATIN *v.* DI-TOLYL-OXINDOLE.

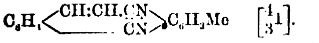
TOLU-(αβ)-NAPHTHAZINE $C_{17}H_{12}N_2$ *i.e.*



$$C_6H_4\left<\begin{array}{l}CH{:}CH.C.N\\ \text{------}\ \ \ C.N\end{array}\right>C_6H_3Me\quad\left[\begin{array}{cc}3&\\&1\\4&\end{array}\right]$$

[180°]. Formed by oxidation of a mixture of tolylene-*o*-diamine (1 mol.) and (β)-naphthol (1 mol.) with K_3FeCy_6. Formed also, together with the isomeride [169°], by the action of (β)-naphthoquinone on tolylene-*o*-diamine (Witt, *B.* 20, 577). Dissolves in conc. H_2SO_4 with violet-red colour. Forms with its isomeride a molecular compound [142°].

Tolu-(αβ)-naphthazine $C_{17}H_{12}N_2$ *i.e.*



$$C_6H_4\left<\begin{array}{l}CH{:}CH.C.N\\ \text{------}\ \ \ C.N\end{array}\right>C_6H_3Me\quad\left[\begin{array}{cc}4&\\&1\\3&\end{array}\right]$$

[169°]. Formed as above, and also, together with amido-benzene *p*-sulphonic acid, by boiling sulpho-benzene-azo-(β)-naphthyl-*p*-tolyl-amine with dilute H_2SO_4, and by boiling 'wool black' $C_6H_4(SO_3H).N_2.C_6H_3(SO_3H).N_2.C_{10}H_5.NHC_7H_7$ with dilute H_2SO_4 (Witt, *B.* 20, 577). Yellow crystals, v. sl. sol. alcohol. Conc. H_2SO_4 forms a brownish-red solution.

TOLUNITRANILIC ACID *v.* NITRO-DI-OXY-TOLUQUINONE.

TOLUOÏN *v.* DI-METHYL-BENZOÏN.

TOLUOL *v.* TOLUENE.

TOLUPHOSPHINIC ACID *v.* PHOSPHOTOLUIC ACID.

TOLUQUINOL *v.* HYDROTOLUQUINONE.

TOLUQUINOLINE *v.* METHYL-QUINOLINE.

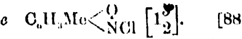
TOLUQUINONE $C_7H_6O_2$ *i.e.* $C_6H_3MeO_2$ [2:4:1]. [69°].

Formation.—1. By oxidation of tolylene-*p*-diamine or of *o*-toluidine (Nietzki, *B.* 10, 832, 1934; *A.* 215, 158; Ladenburg, *B.* 10, 1128).—2. By boiling crude creosol with MnO_2 and dilute H_2SO_4 (Carstanjen, *J. pr.* [2] 23, 425). Separated from accompanying xyloquinone by reduction with SO_2, crystallising the hydrotoluquinone from benzene, and re-oxidising by fuming HNO_3.—3. By oxidation of *m*-xylidine (Nölting a. Baumann, *B.* 18, 1151).

Preparation.—20 g. of *o*-toluidine are dissolved in 600 c.c. of water containing 160 g. of H_2SO_4; 20 g. of finely powdered potassium bichromate are added by degrees, with continual agitation, keeping the temperature at 10°–15°. After standing over night, 33 g. more $K_2Cr_2O_7$ are added; the quinone is then extracted with ether, dried over $CaCl_2$, and the ether removed by distillation. The yield is about 86 p.c. of the theoretical quantity (Schniter, *B.* 20, 2283).

Properties.—Golden-yellow plates smelling like quinone. Very volatile. M. sol. hot water, v. sol. alcohol and ether. Its aqueous solution is turned brown by alkalis. SO_2 reduces it to hydrotoluquinone. Dilute (50 p.c.) H_2SO_4 changes it to isotoluquinone $(C_7H_6O_2)_x$, a powder not melted at 300° (Spica, *G.* 12, 225). An aqueous solution of toluquinone mixed with one of hydrotoluquinone deposits steel-blue needles of the quinhydrone [52°], v. e. sol. water. *o*-Nitroaniline forms [2:4:4:6] $C_6H_3MeO_2.NH.C_6H_4NO_2$ crystallising from alcohol in red crystals decomposing at 200° (Leicester, *B.* 23, 2796). Nitro-*p*-toluidine $C_6H_3Me(NO_2).NH_2$ [1:3:4] forms a homologous body.

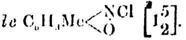
Chlorimide



$$C_6H_3Me\left<\begin{array}{l}O\\ NCl\end{array}\right.\left[\begin{array}{cc}&3\\1&\\&2\end{array}\right]$$

[88°] (Hirsch, *B.* 18, 1514). Formed by the action of a solution of bleaching-powder on the hydrochloride of amido-*o*-cresol. Yellow prisms (from alcohol) volatile with steam. Decomposes violently at 100°-115°. By digestion with $NaHSO_3$ for several hours it is converted into amido-cresol sulphonic acid.

Chlorimide



$$C_6H_3Me\left<\begin{array}{l}NCl\\ O\end{array}\right.\left[\begin{array}{cc}&5\\1&\\&2\end{array}\right]$$

[75°]. Made in like manner from amido-*m*-cresol (Staedel, *A.* 259, 218). Yellow prisms (from alcohol), volatile with steam.

Oxim $C_6H_3MeO(NOH)$ [2:1:4]. *Nitroso-o-cresol.* [135°]. Formed by the action of nitrous acid on *o*-cresol (Nölting a. Kohn, *B.* 17, 370). Formed also by the action of hydroxylamine hydrochloride on toluquinone (Goldschmidt a. Schmid, *B.* 17, 2063). Needles (from water), decomposed by fusion. V. sol. alcohol and ether. Yields nitro-cresol [95°] on oxidation. NaA'3aq. — KA': brown needles, v. sol. water.

Oxim $C_6H_3MeO(NOH)$ [2:4:1]. *Nitroso-m-cresol.* Formed by boiling nitroso-di-methyl-*m*-toluidine with dilute (10 p.c.) NaOHAq (Wurster a. Riedel, *B.* 12, 1799). Formed also by the action of $NO_2.SO_4H$ on *m*-cresol and water at 0° (Bertoni, *G.* 12, 303). Small needles (from water). Decomposes at 145°-150°. Sl. sol. hot water. Gives Liebermann's reaction. Forms an acetyl derivative $C_6H_3MeO(NOAc)$ [92°] crystallising in large prisms.

Di-oxim $C_6H_3Me(NOH)_2$ [2:1:4]. Formed by the action of hydroxylamine on either mono-oxim (Nietzki a. Guitermann, *B.* 21, 430) or by boiling nitroso-*o*- or *m*-toluidine with hydroxylamine hydrochloride (Mehne, *B.* 21, 729). Yellow needles, exploding at 220°-234°, v. sl. sol. benzene, sol. hot water, alcohol, and ether. Reduced by tin and HClAq to tolylene-*p*-diamine. Alkaline K_3FeCy_6 forms di-nitroso-toluene. Ac_2O forms $C_6H_3Me(NOAc)_2$ [120°], crystallising from alcohol in colourless needles.

Ditolylimide $C_6H_3Me(NC_7H_7)_2$. [146°]. Formed by oxidation of tolylene-di-tolyl-diamine in alkaline solution (Green, *C. J.* 63, 1409). Red prisms, v. sol. alcohol, v. e. sol. benzene.

References.—DI-BROMO-, CHLORO-, IODO-, and OXY- TOLUQUINONE.

TOLUQUINOXALINE *v.* METHYL-QUINOXALINE.

***o*-TOLURIC ACID** $C_{10}H_{11}NO_3$ *i.e.* $C_7H_7.CO.NH.CH_2.CO_2H$. *Toluyl-glycocoll*

[162·5°]. Formed from toluyl chloride, amido-acetic acid, and NaOH (Gleditsch a. Möller, *A.* 250, 376). Found in the urine of dogs that have taken *o*-toluic acid. Thick plates, sol. water.

m-**Toluric acid.** [139°]. Formed as above, and also when *m*-xylene or *m*-toluic acid is administered to a dog (G. a. M.; *cf.* Schultzen a. Naunyn, *Z.* 1868, 29). M. sol. water.—$ZnA'_2$4aq.—$CuA'_2$6aq.

p-**Toluric acid.** [161°]. Formed from *p*-toluyl chloride and glycocoll (G. a. M.) and also by passage of *p*-xylene or *p*-toluic acid through the animal body (Kraut, *A.* 98, 360). Plates (from water), sl. sol. cold water, v. sol. alcohol.—$CaA'_2$3aq.—$BaA'_2$5aq.—AgA'.

TOLUYL. The radicle $CH_3.C_6H_4.CO$. The same name has been given to the radicle $CH_3.C_6H_4.CH_2$, which is isomeric with xylyl, and has also been called tolyl, but may be more conveniently named methyl-benzyl. Tolyl is $CH_3.C_6H_4$.

o-**TOLUYL-ACETIC ACID**

Ethyl ether $C_6H_4Me.CO.CH_2.CO_2Et$. Oil, got by boiling the nitrile with alcohol and HCl. Gives a violet colour with $FeCl_3$.

Nitrile $C_7H_7.CO.CH_2.CN$. [74·4°]. Formed by boiling *o*-toluyl-cyano-acetic ether with water (Haller, *C. R.* 108, 1117). Prisms, sol. alcohol and alkalis. Diazobenzene chloride and NaOH form $C_7H_7.CO.CHCy.N_2.C_6H_5$ [125°]. Cold alcoholic HCl forms the hydrochloride of $C_7H_7.CO.CH_2.C(NH).OEt$ [116°].

TOLUYL-ACRYLIC ACID $C_{11}H_{10}O_3$ *i.e.* $C_6H_4(CH_3).CO.CH:CH.CO_2H$. [138°]. Formed by the action of $AlCl_3$ on a mixture of maleic anhydride and toluene (Pechmann, *B.* 15, 888).

TOLUYL ALCOHOL *v.* Tolyl-carbinol.

TOLUYLAMIDE *v. Amide* of Toluic acid.

p-**TOLUYL-*o*-BENZOIC ACID** $C_{15}H_{12}O_3$ *i.e.* [1:4] $C_6H_4Me.CO.C_6H_4.CO_2H$ [1:2]. *Phenyl tolyl ketone carboxylic acid.* Mol. w. 240. [146°]. Formed by the action of phthalic anhydride on toluene in presence of $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 14, 447; *C. R.* 92, 833). Prisms (containing aq) (from alcohol-toluene), v. sl. sol. hot water. Its dilute aqueous solution tastes sweet. Potash-fusion yields benzoic and *p*-toluic acids. Warm conc. H_2SO_4 forms (*β*)-methyl-anthraquinone. — BaA'_2 4aq. — CdA'_2 ½aq. — CuA'_2 4aq.

Methyl ether MeA'. [53°].

Ethyl ether EtA'. [69°].

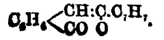
Toluyl-benzoic acid $C_7H_7.CO.C_6H_4.CO_2H$. [222°]. Formed by oxidation of di-tolyl-methane and of *u*-di-tolyl-ethane (Weiler, *B.* 7, 1184; Ador a. Crafts, *C. R.* 85, 1163; O. Fischer, *B.* 7, 1195; Anschütz, *A.* 235, 316). Slender needles (from MeOH), sl. sol. hot water.—KA': tufts of long needles.—AgA'.

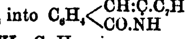
Reference.—Di-chloro-tolyl-benzoic acid.

TOLUYLENE- *v.* Tolylene-.

p-**TOLUYL-PROPIONIC ACID** $C_{11}H_{12}O_3$ *i.e.* $C_7H_7.CO.CH_2.CH_2.CO_2H$. [127°] (C.); [120°] (B.). Formed by the action of succinyl chloride or succinic anhydride on toluene and $AlCl_3$ (Claus, *B.* 20, 1378; Burcker, *Bl.* [2] 49, 448). Plates or needles (from water), v. sol. ether.—BaA'_2 4aq: sol. hot water.—AgA': small needles, insol. Aq.

ω-**TOLUYL-TOLUIC ACID.** *Lactone*


$C_6H_4<\begin{matrix}CH:C.C_7H_7\\CO\ \ O\end{matrix}$. [93°]. Got from nitro-tolyl-methylene-phthalide, HIAq, and P (Heilmann, *B.* 23, 3166). Thin prisms. Converted by alcoholic NH_3 into


$C_6H_4<\begin{matrix}CH:C.C_7H_7\\CO.NH\end{matrix}$ [196°].

oo-**DITOLYL** $C_{14}H_{14}$ *i.e.* [1:2] $C_6H_4Me.C_6H_4Me$ [1:2]. Mol. w. 182. (272°). S.G. $\frac{10.5}{}$ ·9945. Formed from *o*-bromo-toluene and Na (Fittig, *A.* 139, 178). Liquid.

mm-**ditolyl** [1:3] $C_6H_4Me.C_6H_4Me$ [1:3]. (280°) (Schultz, *B.* 17, 468); (288°) (Perrier, *C. R.* 114, 484); (289°) (Stolle, *B.* 21, 1096). S.G. $\frac{16}{4}$ ·9993. Formed by diazotising di-amido-*o*-ditolyl and boiling the product with alcohol. Formed also by the action of Na on *m*-bromo-toluene (P.), and by reduction of di-oxy-*m*-ditolyl and di-chloro-*m*-ditolyl. Oil; yields diphenyl di-*m*-carboxylic acid and isophthalic acid on oxidation.

pp-**ditolyl** [1:4] $C_6H_4Me.C_6H_4Me$ [1:4]. [121°]. S.V. 198·0. Formed by adding Na to a solution of *p*-bromo-toluene in toluene (Zincke, *B.* 4, 396; Louguinine, *B.* 4, 514). Monoclinic prisms (from ether). Yields on oxidation *p*-tolyl-benzoic acid [244°] and diphenyl di-*p*-carboxylic acid (Carnelley, *C. J.* 32, 653). $SbCl_5$ at 360° forms CCl_4 and per-chloro-diphenyl.

om-**Ditolyl** [1:2] $C_6H_4Me.C_6H_4Me$ [1:3]. (270°). Formed from [2:4:1] $C_6H_3Me(NH_2).C_6H_3Me(NH_2)$ [1:3:4] by elimination of amidogen by the diazo-reaction (Schultz, *B.* 17, 471). Yields isophthalic acid on oxidation by CrO_3.

op-**Ditolyl** [1:2] $C_6H_4Me.C_6H_4Me$ [1:4]. (272°-280°). Formed from crude bromo-toluene and Na. It is also one of the products of the passage of a mixture of benzene and toluene through a red-hot tube (Carnelley, *C. J.* 37, 707; 47, 587). Oxidised by CrO_3 and HOAc to *o*-tolyl-*p*-benzoic acid [180°] and terephthalic acid.

Ditolyls have also been obtained by Barbier (*C. R.* 78, 1769) and Varet a. Vienne, *Bl.* [2] **47,** 919).

References.—Di-amido-, Di-bromo-, Di-iodo-, Nitro-amido-, Oxy-amido-, and Oxy-ditolyl.

p-**TOLYL-ACETAMIDINE** $C_9H_{12}N_2$ *i.e.* $CH_3.C(NH).NHC_6H_4Me$ [1:4]. [96°]. Formed from *p*-toluidine hydrochloride and acetonitrile (Bernthsen a. Trompetter, *B.* 11, 1757). Prisms. Alkaline in reaction.—$B''_2H_2PtCl_6$.—$B''H_2C_2O_4$. Prisms, v. sol. water and alcohol.

Di-*o*-tolyl-acetamidine

[1:2] $C_6H_4Me.NH.CMe:NC_6H_4Me$ [1:2]. [136°] (W.); [140°] (L.). Formed by the action of PCl_3 on *o*-toluidine and HOAc (Ladenburg, *B.* 10, 1262), and also by the action of *o*-toluidine on $CMe(SEt):NC_7H_7$ or on $CMeCl:NC_7H_7$ (Wallach a. Wüsten, *B.* 16, 148; *A.* 214, 208). Needles.

Di-*p*-tolyl-acetamidine

[1:4] $C_6H_4Me.NH.CMe:N.C_6H_4Me$ [1:4]. *Acet-tolyl-imid-tolyl-amide.* [120°]. Formed from *p*-toluidine and $CMeCl:NC_7H_7$, which is the product of the action of PCl_5 on acetyl-*p*-toluidine (Wallach a. Fassbender, *A.* 214, 203; *B.* 9, 1214; 16, 148). Formed also from *p*-toluidine and bromopropiolic acid (Mabery a. Krause, *B.* 22, 3307). Prisms (from benzene). Formed also from *p*-toluidine, HOAc, and PCl_3.—$B'_2H_2PtCl_6$.—B'HCl. [200°].

op-**Di-tolyl-acetamidine**

$C_6H_4Me.NH.CMe:NC_6H_4Me$. [142°]. Formed from *o*-toluidine and the product of the action of PCl_5 on acetyl-*p*-toluidine, and also from

p-toluidine and the product of the action of PCl_5 on acetyl-o-toluidine (Wallach a. Pannes, *A.* 214, 209). Formed also from p-toluidine and [1:2] $C_6H_4MeN{:}CMe.SEt$, and from o-toluidine and [1:4] $C_6H_4MeN{:}CMeSEt$; the compounds obtained, [143°] and [140°] respectively, being perhaps isomeric and not identical (Wallach, *B.* 16, 148).

o-**TOLYL-ACETIC ACID** $C_9H_{10}O_2$ *i.e.* [1:2] $C_6H_4Me.CH_2.CO_2H$. [89°]. Formed by saponification of its nitrile (Radziszewski a. Wispeck, *B.* 15, 1747; 18, 1281). Needles, sl. sol. cold water. Yields phthalic acid on oxidation.—CaA'_2 4aq.—AgA'. Plates, sol. hot water

Amide [161°]. Plates, sl. sol. ether.

Nitrile C_9H_9N. (244°). S.G. ^{22} 1·0156. Formed from ω-bromo-o-xylene and KCy. Oil.

m-**Tolyl-acetic acid** [1:3] $C_6H_4Me.CH_2.CO_2H$. [61°]. Formed by saponifying its nitrile, which is obtained from ω-bromo-m-xylene (R. a. W.). Needles, sol. hot water.—CaA'_2 3aq.—AgA'.

Amide [141°]. Sl. sol. cold water.

Nitrile (241°). S.G. ^{22} 1·0022. Oil.

Methyl ether MeA'. (228°). S.G. $^{17.5}$ 1·041. Liquid (Senkowski, *M.* 9, 854).

Ethyl ether EtA'. (238°). S.G. $^{17.5}$ 1·018.

p-**Tolyl-acetic acid** [1:4] $C_6H_4Me.CH_2.CO_2H$. [94°]. Formed in like manner from ω-bromo-p-xylene (R. a. W.; Strassmann, *B.* 22, 1230). Got also by reducing p-tolyl-glyoxylic acid with HI (Claus a. Kroseberg, *B.* 20, 2051). Needles, sl. sol. cold water. Phthalic anhydride and NaOAc yield $C_6H_4\left\langle\begin{matrix}CO\text{———————}\\C(CH.C_6H_4Me)\end{matrix}\right\rangle O$ [151°], whence HNO_2 at 0° forms the compound $C_6H_4\left\langle\begin{matrix}CO\text{———————}\\C(NO_2).CH(NO_2)C_7H_7\end{matrix}\right\rangle O$ [140°], which is converted by treatment with boiling alcohol into $C_6H_4\left\langle\begin{matrix}CO\text{—————}\\C(CNO_2)C_7H_7\end{matrix}\right\rangle O$ [207°], and is reduced by HI and P to $C_6H_4\left\langle\begin{matrix}CH{:}C.C_7H_7\\CO\ .O\end{matrix}\right.$ [116°] (Ruhemann, *B.* 24, 3965).—NaA': needles, sol. water.—CaA'_2 3aq.—AgA': needles, sol. hot water.

Ethyl ether EtA'. (240°).

Amide $C_9H_{11}NO$. [185°]. Plates. Formed from the acid, and also by the action of yellow ammonium sulphide on p-tolyl methyl ketone (Willgerodt, *B.* 21, 534).

Nitrile $C_8H_9.CN$. [18°]. (243°). S.G. ^{22} ·9922.

Reference.—*Nitro-* and *Oxy-*TOLYL-ACETIC ACID.

m-**TOLYL-ACETYLENE** [1:3] $C_6H_4Me.C{:}CH$. *Methyl-styrene.* (164°). Formed by distilling barium m-tolyl-propiolate with lime (Müller, *B.* 20, 1215). Formed also by saturating a solution of m-tolyl-acrylic acid with HBr at 0° and treating the product with NaOHAq. Oil, becoming solid on standing. Gives an explosive red pp. with ammoniacal Cu_2Cl_2. Br forms $C_7H_7.CHBr.CH_2Br$ [45°].

Di-tolyl-acetylene $C_7H_7.C{:}C.C_7H_7$. [136°]. Formed by heating $C_7H_7.CHBr.CHBr.C_7H_7$ with alcoholic potash at 140° (Goldschmiedt a. Hepp, *B.* 6, 1505). Needles (from alcohol).

DI-TOLYL-ACIPIPERAZINE *v.* OXY-DI-TOLYL-PYRAZINE.

Di-tolyl-di-aci-piperazine *v.* DI-OXY-DI-TOLYL-PYRAZINE.

m-**TOLYL-ACRYLIC ACID** $C_{10}H_{10}O_2$ *i.e.* [1:3] $C_6H_4Me.CH{:}CH.CO_2H$. *Methyl-cinnamic acid.* [111°]. Formed by heating m-toluic aldehyde with Ac_2O and NaOAc (Bornemann, *B.* 17, 1474; 20, 1382; Von Miller, *B.* 20, 1213; 23, 1899). Silky needles, v. sol. alcohol, sl. sol. ligroïn. $FeCl_3$ gives a bright-yellow pp. in neutral solutions. Reduced by sodium-amalgam to m-tolyl-propionic acid [43°]. $KMnO_4$ oxidises it to m-toluic acid. Br forms $C_7H_7.C_2H_2Br_2.CO_2H$ [167°].—BaA'_2—AgA'. Crystalline powder.

p-**Tolyl-acrylic acid** [1:4] $C_6H_4Me.CH{:}CH.CO_2H$. [197°]. Formed from p-toluic aldehyde, NaOAc, and Ac_2O (Von Miller, *B.* 23, 1897; *cf.* Kröber, *B.* 23, 1033). Needles (from benzene), sl. sol. hot water. Reduced by HI and P to p-tolyl-propionic acid. Br forms $C_6H_4Me.CHBr.CHBr.CO_2H$.

TOLYL ALCOHOL *v.* TOLYL-CARBINOL.

p-**TOLYL-ALLYL-HYDRAZINE** $C_{10}H_{14}N_2$ *i.e.* $C_7H_7N(C_3H_5).NH_2$. (160°–170° at 90 mm.). Got from tolyl-hydrazine and allyl bromide (Michaelis, *B.* 26, 2178). Oil. Yields $B'HCl$. [129°]. Benzoic aldehyde forms the compound $C_7H_7.N(C_3H_5).N{:}CHPh$ [61°], while cinnamic aldehyde forms the corresponding hydrazide [118°]. Ferric chloride gives the tetrazone $(C_7H_7(C_3H_5)N)_2N_2$ [104°].

o-**TOLYL-ALLYL-THIO-SEMI-CARBAZIDE** $C_7H_7NH.NH.CS.NHC_3H_5$. [105°]. Formed by warming o-tolyl-hydrazine with allyl thiocarbimide (Avenarius, *B.* 24, 268). Needles, insol. water, v. sol. alcohol and CS_2.

p-**Tolyl-allyl-thio-semi-carbazide** [128°]. Formed in like manner (A.). Needles.

o-**TOLYL-ALLYL-THIO-UREA** $C_{11}H_{14}N_2S$ *i.e.* $C_7H_7NH.CS.NHC_3H_5$. *Tolyl-thiosinamine.* [98°]. Formed from o-toluidine and oil of mustard (Jaillard, *Z.* 1865, 441; Maly, *Z.* [2] 5, 258; Weith, *B.* 8, 1528; Prager, *B.* 22, 2998). Pearly crystals, m. sol. ether, v. sol. HOAc. According to Dixon (*C. J.* 55, 622), it melts at 76°. Converted by heating with HClAq into tolyl-propylene-ψ-thio-urea [126°]. Cyanogen passed into its alcoholic solution forms $C_{13}H_{14}N_4S$, which on warming with dilute H_2SO_4 and alcohol gives a pp. of oxalyl-tolyl-allyl-thio-urea $CS\left\langle\begin{matrix}NC_7H_7\\NC_3H_5\end{matrix}\right\rangle C_2O_2$ [157°].

Reference.—OXY-TOLYL-ALLYL-THIO-UREA.

o-**TOLYL-AMIDO-ACETIC ACID** $C_9H_{11}NO_2$ *i.e.* $C_6H_4Me\ NH.CH_2.CO_2H$. *Tolyl-glycocoll.* [150°]. Prepared by the action of chloro-acetic acid and aqueous NaOAc on o-toluidine (Staats, *B.* 13, 137; Cosack, *B.* 13, 1091; Ehrlich, *B.* 16, 204; Bischoff a. Nastvogel, *B.* 22, 1787).—CuA'_2 2aq. Small needles.—CaA'_2 3aq: needles, m. sol. water (Mauthner, *M.* 11, 377).

Ethyl ether EtA'. (281°). S.G. $\frac{20}{20}$ 1·058. Oil (Bischoff, *B.* 25, 2270).

Acetyl derivative $C_7N_7NAc.CH_2.CO_2H$. [212°]. Tables (from dilute alcohol).

Chloro-acetyl derivative $C_7H_7N(CO.CH_2Cl).CH_2.CO_2H$. [117°]. Formed from the acid and chloro-acetyl chloride in ether (Widman, *J. pr.* [2] 38, 304). Rectangular plates, v. sol. hot alcohol, sl. sol. water.

Bromo-acetyl derivative $C_7H_7N(CO.CH_2Br).CH_2.CO_2H$. [124°]. Rectangular plates.

Glycolyl derivative $C_7H_7N(CO.CH_2.OH).CH_2.CO_2H$. [144°]. Formed by boiling the chloro-acetyl derivative with conc. Na_2CO_3Aq (Abenius, *J. pr.* [2] 40, 503). V. e. sol. water. Yields $KA'aq$, $BaA'_2 7aq$, and AgA', and is converted by heating at 160° into $C_7H_7N{<}\begin{matrix}CO.CH_2\\CH_2.CO\end{matrix}{>}O$ [109°], whence alcoholic NH_3 produces $C_7H_7N(CO.CH_2.OH).CH_2.CO.NH_2$ [152°], crystallising in plates (from alcohol).

o-Toluide $C_7H_7.NH.CH_2.CO.NHC_7H_7$. [92°]. Formed by boiling chloro-acetic ether with *o*-toluidine (Ehrlich, *B.* 16, 205). Needles, insol. water and HClAq.

***m*-Tolyl-amido-acetic acid** [1:3]$C_6H_4Me.NH.CH_2.CO_2H$. Formed from chloro-acetic acid and *m*-toluidine in ether (Ehrlich, *B.* 15, 2011). Solid mass.—$CuA'_2 2aq$.

Ethyl ether EtA′. [68°]. Formed from chloro-acetic ether and *m*-toluidine. Six-sided plates, v. sol. alcohol and ether, sl. sol. Aq.

***p*-Tolyl-amido-acetic acid** [1:4]$C_6H_4Me.NH.CH_2.CO_2H$. [119°]. Formed, together with a compound [168°], from *p*-toluidine chloro-acetic acid and NaOAc (dissolved in a little water) at 100° (P. J. Meyer, *B.* 8, 1158; 14, 1323; Staats, *B.* 13, 137; Schwebel, *B.* 10, 2047; Bischoff, *B.* 23, 1997; 25, 2281). Got also by saponifying its ether. Needles (from water). When fused with potash it yields a product which, when dissolved in water, is oxidised by air to an indigo- derivative (Heumann, *B.* 24, 1346). When fused with *p*-chloro-acet-toluide it yields methyl-indigo (Eckenroth, *B.* 24, 693). The compound [168°], formerly supposed to be *p*-tolyl-amido-acetic acid, ought, according to Bischoff a. Hausdörfer (*B.* 25, 2281) to be represented as $CO_2H.CH_2.N(C_7H_7).CH_2.CO.ONH_3C_7H_7$.

Ethyl ether EtA′. [49°]. Formed from chloro-acetic ether and *p*-toluidine. Monoclinic plates, v. sl. sol. hot water.

Amide $C_9H_{12}N_2O$. [163°]. Formed by heating *p*-toluidine with chloro-acetamide. Plates, v. sl. sol. cold water.

Anilide $C_7H_7NH.CH_2.CO.NHPh$. [83°]. Formed by heating chloro-acetic acid with aniline. Needles (from hot water).

p-Toluide $C_7H_7.NH.CH_2.CO.NC_7H_7$. [136°]. Formed in like manner, and also by heating toluidine with the compound of glyoxal with $NaHSO_3$ (Hinsberg, *B.* 21, 112). Plates, v. sl. sol. hot water. Yields a chloro-acetyl derivative [158°].

Nitrile $C_7H_7NH.CH_2.CN$. [126°]. A product of the action of heat on the amide.

Acetyl derivative $C_7H_7.NAc.CH_2.CO_2H$. [175°]. Formed from chloro-acetic ether and $C_7H_7.NAcNa$, the product being saponified with potash (Paal a. Otten, *B.* 23, 2596). Plates (from water).—$NaA'3aq$: plates, v. sol. water.

Imide $(C_7H_7.NH.CH_2.CO)_2NH$. [210°]. Got by heating the acid at 200° and adding NH_3Aq to the product. Needles, sl. sol. water and NH_3Aq (Bischoff).

Di-*o*-tolyl-di-amido-acetic acid $(C_7H_7NH)_2CH.CO_2H$. [240°]. Formed by heating di-chloro-acetic acid with *o*-toluidine (P. Meyer, *B.* 16, 925). Needles, insol. water, sl. sol. alcohol, v. sol. aqueous acids and alkalis.

Reference.—NITRO-TOLYL-AMIDO-ACETIC ACID.

***p*-TOLYL-AMIDO-ACETOPHENONE** [1:4]$C_6H_4Me.NH.CH_2.CO.C_6H_5$. *Phenacyl-p-toluidine.* [134°]. Formed from *p*-toluidine and bromo-acetophenone in alcohol (Lellmann a. Donner, *B.* 23, 167). Tables, v. sol. benzene, m. sol. alcohol. Yields, on nitration, [1:3:4]$C_6H_3Me(NO_2).NH.CH_2Bz$ [165°] and a di-nitro- derivative [156°]. Forms $B'HNO_3$ and $B'HCl$.

***p*-TOLYL-AMIDO-ACRYLIC ETHER** [1:4]$C_6H_4Me.NH.CH:CH.CO_2Et$. [116°]. Formed from *p*-toluidine and formyl-acetic ether (Von Pechmann, *B.* 25, 1053). Yellow plates, insol. water and ligroïn. Alcoholic potash yields plates [144°]. Ac_2O forms acetyl-toluidine.

TRI-*p*-TOLYL-TRI-AMIDO-BENZENE $C_{27}H_{27}N_3$ *i.e.* $C_6H_3(NHC_7H_7)_3$. [187°]. Formed by heating phloroglucin with *p*-toluidine at 210° (Minunni, *B.* 21, 1984). Needles, v. sl. sol. cold alcohol. Conc. H_2SO_4 forms a bluish-green solution, turning black on heating.—$B'''HCl$: amorphous; decomposed by water.—$B'''2HCl$: small needles.—$B'''_2H_2PtCl_6$.

Tri-acetyl derivative [193°]. Plates.

Tri-benzoyl derivative [282°]. Minute prisms.

***p*-TOLYL-AMIDO-BENZOYL-(α)-NAPHTHOQUINONE** $C_6H_5.CO.C_6H_3{<}\begin{matrix}CO.C.NHC_6H_4Me.\\CO.CH\end{matrix}$ [197°]. Formed by boiling *p*-toluidine with benzoyl-(α)-naphthoquinone in alcoholic solution for 15 minutes (Kegel, *A.* 247, 185). Red needles (from HOAc), v. sl. sol. alcohol.

***p*-TOLYL-*o*-AMIDO-BENZYL-AMINE** [4:1] $C_6H_4Me.NH.CH_2.C_6H_4.NH_2$ [1:2]. [80·5°]. Got by reducing *p*-tolyl-*o*-nitro-benzyl-amine (Söderbaum a. Widman, *B.* 23, 2187). Thin leaflets (from alcohol). Ac_2O yields a di-acetyl derivative [186°]. The mono-acetyl derivative $C_7H_7NAc.CH_2.C_6H_4NH_2$ [99°] may be got by reducing $C_7H_7NAc.CH_2.C_6H_4NO_2$.

***o*-TOLYL-α-AMIDO-*n*-BUTYRIC ACID** $C_7H_7.NH.CHEt.CO_2H$. [84°]. Long prisms. Forms an acetyl derivative [116°] and yields propyl-*o*-toluidine on distillation.

Ethyl ether EtA′. (278°). S.G. $\frac{20}{20}$ 1·019. Got by heating *o*-toluidine with α-bromo-butyric ether at 100° (Bischoff a. Mintz, *B.* 25, 2314).

***o*-Tolyl-α-amido-isobutyric acid** $C_7H_7NH.CMe_2.CO_2H$. [62°]. Formed together with the β- isomeride [110°] by the action of KOH and a current of steam on the ether [57°], which is got by heating *o*-toluidine with α-bromo-isobutyric ether (Bischoff a. Mintz, *B.* 25, 2334). The acid [110°] yields an acetyl derivative [219°], sl. sol. ether. On distillation it forms a lactone [95°].

***p*-Tolyl-α-amido-*n*-butyric acid** $C_7H_7NH.CHEt.CO_2H$. [153°–156°]. Got from the ether EtA′ (279°) S.G. $\frac{20}{20}$ 1·011, which is produced when *p*-toluidine is heated with α-bromo-*n*-butyric acid at 105°. Leaflets. Yields propyl-*p*-toluidine on distillation.

Acetyl derivative $C_7H_7NAc.CHEt.CO_2H$. [149°].

***p*-Tolyl-α-amido-isobutyric acid** [1:4] $C_6H_4Me.NH.CMe_2.CO_2H$. [150°]. Formed, together with the β- isomeride, by the action of hot potash in a current of steam on the ether EtA′ [36°], which is got by heating *p*-toluidine with α-bromo-isobutyric acid. Yields an acetyl derivative [146°]. Forms isopropyl-*p*-toluidine on distillation.

_p_-Tolyl-β-amido-isobutyric acid $C_7H_7NH.CH_2.CHMe.CO_2H$. [196°]. Formed as above. Gives an acetyl derivative [206°] and decomposes on distillation into *p*-toluidine and a lactone $C_7H_7N\left<\begin{matrix}CH_2.CHMe\\CO.CMe_2.O\end{matrix}\right>CO$ (?) [170°].

***o*-TOLYL-AMIDO-CROTONIC ACID** [1:2] $C_6H_4Me.NH.CMe{:}CH.CO_2H$.

Methyl ether MeA'. [31°]. Formed by the action of *o*-toluidine on methyl aceto-acetate (Conrad a. Limpach, *B.* 21, 523). Prisms (from alcohol).

Ethyl ether EtA'. Yellowish oil.

_p_-Tolyl-amido-crotonic acid.

Methyl ether MeA'. [60°]. Prisms.

Ethyl ether EtA'. [29°]. Formed from acetoacetic ether and *p*-toluidine.

TOLYL-AMIDO-CYANURIC ACID *v.* *Cyanuric acid*, described under Cyanic acids.

***p*-TOLYL-AMIDO-METHENYL-BENZAMIDOXIM** $CPh\left<\begin{matrix}N.O\\N\end{matrix}\right>C.NH.C_6H_4Me$ [1:4.]. [135°]. Formed by heating *p*-tolyl-thiocarbimide with benzamidoxim (Koch, *B.* 24, 398). Plates (from alcohol), v. sol. ether.

DI-*p*-TOLYL-AMIDO-METHYLENE-*o*-PHENYLENE DIAMINE $C_{21}H_{22}N_4$ *i.e.* $C_6H_4\left<\begin{matrix}NH\\NH\end{matrix}\right>C\left<\begin{matrix}NH.C_7H_7\\NH.C_7H_7\end{matrix}\right.$. [186°]. (above 400°). Formed by heating $C(NC_7H_7)_2$ with *o*-phenylene-diamine at 135° (Moore, *B.* 22, 1639; 3188). Tables (from alcohol), v. sl. sol. boiling water. —Salts: $B'_2 3HCl$. Needles.—$B'_4 3H_2PtCl_6$ 8aq. —$B'H_2SO_4$. Needles, insol. ether, v. sol. hot Aq.

Nitrosamine $C_6H_4\left<\begin{matrix}N(NO)\\N(NO)\end{matrix}\right>C(NC_7H_7.NO)_2$. [130°]. Yellow needles, v. sol. alcohol.

Di-acetyl derivative [143°]. Needles.

Di-benzoyl derivative [185°]. Prisms.

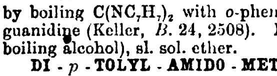
Tetra-benzoyl derivative [274°].

Tetra-*p*-tolyl-tetra-amido-di-methylene-*o*-phenylene-diamine $C_6H_4{:}N_2(C(NHC_7H_7)_2)_2$. [116°]. Formed by heating $C(NC_7H_7)_2$ with *o*-phenylene-diamine at 200° (Moore, *B.* 22, 3195). Needles, v. sol. alcohol. Decomposed by dilute HClAq at 150° into di-*p*-tolyl-urea and *o*-phenylene-diamine. $B'2H_2SO_4$. Needles, sl. sol. cold water.—$B'_2 3HCl$.—$B'_4 3H_2PtCl_6$ 15aq.

Tetra-acetyl derivative [115°].

Tetra-benzoyl derivative [146°].

DI-*p*-TOLYL-AMIDO-METHYLENE-*o*-PHENYLENE-PHENYL-GUANIDINE



$C_6H_4\left<\begin{matrix}N\\N\end{matrix}\right>C{:}NPh\Big>C(NHC_7H_7)_2$. [187°]. Formed by boiling $C(NC_7H_7)_2$ with *o*-phenylene-phenyl-guanidine (Keller, *B.* 24, 2508). Needles (from boiling alcohol), sl. sol. ether.

DI-*p*-TOLYL-AMIDO-METHYLENE-*o*-PHENYLENE-*p*-TOLYL-GUANIDINE $C_6H_4{:}N_2(CNC_7H_7){:}C(NHC_7H_7)_2$. [188°]. Formed by heating *o*-phenylene-*p*-tolyl-guanidine with $C(NC_7H_7)_2$ at 220° (Keller, *B.* 24, 2513). Prisms (from benzene).

DI-*p*-TOLYL-AMIDO-METHYLENE-*o*-TOLYLENE-*p*-TOLYL-GUANIDINE $C_7H_6{:}N_2(C{:}NC_7H_7){:}C(NHC_7H_7)_2$. [210°]. Formed by heating tolylene-tolyl-guanidine together with $C(NC_7H_7)_2$ at 220° (Keller, *B.* 24, 2521). Needles, sl. sol. alcohol.

***o*-TOLYL-AMIDO-METHYL-MALONAMIC ETHER** $CO_2Et.CMe(NHC_7H_7).CO.NH_2$. Formed by dissolving α-cyano-tolyl-α-amido-propionic ether in conc. H_2SO_4 (Gerson, *B.* 19, 2966). Long needles, sol. hot water. Converted by boiling NaOHAq into tolyl-amido-propionic acid.

***p*-TOLYL-AMIDO-*p*-METHYL-OXINDOLE** $C_{16}H_{16}N_2O$ *i.e.* $C_6H_3Me\left<\begin{matrix}NH\\CH(NHC_7H_7)\end{matrix}\right>CO$. [167°]. Formed by heating di-chloro- (or di-bromo-) acetic acid with *p*-toluidine (Duisberg, *B.* 18, 190). Needles, v. sol. hot alcohol. Reduces ammoniacal $AgNO_3$, forming a mirror. Readily absorbs oxygen from the air, forming $C_6H_3Me\left<\begin{matrix}NH\\C(NC_7H_7)\end{matrix}\right>CO$. Alcoholic KOH forms a blood-red solution. B'HCl: crystalline powder.

Di-acetyl derivative $C_{16}H_{14}Ac_2N_2O$. [117°].

Nitrosamine $C_{16}H_{15}N_3O_2$. [c. 220°].

***p*-TOLYL-AMIDO-METHYL-THIAZOLE** $S\left<\begin{matrix}CH - CMe\\C(NHC_7H_7){:}N\end{matrix}\right.$. [125°]. Formed from oxy-methyl-thiazole and *p*-toluidine (Hantzsch a. Weber, *B.* 20, 3130).

TRI-*p*-TOLYL-TRI-AMIDO-NAPHTHALENE $C_6H_4\left<\begin{matrix}C(NHC_7H_7){:}C(NHC_7H_7)\\C(NHC_7H_7){:}CH\end{matrix}\right.$. [160°]. Formed by heating nitroso-ethyl-(α)-naphthylamine with *p*-toluidine at 150° (Fischer a. Hepp, *A.* 256, 244). Needles (from alcohol). Readily oxidised to di-methyl-phenyl-rosinduline.

***o*-TOLYL-AMIDO-(α)-NAPHTHOQUINONE** $C_{17}H_{13}NO_2$ *i.e.* $C_{10}H_5O_2(NHC_7H_7)$. [142°]. Formed from *o*-toluidine and (α)-naphthoquinone (Elsbach, *B.* 15, 689). Red needles, sol. NaOHAq.

_p_-Tolyl-amido-(α)-naphthoquinone $C_{10}H_5O_2(NHC_7H_7)$. [202°]. Formed from (α)-naphthoquinone and *p*-toluidine in hot alcoholic solution (Plimpton, *C. J.* 37, 638). Formed also by the action of *p*-toluidine on (β)-oxy-(α)-naphthoquinone, and by heating *p*-tolyl-amido-(β)-naphthoquinone with HOAc at 150° (Elsbach, *B.* 15, 687). Red needles. Forms a crimson solution in conc. H_2SO_4. Insol. NaOHAq.

Ditoluide $C_6H_4\left<\begin{matrix}C(NC_7H_7){:}C.NHC_7H_7\\C(NC_7H_7){:}CH\end{matrix}\right.$. [147°]. Formed by oxidation of tri-*p*-tolyl-amido-naphthalene (Fischer a. Hepp, *A.* 256, 246). Orange plates.

_o_-Tolyl-amido-(β)-naphthoquinone $C_{10}H_5O_2(NHC_7H_7)$ or $C_{10}H_5(OH)O(NC_7H_7)$. [240°]. Formed from (β)-naphthoquinone and *o*-toluidine (Elsbach, *B.* 15, 689). Red needles, sol. dilute NaOHAq. Not affected by heating with HOAc at 150°. On heating with dilute HClAq it yields (β)-oxy-(α)-naphthoquinone and *o*-toluidine.

_p_-Tolyl-amido-(β)-naphthoquinone [246°]. Formed from (β)-naphthoquinone and *p*-toluidine (Elsbach, *B.* 15, 686). Red needles, sol. hot alcohol and NaOHAq. On heating with HClAq at 130° it is split up into *p*-toluidine and (β)-naphthoquinone.

Methyl ether MeA'. [150°]. Red crystals (Zincke a. Brauns, *B.* 15, 1969).

Ethyl ether EtA'. [137°].

Isopropyl ether PrA'. [139°].

p-Toluide $C_{10}H_5(NHC_7H_7)O(NC_7H_7)$. [183° cor.]. Formed by heating di-bromo-(α)-naphthol with *p*-toluidine (Meldola, *C. J.* 45, 159). Formed also from (β)-naphthoquinone oxim, *p*-toluidine, and HOAc (Bromme, *B.* 21, 391). Orange crystals with green lustre.

DI-*o*-TOLYL-DI-AMIDO-OIAZTHIOLE $C_{16}H_{16}N_4S$ *i.e.* $S<\begin{matrix}C(NHC_7H_7):N\\ C(NHC_7H_7):N\end{matrix}$. [135°]. Formed by boiling an alcoholic solution of *o*-tolyl-thio-urea with dilute HClAq and H_2O_2 (Hector, *B.* 23, 368). V. sol. alcohol. Cyanogen passed into its alcoholic solution forms $C_{16}H_{16}N_4SCy_2$ [89°].—$B'HCl$aq. [219°].—$B'_2H_2PtCl_6$. [192°].—$B'AgNO_3$. White pp.—$B'_2H_2HgCl_4$. [232°]. Needles.—Picrate: $B'C_6H_3N_3O_7$. [201°].

Acetyl derivative $C_{16}H_{15}AcN_4S$. [221°].

Benzoyl derivative $C_{16}H_{15}BzN_4S$. [214°].

Nitrosamine $C_{16}H_{15}(NO)N_4S$. [135°].

Di-*p*-tolyl-di-amido-oiazthiole $C_{16}H_{16}N_4S$. [127°]. Formed in like manner from *p*-tolyl-thio-urea (Hector, *B.* 23, 364). Thick yellowish prisms, v. sol. alcohol. Cyanogen forms $B'Cy_2$ [190°].—$B'HCl$. [233°]. White needles, becoming reddish in air.—$B'_2H_2PtCl_6$ 1½aq. [109°].—$B'AgNO_3$ 1½aq. [177°].—$B'_2H_2HgCl_4$. [114°–119°].—Picrate [238°]. Yellow prisms, sl. sol. alcohol.

Acetyl derivative $C_{16}H_{15}AcN_4S$. [166°].

Benzoyl derivative $C_{16}H_{15}BzN_4S$. [186°].

Nitrosamine $C_{16}H_{15}(NO)N_4S$. [247°].

***o*-TOLYL-*m*-AMIDO-PHENOL** $C_{13}H_{13}NO$ *i.e.* $C_7H_7NH.C_6H_4OH$. (c. 373° cor.). Formed from resorcin, *o*-toluidine, and $CaCl_2$ at 270° (Philip, *J. pr.* [2] 34, 70). Oil. Reduced by hot zinc-dust to hydro-acridine and acridine.

Formyl derivative. [169°]. Tables.

***o*-Tolyl-*p*-amido-phenol** $C_7H_7NH.C_6H_4OH$. [90°]. (367° cor.). Formed from hydroquinone, *o*-toluidine and $CaCl_2$ at 240° (Philip, *J. pr.* [2] 34, 57). White laminæ (from light petroleum). Reduced by distilling with zinc to hydro-acridine and acridine. Converted by heating with conc. HCl into hydroquinone and *o*-toluidine.

Salt.—$B'HCl$: crystalline powder.

Mono-formyl derivative [136·5°].

Di-acetyl derivative [106°]: needles.

Di-benzoyl derivative. [171°].

***p*-tolyl-*m*-amido-phenol** $C_{13}H_{13}NO$ *i.e.* $C_7H_7.NH.C_6H_4.OH$. [92°]. (350° cor.). From resorcin, *p*-toluidine and $CaCl_2$ at 260° for 8 hours (Hatschek a. Zega, *J. pr.* [2] 33, 209). Prisms or needles (from benzene mixed with petroleum ether). Distilled over zinc-dust, it gives C_7H_7NHPh.

Salts.—$B'HCl$; decomposed by water.

Formyl derivative.—$C_7H_7.N(CHO).C_6H_4.OH$. [146°]. V. sol. ether.

Di-benzoyl derivative.—$C_7H_7.NBzC_6H_4.OBz$. [c. 105°]. Gives with fuming HNO_3 a di-nitro-derivative, [110°].

Nitrosamine.—$C_7H_7.N(NO).C_6H_4.OH$. *Oxy-phenyl-tolyl-nitrosamine.* [105°]. Yellow needles (from dil. alcohol).

***p*-Tolyl-*p*-amido-phenol** $C_7H_7.NH.C_6H_4.OH$. [122°]. (350°–360°). From hydroquinone, *p*-toluidine, and $CaCl_2$ 8 hours at 260° (Hatschek a. Zega, *J. pr.* [2] 33, 224). Plates. Heated with zinc-dust it gives phenyl-*p*-tolyl-amine.

Salt.—$B'HCl$. Powder, decomposed by Aq.

Di-acetyl derivative. [101°]. Tables.

Di-benzoyl derivative. [169°].

Nitroso- derivative $C_7H_7.N(NO).C_6H_4.OH$ [130°]; needles. Very unstable.

***o*-TOLYL-α-AMIDO-PHENYL-ACETIC ACID** $NHC_7H_7.CHPh.CO_2H$. [143°]. Formed from α-bromo-phenyl-acetic acid and *o*-toluidine (Stöckenius, *J.* 1878, 781). Plates, almost insol. water.

***p*-Tolyl-α-amido-phenyl-acetic acid.** Formed in like manner, using *p*-toluidine. Insol. water.

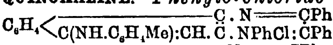
Ethyl ether EtA'. [90°]. Yellowish prisms.

***o*-TOLYL-AMIDO-TRI-PHENYL-METHANE** $CPh_3.NHC_7H_7$. [142°]. Formed from CPh_3Br and *o*-toluidine (Wittich, *B.* 17, 705). Prisms (from ether).

***p*-Tolyl-amido-tri-phenyl-methane** [177°]. Crystals (from ether).

Nitrosamine $CPh_3.NC_7H_7.NO$. [145°–148°].

***p*-TOLYL-AMIDO-DI-PHENYL-NAPHTHO-QUINOXALINE.** *Phenylo-chloride*



$$C_6H_4<\begin{matrix}\overline{\qquad\qquad\qquad\qquad}C.N\!=\!\!=\!CPh\\ C(NH.C_6H_4Me):CH.\,C.NPhCl:CPh.\end{matrix}$$

Got by heating $C_{10}H_5(OEt)<\begin{matrix}N\!=\!\!=\!CPh\\ NPhCl:CPh\end{matrix}$ with *p*-toluidine at 120° (Witt a. Schmidt, *B.* 25, 2005). Bronzed plates, v. sol. alcohol, forming a crimson solution. Conc. H_2SO_4 forms a slate-blue solution, becoming first blue and then violet on dilution.

TRI-*p*-TOLYL-TRI-AMIDO-DI-PHENYL-TOLYL-CARBINOL $C_{41}H_{39}N_3O$. *Tri-tolyl-rosaniline.* The salts are formed by heating rosaniline salts with *p*-toluidine (Hofmann, *A.* 132, 290).—$C_{41}H_{38}N_3Cl$. Small blue crystals (from alcohol), insol. water.

TOLYL-AMIDO-PIPITZAHOIC ACID *v.* *Toluido*-PIPITZAHOIC ACID.

***o*-TOLYL-α-AMIDO-PROPIONIC ACID** $CH_3.CH(NHC_7H_7).CO_2H$. [116°]. Formed by saponification of the nitrile (Tiemann a. Stephan, *B.* 15, 2038; *C. C.* 1886, 470). Got also by boiling *o*-tolyl-amido-methyl-malonic acid with NaOHAq (Gerson, *B.* 19, 2963). White crystals.

Ethyl ether EtA' (278°). S.G. $\frac{20}{20}$ 1·047. Formed from α-bromo-propionic ether and *o*-toluidine (Bischoff a. Hausdörfer, *B.* 25, 2298).

Acetyl derivative $C_7H_7NAc.CHMeCO_2H$. [177°]. Leaflets.

Amide. [125°]. Minute needles.

Nitrile $CH_3.CH(NHC_7H_7).CN$. [73°]. Formed by digesting the cyanhydrin of acetic aldehyde (lactonitrile) with *o*-toluidine.

***p*-Tolyl-α-amido-propionic acid.** [153°]. Formed in like manner. Plates, sl. sol. water and ether. May be sublimed.

Ethyl ether EtA'. [35°]. Tables.

Acetyl derivative [166°].

Amide. [145°]. Needles, sol. hot Aq.

Nitrile. [82°]. Plates, sl. sol. hot Aq.

***p*-Tolyl-β-amido-propionic acid** $C_6H_4Me.NH.CH_2.CH_2.CO_2H$. [86°]. Formed from β-iodo propionic acid and *p*-toluidine (Bischoff a. Mintz, *B.* 25, 2352). Pearly scales, v. e. sol. ether.

Reference. — DI-BROMO-TOLYL-AMIDO-PROPIONITRILE.

***o*-TOLYL-AMIDO-PYROTARTRIMIDE** $\begin{matrix}CH_2.CO\text{—}NH\\ CH_2.C(NHC_7H_7).CO\end{matrix}$. [181°]. Obtained by saponification of *o*-tolyl-amido-pyrotartramic ether, which is formed by the action of H_2SO_4 upon the *a*-cyano-*a*-*o*-toluido-butyric ether (Schiller-Wechler, *B.* 18, 1050). White needles. V. sol. alcohol and benzene, sl. sol. ether and hot water, insol. cold water and ligroïn. Has both acid and basic properties.

DI-*p*-TOLYL-DI-AMIDO-SUCCINIC ACID $CO_2H.CH(NHC_7H_7).CH(NHC_7H_7).CO_2H$. [c. 200°]. Formed, together with 'di-tolil succin' $C_{18}H_{16}N_2O_2$ [228°], by boiling di-bromo-succinic acid with *p*-toluidine (Jungliahn a. Roissert, *B.* 26, 1766). V. sol. alcohol, insol. water. Yields a di-nitroso- derivative [125°], and a di-acetyl derivative $C_{22}H_{24}N_2O_6$ aq, which yields CaA″ aq, BaA″ aq, and anhydrides $C_{22}H_{22}N_2O_5$ [232°], and $C_{22}H_{20}N_2O_4$ [222°]. Na_2A''.—CaA″.—CuA″.

Ethyl ether Et_2A''. [169°]. Needles.

DI-*p*-TOLYL-TRI-AMIDO-TOLUENE $C_6H_2Me(NHC_7H_7)_2(NH_2)$ [1:2:5:4]. [166°]. Formed by reducing amido-toluquinone ditoluide with zinc-dust and HOAc (Green, *C. J.* 63, 1403; *cf.* Barsilowsky, *B.* 6, 1209). Plates (from dilute HOAc). A very feeble base.

DI-*p*-TOLYL-DI-AMIDO-TOLUQUINONE $C_6HMeO_2(NHC_7H_7)_2$ [1:2:5:4:6]. [178°]. Formed from azotoline, MeOH, and conc. H_2SO_4 (Fischer a. Hepp, *A.* 262, 251). Brownish-red needles.

Di-*p*-tolyl-di-amido-toluquinone $C_6HMeO_2(NHC_7H_7)_2$ [1:2:5:3:6]. [241°]. Formed by boiling toluquinone with *p*-toluidine and alcohol (Fischer a. Hepp, *A.* 256, 259). Yellow needles.

Di-*p*-tolyl-di-amido-toluquinone *p*-toluide $C_{28}H_{27}N_3O$. [191°]. Claret-red plates (Fischer a. Hepp, *B.* 21, 676).

TOLYLAMINE is Toluidine (*q.v.*).

Di-*o*-tolyl-amine $NH(C_6H_4Me[1:2])_2$. (312° i.V.) at 728 mm. (Graebe, *A.* 238, 363). Obtained, together with diphenylamine by heating *o*-toluidine with aniline hydrochloride at 280° (Girard a. Willm, *Bl.* [2] 25, 248). Formed also by heating *o*-cresol with $ZnBr_2$, ammonia, and NH_4Cl at 335° (Merz a. Müller, *B.* 20, 547). Oil.

Di-*m*-tolyl-amine $NH(C_7H_7)_2$. (322°). Formed in like manner (Cosack, *B.* 13, 1091; Merz a. Müller, *B.* 20, 549). Oil, volatile with steam. Sl. sol. acids, v. sol. alcohol.

Acetyl derivative $NAc(C_7H_7)_2$. [43°].

Nitrosamine $(C_7H_7)_2N.NO$. [103°].

Di-*p*-tolyl-amine $NH(C_7H_7)_2$. [79°]. (331° i.V.) (Graebe, *A.* 238, 363). Formed by heating *p*-toluidine with its hydrochloride (Girard, *A.* 140, 346; Gerber, *B.* 6, 446). Formed also by heating *p*-cresol with $ZnCl_2$, ammonia, and NH_4Cl at 335° (Merz a. Müller, *B.* 20, 546). White needles. Its salts are decomposed by water.

Nitrosamine $(C_7H_7)_2N.NO$. [103°]. Yellow trimetric crystals (Lehne, *B.* 13, 1514; Cosack).

Acetyl derivative $(C_7H_7)_2NAc$. [85°].

Benzoyl derivative $(C_7H_7)_2NBz$. [125°].

References.—Tetra-bromo- and Nitro- Di-tolyl-amine.

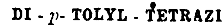
DI-*p*-TOLYL-ISOAMYL-AMINE $C_{19}H_{25}N$ *i.e.* $(C_7H_7)_2NC_5H_{11}$. (290°–300° at 15 mm.). Formed by heating di-*p*-tolyl-amine with isoamyl alcohol and HCl in sealed tubes (Girard, *Bl.* [2] 24, 120).

TOLYL-ANILINE *v.* Phenyl-toluidine.

TOLYL-ARSINE *v.* Arsenic.

TOLYL-AURAMINE $C_{24}H_{27}N_3$ *i.e.* $C_6H_4Me.N:C(C_6H_4NMe_2)_2$. Formed from auramine hydrochloride and *p*-toluidine (Fehrmann, *B.* 20, 2853). Decomposed by H_2S in alcoholic solution at 50° into $CS(C_6H_4NMe_2)_2$ and *p*-toluidine.—$B'_2H_2PtCl_6$. Red flakes, v. sl. sol. water.

TOLYL-AZIMIDO-TOLUENE *v.* Azimido-compounds.



DI-*p*-TOLYL-TETRAZINE $C_{16}H_{16}N_4$ *i.e.* $C_6H_4Me.N{<}\genfrac{}{}{0pt}{}{N{=}CH}{CH{:}N}{>}N.C_6H_4Me$. [185°]. Mol. w. 269 (obs.). Formed by the action of chloroform and alcoholic potash on *p*-tolyl hydrazine (Ruhemann, *C. J.* 55, 218; 57, 51). Yellow plates (from hot alcohol). Yields a nitro-derivative $C_{16}H_{15}(NO_2)N_4$ [144°].

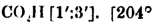
TOLYL-DISAZO-compounds *v.* Disazo-compounds.

TOLYL BENZAMIDE *v.* *Benzoyl derivative* of Toluidine.

***p*-TOLYL-BENZAMIDINE** $C_{14}H_{14}N_2$ *i.e.* $C_6H_5.C(NC_7H_7).NH_2$. [99°]. Formed from benzonitrile and toluidine hydrochloride (Bernthsen, *B.* 8, 1319; 9, 429). Forms a crystalline nitrate and oxalate.

Di-*p*-tolyl-benzamidine $C_6H_5.C(NC_7H_7).NHC_7H_7$. [131°]. Formed by the action of *p*-toluidine on benzonitrile, and on ω-chloro-benzylidene-*p*-toluidine $C_7H_7N:CCl.C_6H_5$ (Bernthsen; Just, *B.* 19, 981). May be sublimed.

Reference.—Amido-tolyl-benzamidine.



***p*-TOLYL-BENZAMIDOXIM** $C_{14}H_{14}N_2O$ *i.e.* $C_6H_5.C(NOH).NHC_7H_7$. [176°]. Formed by heating hydroxylamine hydrochloride with $C_6H_5.CS.NHC_7H_7$ and Na_2CO_3 at 100° (H. Müller, *B.* 22, 2406). White needles, sl. sol. hot water.—B′HCl: white needles, sl. sol. water. $ClCO_2Et$ converts it into $C_6H_5.C{<}\genfrac{}{}{0pt}{}{N.O}{NC_7H_7}{>}CO$. [163°].

TOLYL-BENZENE *v.* Methyl-diphenyl.

Tri-*p*-tolyl-benzene $C_{27}H_{24}$ *i.e.* $C_6H_3(C_7H_7)_3$. [171°]. Formed by passing dry HCl into *p*-tolyl methyl ketone for some days (Claus, *J. pr.* [2] 41, 402). Needles. Oxidised by CrO_3 to $C_6H_3(CO_2H)_3$. Yields $C_{27}H_{21}Br_3$ [212°].

***p*-TOLYL-BENZIMIDO PHENYL ETHER** $C_6H_5.C(NC_7H_7).OPh$. [120°]. Formed from $C_6H_5.CCl:NC_7H_7$ and NaOPh (Hantzsch, *B.* 26, 927).

***om*-TOLYL-BENZOIC ACID** [1:3] $C_6H_4Me.C_6H_4.CO_2H$ [1′:3′]. [204°]. Formed by oxidation of [1:3] $C_6H_4Me.C_6H_4Me$ [1′:3′] with dilute HNO_3 (Perrier, *C. R.* 114, 484). Silky needles, sol. alcohol, m. sol. Aq.

***pp*-Tolyl-benzoic acid** [1:4] $C_6H_4Me.C_6H_4.CO_2H$ [1′:4′]. [244°]. Formed by oxidation of *pp*-ditolyl by CrO_3 and HOAc (Carnelley, *J.* 1877, 384). Sl. sol. hot water.—AgA′.

***op*-Tolyl-benzoic acid.** [180°]. Formed by oxidation of [1:2] $C_6H_4Me.C_6H_4.Me$ [1′:4′] (Carnelley, *C. J.* 37, 707). Insol. water, sol. hot alcohol.

TOLYL-BENZYL-AMINE *v.* Benzyl-toluidine.

***p*-TOLYL-BENZYL-ISOBUTYL-UREA** $C_{19}H_{24}N_2O$. [41°]. Got from *p*-tolyl-benzyl-carbamic chloride and isobutylamine (Hammerich, *B.* 25, 1824). Crystals (from ligroïn).

p-**TOLYL-BENZYL-CARBAMIC CHLORIDE** $(C_6H_4Me)N(CH_2Ph).COCl$. Formed from *p*-tolyl-benzyl-amine and $COCl_2$ (Hammerich, *B.* 25, 1822). Oil.

p-**TOLYL-BENZYL-CARBINOL** $C_{15}H_{16}O$ *i.e.* $C_6H_4Me.CH(OH).CH_2Ph$. [66°]. (above 360°). Formed by reducing *p*-tolyl benzyl ketone in alcoholic solution by Na (Mann, *B.* 14, 1646). Small concentric needles, sol. alcohol and ether.

p-**TOLYL-BENZYLENE-ACETAMIDINE** $C_{16}H_{16}N_2$ *i.e.* $C_6H_4{<}\begin{matrix}CH_2.NC_7H_7\\N = CMe\end{matrix}$. [79°]. Formed by reduction of the acetyl derivative of *o*-nitro-benzyl-*p*-toluidine in acetic acid solution with tin and HCl (Lellmann a. Stickel, *B.* 19, 1610). Small glistening plates. V. sol. alcohol, ether, and chloroform.

p-**TOLYL BENZYL KETONE** $C_{15}H_{11}O$ *i.e.* $C_6H_4Me.CO.CH_2Ph$. [109°]. (above 360°). Formed by the action of $AlCl_3$ on a mixture of phenyl-acetyl chloride and toluene (Mann, *B.* 14, 1646; Strassmann, *B.* 22, 1229). Plates, sol. alcohol and ether. Na added to its alcoholic solution forms the carbinol and an acid $C_{19}H_{20}O_2$ [′3°].

Oxim [131°]. Plates, insol. water.

o-**TOLYL BENZYL OXIDE** $C_{14}H_{11}O$ *i.e.* [1:2] $C_6H_4Me.O.CH_2Ph$. (285°–290°). Oil (Staedel, *B.* 14, 899). Converted by HNO_3 (S.G. 1·5) into a tri-nitro- derivative [145°].

m-**Tolyl benzyl oxide.** [43°]. (300°–305°). Tables (from alcohol), v. sol. ether.

p-**Tolyl benzyl oxide** [41°]. Formed from $C_6H_4Me.OK$ and CH_2PhCl (Frische, *A.* 224, 154). Crystals. Converted by HNO_3 (S.G. 1·5) into di-nitro-*p*-cresol [84°].

TOLYL-BENZYL-ISOPHOSPHINE $C_{14}H_{15}P$ or $C_{27}H_{28}P_2$. [187°]. An indifferent body formed by the action of zinc on a mixture of benzyl chloride and $C_6H_4MePCl_2$ (Michaelis a. Gleichmann, *B.* 15, 1963).

p-**TOLYL BENZYL SULPHONE** $C_6H_4Me.SO_2.CH_2Ph$. [145°]. Formed by the action of benzyl chloride on sodium toluene *p*-sulphinate (Otto, *B.* 13, 1278). Needles, sol. hot alcohol.

p-**TOLYL-BENZYL-THIO-SEMICARBAZIDE** $C_{15}H_{17}N_3S$. [121°]. Formed from benzyl thiocarbimide and *p*-tolyl-hydrazine (Dixon, *C. J.* 61, 1022). Prisms, sl. sol. cold alcohol.

o-**TOLYL-BENZYL-THIO-UREA** $C_{15}H_{16}N_2S$ *i.e.* $C_6H_4MeNH.CS.NHCH_2Ph$. [139°]. Formed by boiling *o*-tolyl-thiocarbimide with benzylamine in alcohol (Dixon, *C. J.* 59, 556). Tufts of prisms, m. sol. hot alcohol.

m-**Tolyl-benzyl-thio-urea.** [114°]. Formed from benzyl-thiocarbimide and *m*-toluidine. Vitreous crystals, v. sl. sol. hot Aq.

p-**Tolyl-benzyl-thio-urea** [121°]. Crystals.

p-**TOLYL-BENZYL-UREA** $CH_2Ph.NH.CO.NHC_6H_4Me$. [181°]. Formed from *p*-tolyl cyanate and benzylamine (Kühn a. Henschel, *B.* 21, 505).

p-**Tolyl-di-benzyl-urea** $C_{22}H_{22}N_2O$ *i.e.* $(CH_2Ph)_2N.CO.NHC_6H_4Me$. [169°]. Got from $(C_7H_7)_2N.COCl$ and *p*-toluidine (Hammerich, *B.* 25, 1820). Needles (from alcohol), insol. ether.

p-**Tolyl-di-benzyl-urea** $C_{22}H_{22}N_2O$ *i.e.* $CH_2PhN(C_6H_4Me).CO.NH.CH_2Ph$. [85°]. Formed from tolyl-benzyl-carbamic chloride and benzylamine (H.). Prisms, v. sol. alcohol.

Di-*p*-tolyl-benzyl-urea $C_{22}H_{22}N_2O$. [115°]. Formed from *p*-tolyl-benzyl-carbamic chloride and *p*-toluidine. Needles, v. sol. hot alcohol.

Di-*p*-tolyl-di-benzyl-urea $(CH_2PhN(C_6H_4Me))_2CO$. [93°]. Got from *p*-tolyl-benzyl-carbamic chloride and *p*-tolyl-benzyl-amine. Crystalline, sol. alcohol.

DI-*p*-TOLYL-BIURET $(C_6H_4MeNH.CO)_2NH$. [c. 220°]. Formed from *p*-tolyl-urea and *p*-tolyl cyanate at 160° (Kühn a. Henschel, *B.* 21, 506). White needles (from alcohol).

Tri-*p*-tolyl-biuret $(C_6H_4MeNH.CO)_2NC_6H_4Me$. [156°]. Formed from di-*p*-tolyl-urea and *p*-tolyl cyanate.

p-**TOLYL-BORIC ACID** $C_6H_4Me.B(OH)_2$. [240°]. Formed by the action of water on boron-*p*-tolyl-dichloride (*v.* vol. i. p. 531). Needles, sol. hot water. $HgCl_2$ gives a white pp. of C_7H_7HgCl.

TOLYL-BROMO-ETHYLENE *v.* BROMO-TOLYL-ETHYLENE.

TOLYL BROMO-METHYL KETONE $C_6H_4Me.CO.CH_2Br$. [55°]. Formed by the action of hot water on di-*exo*-bromo-*eso*-methyl-atrolactic acid (Böttinger, *B.* 14, 1598). Crystals, volatile with steam, sol. water and ether.

p-**TOLYL BROMO-METHYL SULPHONE** $C_6H_4Me.SO_2.CH_2Br$. [92°]. Formed by the action of bromine on an aqueous solution of $C_7H_7.SO_2.CH_2.CO_2H$ (Otto, *J. pr.* [2] 40, 544). Formed also from $C_7H_7.SO_2Na$ and CH_2Br_2. Thin monoclinic needles, sol. hot alcohol.

p-**Tolyl di-bromo-methyl sulphone** $C_6H_4Me.SO_2.CHBr_2$. [117°]. Formed from tolyl-sulphono-acetic acid and Br (O.). Monoclinic prisms, v. sol. hot alcohol.

TOLYL-BUTANE *v.* BUTYL-TOLUENE.

m-**TOLYL-BUTYLENE** $C_6H_4Me.CH_2.C_3H_5$. (195°). Formed from $C_6H_4Me.CH_2Cl$, allyl iodide, and Na (Aronheim, *B.* 9, 1790). Oil. Yields a liquid dibromide.

p-**TOLYL-*p*-BUTYL-PHENYL-THIO-UREA** $C_6H_4Me.NH.CS.NH.C_6H_4.C_4H_9$. [137°]. Formed from isobutyl-phenyl-amine and *p*-tolyl-thio-carbimide (Mainzer, *B.* 16, 2024). Plates, sol. alcohol and ether.

DI-*p*-TOLYL-ISOBUTYL-UREA $C_{19}H_{24}N_2O$. [119°]. Formed from $(C_7H_7)_2N.COCl$ and isobutylamine (Hammerich, *B.* 25, 1822). Prisms, v. sol. alcohol and ether.

m-**TOLYL-ISOBUTYRIC ACID** $C_6H_4Me.CH_2.CHMe.CO_2H$. [92°]. Formed by oxidation of *m*-isobutyl-toluene by dilute HNO_3 (Kelbe, *B.* 16, 620). Needles (from ligroïn).—AgA′: pp.

Reference.—NITRO-TOLYL-ISOBUTYRIC ACID.

o-**TOLYL-CARBAMIC ACID** $C_8H_9NO_2$ *i.e.* $C_6H_4Me.NH.CO_2H$.

Ethyl ether EtA′. [42°] (C.); [46°] (L.). Formed from *o*-toluidine and $ClCO_2Et$ (Cosack, *B.* 12, 1450; Nevile a. Winther, *B.* 12, 2324). Formed also from $C_6H_4Me.CCl{:}NCl$ and alcoholic potash (Lachmann, *B.* 12, 1349). Tables, sol. alcohol and benzene. Volatile with steam. Yields *o*-tolyl cyanate on distilling with P_2O_5.

Isobutyl ether C_4H_9A'. (275°–280°). Oil (Mylius, *B.* 5, 974). Partially decomposed on distillation into tolyl cyanate and isobutyl alcohol.

Benzyl ether CH_2PhA'. [84°]. Formed from *o*-tolyl cyanate and benzyl alcohol (Gattermann a. Cantzler, *B.* 25, 1087). Needles

Phenyl ether PhA'. [92°]. Formed by boiling di-*o*-tolyl-urea with di-phenyl carbonate for some hours (Eckenroth a. Rückel, *B.* 23, 699). Crystals (from ligroïn).

m-Phenylene ether $C_6H_4A'_2$. [154°]. Formed by heating *o*-tolyl cyanate with resorcin at 120° (G. a. C.). Colourless plates.

p-Phenylene ether $C_6H_4A'_2$. [206·5°]. Formed by heating *o*-tolyl cyanate with hydroquinone at 150°.

o-Tolyl ether C_7H_7A'. [126°]. Formed from *o*-tolyl cyanate and *o*-cresol (G. a. C.). Needles.

(β)-*Naphthyl ether* $C_{10}H_7A'$. [149°]. Formed by heating *o*-tolyl cyanate with (β)-naphthol at 160° (G. a. C.). Plates.

Di-phenyl-ethylene ether $C_2H_2Ph_2A'_2$. [234°]. Formed by heating *o*-tolyl cyanate with hydrobenzoïn at 100° (Auwers, *B.* 24, 1778). Needles. An isomeride [163°] is obtained from isohydrobenzoïn.

***m*-Tolyl-carbamic acid** $[1:3]C_6H_4Me.NH.CO_2H$.

Ethyl ether $C_{10}H_{13}NO_2$. Prepared from *m*-toluidine and chloro-formic ether (Cosack, *B.* 13, 1090). Oil, v. sol. alcohol and ether.

***p*-Tolyl-carbamic acid** $[1:4]C_6H_4Me.NH.CO_2H$.

Ethyl ether EtA'. [52°]. Formed from *p*-toluidine and $ClCO_2Et$ (Hofmann, *Pr.* 19, 108; *B.* 3, 656). Monoclinic prisms, v. sol. alcohol (Levin, *J.* 1882, 384).

Phenyl ether PhA'. [115°]. Formed by distilling di-*p*-tolyl-urea with di-phenyl carbonate (Eckenroth a. Rückel, *B.* 23, 698). Needles (from hot ligroïn).

Di-*p*-tolyl-carbamic acid $(C_7H_7)_2N.CO_2H$.

Ethyl ether EtA'. [62°]. Formed from $(C_7H_7)_2N.COCl$ and NaOEt (Hammerich, *B.* 25, 1824). Large plates, v. sol. alcohol and ether.

Chloride $(C_6H_4Me)_2N.COCl$. [103°]. Formed from $COCl_2$, a solution of di-*p*-tolylamine in benzene, and conc. NaOHAq (Hammerich, *B.* 25, 1821). Needles (from alcohol), v. e. sol. ether. AgCy forms the compound $(C_7H_7)_2N.CO.CN(AgCy)_2$ crystallising in needles which begin to melt at 103°.

***o*-TOLYL-CARBAMINE** $[1:2]C_6H_4Me.N:C$. (184°). S.G. ^{24} ·968. Formed by the action of alcoholic potash on *o*-toluidine and chloroform (Nef, *A.* 270, 309). Oil, volatile with steam. When heated at 245° for 3 hours it changes to the isomeric *o*-toluic nitrile. Heated with S in CS_2 at 130° it yields *o*-tolyl thiocarbimide. H_2S at 100° forms $C_6H_4Me.NH.CHS$ [101°].

Chloride $C_6H_4Me.N:CCl_2$. (215°). Formed by passing chlorine into a chloroform solution of the carbamine.

***p*-Tolyl-carbamine** $C_6H_4Me.N:C$. (99° at 36 mm.). Formed in like manner from *p*-toluidine (Nef). Oil.

Chloride $C_6H_4Me.N:CCl_2$. (226°). Converted by *p*-toluidine into tri-*p*-tolyl-guanidine.

***o*-TOLYL-SEMI-CARBAZIDE** $C_8H_{11}N_3O$ *i.e.* $NH_2.CO.N_2H_2C_7H_7$. [160°]. Formed by heating *o*-tolyl-hydrazine with urea (Pinner, *B.* 21, 1219). Flat needles, m. sol. water.

***p*-Tolyl-semi-carbazide** $C_8H_{11}N_3O$. [158°]. Sl. sol. cold water. Reduces Fehling's solution.

Di-*p*-tolyl-carbazide $CO(NH.NHC_7H_7)_2$. [201°]. Formed from *p*-tolyl-hydrazine and carbamic ether (Preund, *B.* 24, 4197). Tables, insol. water, v. sol. hot alcohol.

TOLYL-CARBIMIDE v. TOLYL ISOCYANATE, vol. ii. p. 316.

***o*-TOLYL-CARBINOL** $C_8H_{10}O$ *i.e.* $[1:2]C_6H_4Me.CH_2OH$. *ω-Oxy-o-xylene.* Mol. w. 122. [34°]. (223° i.V.). S.G. ^{49} 1·02. S. 1 in the cold; 1·5 at 100°. Formed by boiling *ω*-bromo-*o*-xylene with KOHAq (Colson, *Bl.* [2] 43, 8; *A. Ch.* [6] 6, 116). Formed also by reducing the aldehyde $C_6H_4Me.CHO$ (Raymann, *Bl.* [2] 27, 498), by the action of HNO_2 on the amine $C_6H_4Me.CH_2.NH_2$ (Kröber, *B.* 23, 1028), and by reducing *o*-toluic amide in acid solution by sodium-amalgam (Hutchinson, *B.* 24, 174). Needles, v. sol. alcohol and ether, sol. hot water. Oxidised by alkaline $KMnO_4$ to *o*-toluic acid [103°].

***m*-Tolyl-carbinol** $[1:3]C_6H_4Me.CH_2.OH$. (217°). S.G. ^{0} 1·036 (C.); ^{17} ·916 (R. a. W.). S. 5 in the cold. Formed by boiling the bromide $C_6H_4Me.CH_2Br$ with alkalis (C.). Liquid, v. sol. alcohol and ether, sl. sol. cold water. Yields *m*-toluic acid [108°] on oxidation.

Ethyl ether $C_7H_7.CH_2.OEt$. (202°) at 740 mm. S.G. ^{17} ·93. Oil.

Acetyl derivative $C_7H_7.CH_2.OAc$. (226°). Formed from $C_7H_7.CH_2Br$ and KOAc (Radziszewski a. Wispek, *B.* 15, 1747). Oil.

***p*-Tolyl-carbinol** $[1:4]C_6H_4Me.CH_2OH$. [59°]. (217°). Formed from *p*-toluic aldehyde and alcoholic potash (Cannizzaro, *C. R.* 54, 1225; *A.* 124, 255). Needles, sl. sol. cold water.

Ethyl ether $C_8H_9.OEt$. (203°) at 740 mm. S.G. ^{17} ·93. Formed from *ω*-bromo-*p*-xylene and alcoholic potash (Radziszewski a. Wispek, *B.* 15, 1745). Oil.

Di-tolyl-carbinol $(C_6H_4Me)_2CH.OH$. [69°] (W.); [62°] (Ador a. Crafts, *B.* 10, 2175). Formed by reducing di-tolyl ketone with sodium-amalgam (Weller, *B.* 7, 1184). Needles (from alcohol), insol. water.

Reference.—OXY-TOLYL-CARBINOL.

TOLYL-CARBINYL-AMINE v. METHYL-BENZYL-AMINE.

DI-*p*-TOLYL-CARBINYL AMINE $(C_7H_7)_2CH.NH_2$. [93°]. Formed by reducing the oxim of di-*p*-tolyl ketone in alcoholic solution with sodium-amalgam and HOAc at 60° (Goldschmidt a. Stöcker, *B.* 24, 2798). Tables.—B'HCl. [235°]. White needles.

Acetyl derivative [159°]. Needles.

TOLYL-CARBINYL-UREA v. METHYL-BENZYL-UREA.

Di-*p*-tolyl-carbinyl-urea $NH_2.CO.NH.CH(C_7H_7)_2$. [152°]. Formed from the hydrochloride of the amine and KCyO (Goldschmidt, *B.* 24, 2799). Needles.

DI-*p*-TOLYL-CARBONATE $(C_7H_7O)_2CO$. [115°]. Formed, together with di-ethyl carbonate, by heating *p*-tolyl ethyl carbonate at 300° (Bender, *B.* 19, 2268). V. sl. sol. cold alcohol.

DI-TOLYL DICARBOXYLIC ACID $[3:4:1]C_6H_3Me(CO_2H).C_6H_3Me(CO_2H)[1:3:4]$ [over 300°]. Formed by heating its nitrile with dilute H_2SO_4 (Löwenherz, *B.* 25, 1036). Plates, insol. water, sl. sol. hot alcohol.

Nitrile $C_{14}H_{12}(CN)_2$. [190°]. Formed from di-amido-ditolyl by Sandmeyer's diazo- reaction. Needles, m. sol. cold alcohol.

Reference.—OXY-DITOLYL DICARBOXYLIC ACID.

TOLYL CHLORIDE v. *ω*-CHLORO-XYLENE.

p-**TOLYL CHLORO-BENZYL SULPHONE** $C_6H_4Me.SO_2.CHCl.C_6H_5$. [203°]. Formed by heating sodium toluene *p*-sulphinate with benzylidene chloride (Otto, *J. pr.* [2] 40, 519). Needles (from HOAc).

p-**TOLYL CHLORO-ETHYL SULPHONE** [1:4]$C_6H_4Me.SO_2.CHCl.CH_3$. [48°]. Formed by boiling $CH_3.CCl_2.CO_2Na$ (1 mol.) with $C_7H_7.SO_2Na$ (2 mols.) in aqueous solution. Formed also by heating ethylidene chloride (2·5 g.) with sodium toluene *p*-sulphinate (4·5 g.) and alcohol at 150° (Otto, *J. pr.* [2] 40, 515, 534). Trimetric tables, v. sol. hot alcohol. Does not act upon $C_7H_7.SO_2Na$ even at 200°.

p-**Tolyl chloro-ethyl sulphone** $C_6H_4Me.SO_2.CH_2.CH_2Cl$. [79°]. Formed from $C_6H_4Me.SO_2.CH_2.CH_2.OH$ and PCl_5 (Otto, *J. pr.* [2] 30, 357). Needles or plates, v. sol. hot alcohol.

p-**TOLYL CHLORO-METHYL SULPHONE** $C_6H_4Me.SO_2.CH_2Cl$. [84°]. Formed by heating an aqueous solution of $CHCl_2.CO_2Na$ (1 mol.) with $C_7H_7.SO_2Na$ (2 mols.) on the water-bath (Otto, *J. pr.* [2] 40, 528). Tables (from benzene), v. sol. hot alcohol.

p-**Tolyl di-chloro-methyl sulphone** $C_6H_4Me.SO_2.CHCl_2$. [114°]. Formed by passing chlorine into a warm aqueous solution of $C_7H_7.SO_2.CH_2.CO_2H$ (Otto, *J. pr.* [2] 40, 544). Crystals, insol. water, v. sol. hot alcohol.

TOLYL-CRESOL $C_6H_4Me.CH_2.C_6H_4.OH$. (250°–255° at 10 mm.). Formed by heating ω-chloro-xylene with phenol and zinc filings (Mazzara, *G.* 9, 421). Oil, sol. alcohol, ether, and alkalis. Not coloured by $FeCl_3$.

Acetyl derivative (250° at 9 mm.). Decomposed in moist air into HOAc and tolyl-cresol.

p-**TOLYL-CUMINYL-AMINE** $C_{17}H_{21}N$ *i.e.* $C_6H_4Me.NH.CH_2.C_6H_4Pr$. [36°]. (above 200°). Formed by the reduction by sodium-amalgam of the product of the action of cuminol on *p*-toluidine (Uebel, *A.* 245, 293). Plates or prisms.—B'HCl. Plates or needles, sl. sol. hot Aq.

Nitrosamine $C_{17}H_{20}N.NO$. [67°]. Prisms.

p-**TOLYL-CUMINYL-UREA** $C_{18}H_{22}N_2O$ *i.e.* $C_{10}H_{13}.NH.CO.NHC_6H_4Me$. [150°]. Formed from cuminylamine and *p*-tolyl cyanate (Goldschmidt a. Gessner, *B.* 22, 928). Needles, v. sol. alcohol.

p-**TOLYL-CUMYLIDENE-AMINE** $C_6H_4Me.N:CH.C_6H_4Pr$. [51°]. Formed from cuminic aldehyde (cuminol) and *p*-toluidine in alcoholic solution (Uebel, *A.* 245, 292). Yellowish plates (from alcohol). Decomposed into the parent substances by heating with acids and alkalis.

p-**TOLYL-ψ-CUMYL-UREA** $C_6H_4Me.NH.CO.NH.C_6H_2Me_3$. [218°]. Formed from ψ-cumidine and *p*-tolyl cyanate (Goldschmidt a. Bardach, *B.* 25, 1361). Needles.

o-**TOLYL-CYANAMIDE** $C_6H_4Me.NH.CN$. [77°]. Formed by heating $C_7H_7NH.CS.NH.OH$ or by the action of hydroxylamine on *o*-tolyl thiocarbimide (Tiemann, *B.* 22, 1940; Voltmer, *B.* 24, 881). Tables, v. sol. alcohol and KOHAq, m. sol. water.

DI-*o*-TOLYL-CYANAMIDE $C_{15}H_{14}N_2$ *i.e.* $C(NC_7H_7)_2$. *Carboditolylimide.* (above 300°). Formed by heating the alkyl derivatives of di-*o*-tolyl-thio-urea (Will a. Bielschowski, *B.* 15, 1317). Amorphous, v. sol. benzene. Converted by dilute HClAq into di-*o*-tolyl-urea.

Di-*p*-tolyl-cyanamide $C_{16}H_{14}N_2SO$ or $C(NC_7H_7)_2$. [60°]. (above 230°). Formed by the action of HgO on a benzene solution of di-tolyl-thio-urea (Will, *B.* 14, 1488). Thick prisms, sol. benzene and ether. On heating with aniline it gives phenyl-di-tolyl-guanidine. Acids and alkalis convert it into di-*p*-tolyl-urea. On distillation it yields compounds melting at 49° to 60° and at 149° (Schall a. Paschkowetzky, *B.* 25, 2892). Phenyl-hydrazine at 190° forms $C_{36}H_{36}N_8$ [163°], which crystallises from alcohol in plates, and yields B'_34HCl and $B'_32H_2PtCl_6$. On heating with phenyl-hydrazine at 165° there is formed $N_2PhH:C(NC_7H_7)_2$ [138°], crystallising in pale-red needles, yielding $B'_2H_2PtCl_6$ (Wessel, *B.* 21, 2274). Tolylene-*o*-diamine at 140° forms $C_{22}H_{24}N_4$ [196°], which yields B'_23HCl [143°] (Dahm a. Gasiorowski, *B.* 19, 3057).

TOLYL CYANATE *v.* Cyanic acid.

TOLYL CYANIDE *v.* *Nitrile* of Toluic acid.

TOLYL-CYANURIC ACID *v.* Cyanic acids.

TOLYLENE ALCOHOL *v.* Di-oxy-xylene.

TOLYLENE-DI-ALLYL-DI-THIO-DI-UREA [1:2:3] $C_6H_3Me(NH.CS.NHC_3H_5)_2$. [152°]. Formed from *c*-tolylene-*o*-diamine and oil of mustard (Lellmann, *A.* 228, 246). Needles (from alcohol), decomposed on fusing into tolylene-thio-urea and di-allyl-thio-urea.

Tolylene-di-allyl-di-thio-di-urea [1:3:4] $C_6H_3Me(NH.CS.NHC_3H_5)_2$. [150°]. Formed from *i*-tolylene-*o*-diamine and oil of mustard (Lellmann, *A.* 221, 24). Decomposed by heat like the preceding isomeride; melting a second time at 210°–230°.

Tolylene-di-allyl-di-thio-di-urea [1:2:5] $C_6H_3Me(NH.CS.NHC_3H_5)_2$. [175·5°]. Formed from tolylene-*p*-diamine and allyl thio-carbimide (Lellmann a. Würthner, *A.* 228, 209). Plates or prisms, nearly insol. ether.

Tolylene-di-allyl-di-thio-di-urea. [151°]. Formed from tolylene-*m*?-di-amine and allyl thiocarbimide. Prisms (from alcohol), insol. ether, v. sol. HOAc. Melts without decomposition.

TOLYLENE-DI-AMIDO-DI-ACETIC ETHER [1:2:4] $C_6H_3Me(NH.CH_2.CO_2Et)_2$. [70°]. Formed from tolylene-*m*-diamine and chloro-acetic ether (Zimmermann a. Knyrim, *B.* 16, 516). Needles (from water).

c-**TOLYLENE-*o*-DIAMINE** $C_7H_{10}N_2$ *i.e.* $C_6H_3Me(NH_2)_2$ [1:2:3]. Mol. w. 122. [62°]. (255°). Formed from $C_6H_3Me(NH_2)(NO_2)$ [1:2:3] by reducing with Sn and HCl (Lellmann, *A.* 228, 243). Reddish crystals, smelling of acetamide. —B''2HCl. Sol. water, ppd. by HCl.

c-**Tolylene-*m*-diamine** $C_6H_3Me(NH_2)_2$ [1:2:6]. [104°]. Formed by reduction of nitro-toluidine [92°], or of liquid di-nitro-toluene (Ullmann, *B.* 17, 1960). Prisms, sol. hot water. Gives a brown colour with nitrous acid. CrO_3 and $FeCl_3$ give a brown colour.—B'HCl: crystals, v. e. sol. water.

i-**Tolylene-*m*-diamine** $C_6H_3Me(NH_2)_2$ [1:2:4]. [99°]. (c. 280°). Formed by reducing di-nitro-toluene (Hofmann, *Pr.* 11, 518) by reducing (4,1,2)-nitro-toluidine (Nölting a. Collin, *B.* 17, 268), and by the action of $SnCl_2$ on amido-toluene-azo-amido-cresol (Graeff, *A.* 229, 348). Needles (from water), v. sol. alcohol, ether, and hot water. Chloroformic ether, $ClCO_2Et$, forms [1:2:4] $C_6H_3Me(NH_2)(NH.CO_2Et)$ [91°], and chiefly $C_6H_3Me(NH.CO_2Et)_2$ [137°] (Schiff, *A.* 268, 314). Phenyl-thio-carbimide yields $CO_2Et.NH.C_6H_3Me.NH.CS.NHPh$ [155°]. Heptoic aldehyde in the cold forms $C_7H_6N_2(C_7H_{14})_2$, but when heated it yields an orange mass which forms a highly fluorescent solution (Schiff a. Vanni, *A.* 253, 319). Benzoic aldehyde forms $C_7H_6(N{:}CHPh)_2$ [122°–128°], while cinnamic aldehyde gives $C_7H_6(NC_9H_8)_2$ [162°] (Schiff, *A.* 140, 98; 239, 384). $Cl.CO.CO_2Et$ forms $C_6H_3Me<\begin{matrix}NH.CO\\NH.CO\end{matrix}$ [c. 260°] and [1:2:4] $C_6H_3Me(NH_2).NH.CO.CO_2Et$ [170°], which yields an acetyl derivative [192°]. Phenyl-thiocarbimide forms the compound $NHPh.CS.NH.C_6H_3Me.NH.CO.CO_2Et$ [155°] and $C_6H_3Me<\begin{matrix}NH.CS\\NH.C_2O_2\end{matrix}>NPh$ [198°] (Schiff, *A.* 268, 307). Tolylene-*m*-diamine heated with citric acid at 125° forms $C_{13}H_{12}N_2O_5$, crystallising from boiling alcohol in minute octahedra, decomposing at about 187° (Schneider, *B.* 21, 665). Acetyl-acetone at 100° forms a syrup, which when heated with H_2SO_4 yields $C_{12}H_{14}N_2$ [191°] (Combes, *C. R.* 108, 1252).—$B''HCl$.—$B''2HCl$.—$B''2HBr$.—$B''H_2SO_4$ 2aq: prisms. S. 5·6 at 19·5 (Beilstein a. Kuhlberg, *A.* 158, 351).—$B''H_2PtCl_6$.—$B''2HCyS$. Prisms (Lussy, *B.* 7, 1265).

o-Acetyl derivative $C_6H_3Me(NHAc)NH_2$ [1:2:4]. [140°]. Formed from $C_6H_3Me(NH_2)(NO_2)$ [107°] by acetylation and reduction (Wallach, *A.* 234, 350). Needles.—$B'_2H_2PtCl_6$.

p-Acetyl derivative $C_6H_3Me(NH_2)(NHAc)$ [1:2:4]. [160°]. Formed by acetylating the diamine, and got also by reducing $C_6H_3Me(NO_2)(NHAc)$ [1:2:4] (Tiemann, *B.* 3, 221; Wallach, *B.* 15, 2826, 2831). Long white needles.

Di-acetyl derivative $C_6H_3Me(NHAc)_2$. [224°]. Got by boiling the base with Ac_2O or HOAc (Koch, *A.* 153, 132; Tiemann, *B.* 3, 8; Ladenburg, *B.* 8, 1211). Needles.

Benzoyl derivative $C_6H_3Me(NO_2)(NHBz)$ [1:2:4]. [142°]. Got by reducing $C_6H_3Me(NO_2)(NHBz)$ (Bell, *B.* 7, 1505).

Di-benzoyl derivative [224°]. Tables, sl. sol. alcohol (Ruhemann, *B.* 14, 2656).

Thiobenzoyl derivative $C_6H_3Me(NH_2)NH.CSPh$. [197°] (Bernthsen a. Trompetter, *B.* 11, 1760).

Phthalyl derivative $C_6H_3Me<\begin{matrix}NH.CO\\NH.CO\end{matrix}>C_6H_4$. [192°]. Formed from the base and phthalic anhydride (Biedermann, *B.* 10, 1161). Needles, split up by dilute HCl into phthalic acid and a base $C_{37}H_{31}N_6O_4$.

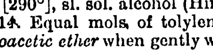
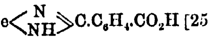
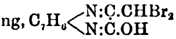
Di-phthalyl derivative $C_6H_3Me(NC_8H_4O_2)_2$. [233°]. Crystals, insol. water and alcohol.

***s*-Tolylene-*m*-diamine** $C_6H_3Me(NH_2)_2$ [1:3:5]. (284°). Formed by reducing *s*-di-nitro-toluene (Staedel, *A.* 217, 202). Syrup.—$B''H_2SO_4$.—$B''H_2SnCl_4$: crystals, v. sol. water.

Tolylene-*p*-diamine $C_6H_3Me(NH_2)_2$ [1:2:5]. [64°]. (274°). Formed by reducing (5,1,2)- and (2,1,5)- nitro-toluidines (Beilstein a. Kuhlberg, *A.* 158, 352; Fileti a. Crosa, *G.* 18, 306), and $C_6H_4Me.N_2.C_6H_3Me.NH_2$ [2:1:5] or [5:1:2] (Nietzki, *B.* 10, 832, 1158). Plates (from benzene), v. sol. water, alcohol, and ether. Forms toluquinone on oxidation. $FeCl_3$ added to a solution of tolylene-*p*-diamine hydrochloride mixed with *o*-toluidine gives an intense green colour.—$B''2HCl$. Plates.—$B''H_2SO_4$. S. ·84 at 11·5°.

Di-acetyl derivative $C_6H_3Me(NHAc)_2$. [220°]. Prisms (from dilute alcohol) (Nietzki, *B.* 10, 1157; 12, 2237).

Tolylene-*o*-diamine $C_6H_3Me(NH_2)_2$ [1:3:4]. [88·5°]. (265°). Formed by reducing (3 1,4)-nitro-*p*-toluidine (Beilstein a. Kuhlberg, *A.* 158, 351; Graeff, *A.* 229, 343). Plates, m. sol. cold water. Its aqueous solution quickly blackens when exposed to air. $FeCl_3$ forms by oxidation $C_{14}H_{13}N_3O$, crystallising from wood spirit in brownish-red plates [247°] (O. Fischer a. Sieder, *B.* 23, 3802).

Reactions.—1. *Benzoic aldehyde* at 140° forms $C_{21}H_{18}N_2$ or $C_7H_6<\begin{matrix}N(C_7H_7)\\N\end{matrix}>CPh$ [195·5°] (Ladenburg, *B.* 11, 591, 1656; Hinsberg, *B.* 19, 2026; 20, 1585), which yields $B'MeI$ [209°], $B'EtI$ [181°], and $B'EtI_3$ [125°], and is oxidised by $KMnO_4$ to an acid $C_{21}H_{16}N_2O_2$ [254°].—2. *Furfuraldehyde*, acting on the hydrochloride, forms $C_{17}H_{14}N_2O_2$ [128·5°], which yields $B'MeI$ [195·5°], $B'MeI_3$ [128°], and $B'MeI_5$ [109°].—3. *Acetic aldehyde* (2 mols.) added to a cold solution of the base (1 mol.) in glacial acetic acid forms $C_7H_6<\begin{matrix}NEt\\N\end{matrix}>CMe$ (Hinsberg).—4. *Anisic aldehyde*, added to a dilute aqueous solution of tolylene-*o*-diamine hydrochloride containing a little alcohol, forms $C_{23}H_{22}N_2O_2$ [152°–156°], which separates on addition of ammonia (L.).—5. *Salicylic aldehyde* at 110° forms $C_{28}H_{22}N_4O_3$ [106° 110°], and at 135° it forms azurine $C_{35}H_{32}N_4O_3$ [250·5°], which exhibits blue fluorescence in alkaline solutions.—6. *Glucose* (2 mols.) added to an alcoholic solution of tolylene-*o*-diamine forms $C_7H_6(N{:}C_6H_{12}O_5)_2$, crystallising in satiny needles, v. sol. water [c. 160°], which gives a red colour with $FeCl_3$. Glucose converts tolylene-*o*-diamine acetate into amorphous 'glycodiamido-toluene' $C_{13}H_{18}N_2O_5$, m. sol. water (Hinsberg, *B.* 20, 495; Griess a. Harrow, *B.* 20, 2209). Glucoson $C_6H_{10}O_6$ acts in aqueous solution on phenylene-*o*-diamine, forming $C_{13}H_{16}N_2O_4$ [c. 180°] (E. Fischer, *B.* 22, 93).—7. *Arabinose* forms $C_{12}H_{16}N_2O_4$ [238°] (G. a. H.).—8. *Acrolein* in boiling aqueous solution forms tolylene-*o*-diamine acroson [185°] (Fischer a. Tafel, *B.* 22, 99).—9. *Formic aldehyde* forms $C_{18}H_{20}N_4$ [222°] (Fischer a. Wrezinski, *B.* 25, 2713).—10. *Butyric aldehyde* forms tolylene-butenyl-diamine $C_7H_6<\begin{matrix}NH\\N\end{matrix}>CPr$ [158°], and the compound $C_{15}H_{22}N_2$ or $C_7H_6<\begin{matrix}N(C_4H_9)\\N\end{matrix}>CPr$ (Hinsberg, *B.* 20, 1590).—11. *Nitrous acid* or, better, amyl nitrite acting on a salt of tolylene-*o*-diamine forms azimido-toluene $C_7H_7N_3$ [84°] (323°), which is v. sol. alcohol and hot toluene (Zincke a. Lawson, *A.* 240, 115; *cf.* Ladenburg, *B.* 9, 220; Bössneck, *B.* 19, 1759; Nölting a. Abt, *B.* 20, 3001). Azimido-toluene forms the salts $B'_2H_2PtCl_6$, $NaC_7H_6N_3$, $Hg(C_7H_6N_3)_2$ [235°], and $AgC_7H_6N_3$. AcCl converts azimido-toluene into the (β)-acetyl derivative $C_7H_6{<}\substack{N\\N}{>}NAc$ [94°], while the isomeric (α)-acetyl derivative $C_7H_6{<}\substack{NAc\\N}{>}N$ [132°] is formed by the action of nitrous acid on the acetyl derivative of tolylene-o-diamine.—12. Boiling *chloro-acetic ether* forms oxytoluquinoxaline dihydride and a compound $C_{18}H_{16}N_2O_3$ (?) [147°], whence HNO_3 forms a compound [248°] (Hinsberg, *A.* 237, 365).—13. *Isatin* yields $C_{15}H_{11}N_3$ [290°], sl. sol. alcohol (Hinsberg, *A.* 237, 344).—14. Equal mols. of tolylene-o-diamine and *acetoacetic ether* when gently warmed together eliminate H_2O, and form a condensation product $C_{13}H_{18}N_2O_2$ [82°]; if this is heated at 100°–120° acetic ether is evolved, and a tolylene-ethenyl-o-diamine  $C_6H_3Me{<}\substack{NH\\N}{>}C.CH_3$ is produced (Ladenburg a. Rügheimer, *B.* 12, 953; Witt, *B.* 19, 2977, 3299).—15. *Chloro-aceto-acetic ether* forms $C_7H_6(NH)_2CMe.CHCl.CO_2Et$ [110°], crystallising in needles (Autenrieth a. Hinsberg, *B.* 25, 606).—16. *Oxydehydracetic acid* forms $C_8H_8O_5(C_6H_3Me(NH_2)_2)$ [147°] (Feist, *B.* 25, 325).—17. *o-Aldehydo-benzoic acid* in hot water forms  $C\,H_3Me{<}\substack{N\\NH}{>}C.C_6H_4.CO_2H$ [258°] (Bistrzycki, *B.* 23, 1043).—18. *Di-oxy-quinone* forms di-oxy-methyl-phenazine $C_{13}H_{10}N_2O_2$ [c. 265°], which yields a di-acetyl derivative [160°]. 19. *Opianic acid* gives, in alcoholic solution at 0°, the acid $C_6H_3Me:(N_2H):C.C_6H_2(OMe)_2.CO_2H$, crystallising in needles, decomposing at 234° (Bistrzycki, *B.* 24, 627).—20. *Di-bromo-pyruvic acid* (1 mol.) forms, on boiling,  $C_7H_6{<}\substack{N:C.CHBr_2\\N:C.OH}$ [235°].

Salts.—B''2HCl. Needles (Hübner, *A.* 209, 364).—$B''H_2SO_4$ 1½aq. Scales. S. 9·29 at 19·5°.—$B''2H_2C_2O_4$ aq (Hinsberg, *B.* 16, 1532).

Compound with pyrocatechin $B''C_6H_6O_2$. [78°]. Needles (from ligroïn) (Merz, *B.* 19, 726).

Compound with cyanogen $B''Cy_2$ aq. [c. 244°]. Formed by passing cyanogen into an alcoholic solution of the base (Bladin, *B.* 18, 666). Crystals, m. sol. alcohol and ether. Converted by heating with water into NH_3 and two isomeric compounds $C_9H_9N_3O$, one melting at 290°, the other beginning to decompose at 230°–240°. $B''Cy_2$ yields the salts $B''Cy_2HCl$ 1½aq, $B''Cy_22HCl$, $B''Cy_2H_2PtCl_6$ 2aq, minute needles, $(B''Cy_2)_2H_2PtCl_6$ 2aq, and $B''Cy_2H_2SO_4$ aq: minute tables.

p-Acetyl derivative
$C_6H_3Me(NH_2)(NHAc)$ [1:3:4]. [131°]. Formed by reducing $C_6H_3Me(NO_2)(NHAc)$ with iron and dilute HOAc (Boessneck, *B.* 19, 1757). Plates (from water). Converted by nitrous acid into acetyl-azimido-toluene. On distillation it yields tolylene-acetamidine $C_6H_3Me{<}\substack{N\\NH}{>}CMe$ [203°] (Niementowski, *B.* 25, 861).

Di-acetyl derivative $C_6H_3Me(NAcH)_2$. [216°]. Formed by boiling the base with Ac_2O (Bistrzycki, *B.* 23, 1878). Thin prisms (from water). Yields HOAc and tolylene-acetamidine on distillation.

Di-propionyl derivative
$C_6H_3Me(NH.CO.Et)_2$. [133°]. Formed in like manner (B.). Yields tolylene-propenyl-amine [166°] on distillation.

Benzoyl derivative
$C_6H_3Me(NH_2)(NHBz)$ [1:3:4]. [194°]. Formed by reduction of $C_6H_3Me(NO_2)(NHBz)$ with tin and HClAq (Hübner, *A.* 208, 314). Crystals, split up by distillation into water and tolylene-benzamidine [240°].

Di-benzoyl derivative $C_6H_3Me(NHBz)_2$. [264°]. Got by shaking tolylene-o-diamine with BzCl and NaOHAq (Hinsberg, *A.* 254, 255), by the action of Bz_2O on the diamine (Bistrzycki, *B.* 23, 1879; 24, 631), and by the action of BzCl on the benzoyl derivative (Hübner, *A.* 208, 314). Needles (from HOAc).

o-Chloro-benzoyl derivative
$C_6H_3Me(NH_2).NH.CO.C_6H_4Cl$. [153°] (Schreib, *B.* 13, 467). Converted by benzoyl chloride into $C_6H_3Me(NHBz).NH.CO.C_6H_4Cl$ [178°].

Di-cinnamyl derivative
$C_6H_3Me(NH.CO.C_8H_7)_2$. [206°]. Formed from tolylene-o-diamine and cinnamic anhydride (B.). Groups of small needles (from dilute alcohol).

Oxalyl derivative $C_2O_2(NH.C_7H_6.NH_2)_2$. [above 300°]. Obtained by the reduction of $C_2O_2(NH.C_7H_6.NO_2)_2$ (Hinsberg, *B.* 15, 2691). Small needles (from alcohol-ligroïn). On fusion it splits up into Aq and $C_{16}H_{14}N_4$ [193°].—Salts.—$B''H_2Cl_2$ aq.—$B''H_2PtCl_6$.—$B''H_2SO_4$ 5aq. Colourless needles.

Phthalyl derivatives.
The compounds $C_6H_3MeN_2H_2(C_8H_4O_2)$ [104°] and $C_6H_3Me(NC_8H_4O_2)_2$ [272°] are known (Biedermann, *B.* 10, 1165; Ladenburg, *B.* 10, 1125).

Benzene-sulphonyl derivative
$C_6H_3Me(NH_2).NH.SO_2Ph$. The hydrochloride, B'HCl, is formed by the action of benzene sulphonic chloride on tolylene-o-diamine in benzene (Bistrzycki a. Cybulski, *B.* 24, 633; *cf.* Lellmann, *A.* 221, 18).

Phenyl-acetyl derivative
$C_6H_3Me(NH_2).NH.CO.CH_2Ph$. [195°]. Formed from tolylene-o-diamine and phenylacetyl chloride (B. a. C.). Needles, v. sol. hot alcohol.

Di-phenylacetyl derivative
$C_6H_3Me(NH.CO.CH_2Ph)_2$. [176°]. Needles, insol. ether, v. sol. hot. alcohol.

References.—Bromo-, Chloro-, and Nitro-Tolylene-diamine.

TOLYLENE-DIAMINE SULPHINIC ACID *v.* Di-amido-toluene sulphinic acid.

TOLYLENE-*o*-DIAMINE SULPHONIC ACID $C_6H_2Me(NH_2)_2.SO_3H$ [1:2:3:5]. Formed by reducing nitro-toluidine sulphonic acid (Nietzki a. Pollini, *B.* 23, 139). Needles. Forms azines with o-diketones.

c-Tolylene-*m*-diamine sulphonic acid
$C_7H_{10}N_2SO_3$ *i.e.* $C_6H_2Me(NH_2)_2SO_3H$ [1:2:6:4]. S. ·07 at 14°. Formed from toluene *p*-sulphonic acid by nitration and reduction (Schwanert, *A.* 186, 360; Marckwald, *A.* 274, 349). Prisms, not melted at 280°.—BaA'_2 4aq.—HA'HCl 2aq.—HA'HBr 2aq.—$HA'HNO_3$ aq: needles, sl. sol. alcohol.—$(HA')_2H_2SO_4$ aq: plates.

Tolylene-*m*-diamine sulphonic acid
$C_6H_2Me(NH_2)_2.SO_3H$ [1:2:4:5]. S. ·1054 at 10°. Got by reduction of $C_6H_2Me(NO_2)(NH_2).SO_3H$ [1:2:4:5] with $SnCl_2$ (Limpricht a. Foth, *B.* 18, 2185; *A.* 230, 309). Small prisms.—KA' aq.—BaA'_2 5½aq.—HA'HCl aq.—HA'HBr aq: prisms,

Tolylene-*m* diamine sulphonic acid $C_6H_2Me(NH_2)_2.SO_3H$ [1:2:4:*x*]. Formed from tolylene-*m*-diamine and fuming H_2SO_4 (Wiesinger, *B.* 7, 464). Small prisms.—NaA′ 4aq.—KA′ aq.—MgA'_2 5aq.—CaA'_2 6½aq.—SrA'_2 7aq.—BaA'_2 6½aq.—MnA'_2 3aq.

TOLYLENE - DIAMINE THIOSULPHONIC ACID *v.* vol. i. p. 188.

TOLYLENE-BENZAMIDINE *v.* BENZENYL-TOLYLENE-DIAMINE.

TOLYLENE-BENZENYL-DIAMINE *v.* BENZENYL-TOLYLENE-DIAMINE.

***p*-TOLYLENE-BENZYL-DI-AMINE** [1:2:5] $C_6H_3Me(NH_2).NHCH_2Ph$. Got by reducing *p*-nitroso-benzyl-*o*-toluidine by alcoholic ammonium sulphide (Boeddinghaus, *A.* 263, 309).—B″2HCl. Needles, sl. sol. alcohol.

TOLYLENE BLUE $C_{15}H_{18}N_4HCl$. Formed by mixing solutions of nitroso-dimethyl-aniline hydrochloride and (1,2,4)-tolylene-*m*-diamine (Witt, *C. J.* 35, 358; *B.* 12, 931). Prisms (containing aq) with coppery lustre, forming blue solutions in water and alcohol. Acids turn the solutions reddish-brown. Alkalis pp. the base as a tarry mass. Tin and HClAq reduce it to the leuco- base, which forms a deliquescent hydrochloride and crystalline $(C_{15}H_{20}N_4)HSnCl_3$. On boiling tolylene-blue with water for some time part is reduced to leuco-tolylene blue and part oxidised to tolylene red $C_{15}H_{16}N_4$. Tolylene blue heated in aqueous solution containing HOAc for 12 hours at 40° forms tolylene violet $C_{14}H_{14}N_4$, characterised by an insoluble sulphate. Hydrated tolylene-violet $C_{14}H_{14}N_4$ aq is a scarlet powder which dissolves in alcohol and in ether, forming solutions with orange fluorescence.

Tolylene red

$$\left[1\begin{smallmatrix}3\\4\end{smallmatrix}\right] C_6H_3(NMe_2)\Big\langle\begin{smallmatrix}N\\N\end{smallmatrix}\Big\rangle C_6H_2Me(NH_2) \left[\begin{smallmatrix}3\\4\end{smallmatrix}:6:1\right]$$

(Bernthsen a. Schweitzer, *A.* 236, 332; Andresen, *B.* 19, 2217). Orange-red needles (containing 4aq). Forms a red fluorescent solution in alcohol. Its neutral salts are red, its acid salts are blue. By elimination of NH_2 by the diazo-reaction it is converted into di-methyl-amido-methyl-phenazine.

Isomeride of tolylene red

$$\left[1\begin{smallmatrix}3\\4\end{smallmatrix}\right] C_6H_3(NMe_2)\Big\langle\begin{smallmatrix}N\\N\end{smallmatrix}\Big\rangle C_6H_2Me(NH_2)\left[\begin{smallmatrix}3\\4\end{smallmatrix}5:1\right].$$

Formed from chloro-di-nitro-toluene and di-methyl-*p*-phenylene-diamine and reduction of the product (Witt, *B.* 25, 3008). Coppery needles, sol. warm water.

TOLYLENE-BUTENYL-DIAMINE *v.* BUTENYL-TOLYLENE-DIAMINE.

TOLYLENE-DICARBAMIC ETHER *v. i-*TOLYLENE-*m*-DIAMINE.

TOLYLENE DICYANATE $C_9H_6N_2O_2$ *i.e.* [1:2:4] $C_6H_3Me(N:CO)_2$. [94°]. Formed from tolylene *m*-diamine and $COCl_2$ (Snape, *C. J.* 49, 258). Needles, sol. ether. When heated with phenol at 130° it yields $C_6H_3Me(NH.CO_2Ph)_2$ [147·5°] crystallising in needles.

TOLYLENE-ETHENYL-DIAMINE $C_9H_{10}N_2$ *i.e.* $C_6H_3Me\Big\langle\begin{smallmatrix}N\\NH\end{smallmatrix}\Big\rangle CMe$. [203°] (Niementowski, *B.* 25, 861). (350°) (Nölting a. Witt, *B.* 17, 81). Formed by boiling (1,3,4)-tolylene-*o*-diamine with HOAc (Ladenburg, *B.* 8, 677) by reducing the acetyl derivative of nitro-*p*-toluidine (Hobrecker, *B.* 5, 920), and by adding aldehyde to a solution of tolylene-*o*-diamine in very dilute HOAc (Hinsberg, *B.* 20, 1589). Tables (from water). Forms with acetone and SO_2 the compound $(C_9H_{10}N_2C_3H_6O)SO_2$ (Boessneck, *B.* 21, 1909).—$B'_2H_2PtCl_6$.—$B'HNO_3$.

TOLYLENE-ETHENYL-ETHYL-DIAMINE $C_{11}H_{14}N_2$ *i.e.* $\begin{array}{l}CMe{:}CH.C.N\\CH\ {:}CH.C.NEt\end{array}\Big\rangle CMe$. [166°]. Formed from [1:3:4] $C_6H_3Me(NH_2).NHEt$ and Ac_2O (O. Fischer, *B.* 26, 200).

Tolylene-ethenyl-ethyl-diamine $\begin{array}{l}CMe{:}CH.C.NEt\\CH\ {:}CH.C.N\end{array}\Big\rangle CMe$. [93°]. Got by ethylation of tolylene-ethenyl-diamine (Hübner, *A.* 210, 351). Formed also by the action of aldehyde (2 mols.) on tolyene-*o*-diamine (1 mol.) (Hinsberg, *B.* 20, 1585) and by heating $C_6H_3Me(NO_2)NEtAc$ with zinc-dust and HOAc (Niementowski, *B.* 20, 1884). Needles (containing 3aq). Combines with ethyl iodide, forming B′EtI and $B'EtI_3$ [111°], which yield B′EtOH and $B'Et_2PtCl_6$. Salts.—K′HI aq [143°].—$B'HNO_3$ aq. [99°]. Melts at 95° when anhydrous.—$B'C_6H_3N_3O_7$. Crystals, sl. sol. alcohol.

TOLYLENE-ETHYL-DIAMINE $\begin{array}{l}CMe{:}CH.C.NH_2\\CH\ {:}CH.C.NHEt\end{array}$ [55°]. Formed by reduction of nitro-ethyl-*p*-toluidine (Gattermann, *B.* 18, 1184; Fischer, *B.* 26, 199). White plates, quickly blackened by light and air. Rotates on water.

Reactions.—1. Bisulphide of carbon yields $C_6H_3Me\Big\langle\begin{smallmatrix}N\\NEt\end{smallmatrix}\Big\rangle C.SH$ [139°].—2. Ac_2O forms tolylene-ethenyl-ethyl-diamine [166°].—3. Benzoic aldehyde yields $C_6H_3Me\Big\langle\begin{smallmatrix}N\\NEt\end{smallmatrix}\Big\rangle CPh$; while *o*- and *p*-nitro- and *o*-oxy- benzoic aldehydes from corresponding bodies [170°], [176°], and [78°].

Salts.—B′HCl. [176°].—$B'_2H_2C_2O_4$. [151°].

Tolylene-ethyl-diamine $C_6H_3Me(NHEt).NH_2$ [1:2:5]. (264° cor.). Formed by reducing nitroso-ethyl-*o*-toluidine (Koch, *A.* 243, 307). Oil, v. sol. ether.—B″2HCl. [124°]. Crystals, insol. ether.

Tolylene-ethyl-diamine $C_6H_3Me(NH_2)(NHEt)$ [1:2:4]. (282° uncor.). Formed by reduction of nitro-ethyl-*p*-toluidine (Nölting a. Stricker, *B.* 19, 549). Oil. Gives the reactions characteristic of *m*-diamines.

Tolylene-di-ethyl-diamine $C_6H_3Me(NHEt)_2$ [1:3:4]. (265° uncor.). Oil (Hinsberg, *A.* 265, 191). Turns black in air.

Tolylene-di-ethyl-diamine $C_6H_3Me(NEt_2)(NH_2)$ [1:2:5]. (240° i.V.). Formed by reducing nitro-di-ethyl-*o*-toluidine (Bernthsen, *B.* 25, 3138). Oil. $FeCl_3$ slowly gives a purple colour in an aqueous solution of the sulphate. $Na_2S_2O_3$ and $K_2Cr_2O_7$ added to its solution in HOAc slowly ppt. $SO_3H.S.C_6H_2Me(NEt_2)(NH_2)$ [210°-215°].—$B'H_2SO_4$. Large colourless tables.

DI-TOLYLENE-ETHYLENE-TETRA-AMINE *v.* ETHYLENE-DI-TOLYLENE-TETRA-AMINE.

TOLYLENE-DI-ETHYL-DI-THIO-DI-UREA [1:3:4] $MeC_6H_3(NH.CS.NHEt)_2$. [149°]. Got from ethyl mustard oil (5·5 g.) and tolylene-diamine (3 g.) in alcohol (15 c.c.) (Lellmann, *A.* 221, 23). V. sol. alcohol, more sol. HOAc, sl. sol. water. Decomposes when melted into tolylene-thio-urea, $Me.C_6H_3(NH)_2CS$, and $CS(NHEt)_2$.

(1.2.4)-Isomeride [225°]. Formed from tolylene-di-thio-di-urea and EtI at 105° (Lussy, *B.* 8, 668). Crystals.

TOLYLENE-DI-ETHYL-DI-UREA [1:2:4]$C_6H_3Me(NH.CO.NHEt)_2$. [175°]. Formed by heating tolylene-urea with EtI at 110° (Lussy, *B.* 8, 292). Crystals, v. sol. alcohol and ether.

TOLYLENE HYDRATE *v.* Phenyl-benzyl-carbinol.

DI-TOLYLENE KETONE OXIDE

$\left[1\begin{smallmatrix}3\\4\end{smallmatrix}\right]C_6H_3Me<\begin{smallmatrix}O\\CO\end{smallmatrix}>C_6H_3Me\left[\begin{smallmatrix}3\\4\end{smallmatrix}1\right]$. [166°]. Formed by heating oxytoluic acid with Ac_2O (Weber, *B.* 25, 1745). White flakes, sol. alcohol and ether.

TOLYLENE MERCAPTAN $C_6H_3Me(SH)_2$ [1:2:4]. *Dithiocresorcin.* [37°]. (263°) (Klason, *B.* 20, 355).

Di-tolylene mercaptan $HS.C_6H_3Me.C_6H_3Me.SH$. [113°]. Formed from the diazo- compound of di-amido-*o*-ditolyl by combination with potassium xanthate at 70°–75° and saponification of the resulting oil with alcoholic potash (Leuckart, *J. pr.* [2] 41, 214). Yellowish plates, v. sol. alcohol and ether.

Methyl ether [118°]. Needles.

TOLYLENE METHENYL-AMIDINE $C_8H_8N_2$ *i.e.* $C_6H_3Me<\begin{smallmatrix}N\\NH\end{smallmatrix}\gg CH$. [114°]. Formed by boiling from (1,3,4)-tolylene-diamine with formic acid (Ladenburg, *B.* 10, 1123; O. Fischer, *B.* 22, 644).—$B'_2H_2PtCl_6$. Yellow prisms.

TOLYLENE-METHENYL-DIAMINE *v.* Methenyl-tolylene-diamine and the preceding body.

TOLYLENE METHENYL - METHYL - DIAMINE $C_9H_{10}N_2$ *i.e.* $\begin{array}{l}CMe{:}CH.C.N\\CH\ {:}CH.C.NMe\end{array}\gg CH$. [94°]. Formed by heating $C_7H_6(NH_2).NHMe$ with formic acid (O. Fischer, *B.* 26, 195).

Isomeride $\begin{array}{l}CMe{:}CH.C.NMe\\CH\ {:}CH.C.N\end{array}\gg CH$. (279°). Formed by heating tolylene-methenyl-amidine with MeI (O. Fischer, *B.* 22, 644). Formed also from (1,3,4)-tolylene-diamine and formic aldehyde (Fischer a. Wreszinski, *B.* 25, 2711). Oil. —B'HI aq.—B'HCl. Prisms (from HClAq).

TOLYLENE-METHYL-DIAMINE [1:3:4] $C_6H_3Me(NH_2).NHMe$. [44°]. Formed by reducing nitro-methyl-*p*-toluidine (Gattermann, *B.* 18, 1487; O. Fischer, *B.* 26, 194). Formed also by heating methyl-*p*-amido-toluene-azo-benzene sulphonic acid with $SnCl_2$ and HClAq (Bamberger a. Wulz, *B.* 24, 2082). Four-sided tables.

Reactions.—1. *Acetic anhydride* yields $C_7H_6<\begin{smallmatrix}NH\\NMe\end{smallmatrix}\gg CMe$ [142°].—2. CS_2 reacts, forming $C_7H_6<\begin{smallmatrix}NH\\NMe\end{smallmatrix}>CS$ [194°].—3. *Benzoic aldehyde* forms $C_7H_6<\begin{smallmatrix}N\\NMe\end{smallmatrix}\gg CPh$ [127°], while *o*-nitro- and *o*-oxy-benzoic aldehyde form corresponding bodies [153°] and [180°].

Salts.—B'HCl. [175°-180°]. Plates (from alcohol).—$B'H_2C_2O_4$. [124°].—$B'C_6H_3N_3O_7$. [164°].

Tolylene-di-methyl-diamine $C_6H_3Me(NMe_2)(NH_2)$ [1:5:2]. [28°]. (270°). Formed by reducing nitroso-di-methyl-*m*-toluidine (Wurster a. Riedel, *B.* 12, 1801; 13, 126). Needles or prisms; v. sol. water, alcohol, and ether. Yields toluquinone on oxidation.

Acetyl derivative [158°].—$B'_2H_2PtCl_6$4aq.

Tolylene-di-methyl-diamine $C_6H_3Me(NMe_2)(NH_2)$ [1:2:5]. [47°]. (240° i.V.). Formed by reducing nitro-di-methyl-*o*-toluidine (Bernthsen, *B.* 25, 3134). $FeCl_3$ gives an intense bluish-red colour in neutral solutions. $Na_2S_2O_3$ and $K_2Cr_2O_7$ added to the acetic acid solution ppt. $C_6H_2Me(NMe_2)(NH_2)S.SO_3H$ [c. 240°]. **Salt.**—$B'_2H_2SO_4$. Needles, v. e. sol. water.

Tolylene-tetra-methyl-diamine $C_6H_3Me(NMe_2)_2$ [1:2:5]. (c. 260°). Formed by heating the preceding body with MeOH and HCl at 180° (W. a. R.). Liquid. Coloured blue in aqueous solution by $FeCl_3$.

Methylo-iodide B'MeI. [160°]. Needles.

Tolylene-tetra-methyl-diamine $C_6H_3Me(NMe_2)_2$[1:3:4]. (226°) at 717 mm. Got by methylation (Niementowski, *B.* 20, 1888). Liquid, v. sl. sol. water. $FeCl_3$ at 40° to 50° gives a reddish-brown colour. HNO_3 added to its solution in H_2SO_4 gives a red colouration.—$B'_2H_2PtCl_6$.—$B'HHgCl_3$.—$B'C_6H_3N_3O_7$. Yellow tables.

Reference.—Nitro-tolylene-tetra-methyl-diamine.

TOLYLENE-METHYL-ETHENYL-AMIDINE $C_{10}H_{12}N_2$ *i.e.* $\begin{array}{l}CMe{:}CH.C.N\\CH\ {:}CH.C.NMe\end{array}\gg CMe$. [142°]. Formed, together with $C_{10}H_{12}N_2O$ [163°], which crystallises with 2aq, by reducing the compound $C_6H_3Me(NO_2).NMeAc$ (Niementowski, *B.* 20, 1878), and by acting on tolylene-methyl-diamine with Ac_2O (O. Fischer, *B.* 26, 196). Needles (from hot water). $B'_2H_2PtCl_6$ (dried at 100°). [234°-244°].—B'HCl ½aq.—B'MeI. [221°]. —B'MeOH. [115°-135°].

TOLYLENE-TETRA-METHYL DI-PYRROLE TETRACARBOXYLIC ACID $C_{23}H_{22}N_2O_8$ *i.e.* [1:2:4]$C_6H_3Me\left(N<\begin{array}{l}CMe{:}C.CO_2H\\CMe{:}C.CO_2H\end{array}\right)_2$. [248°]. Sl. sol. hot alcohol and ether.

Ethyl ether Et_4A^{iv}. Formed by heating di-acetyl-succinic ether with tolylene-*m*-diamine and HOAc at 150° (Knorr, *A.* 236, 314). Oil.

TOLYLENE-METHYL-THIO-UREA $\begin{array}{l}CMe{:}CH.C.NH\\CH\ {:}CH.C.NMe\end{array}>CS$. [194°]. Formed from $C_7H_6(NH_2)(NHMe)$ and CS_2 (Fischer, *B.* 26, 196). Needles (from alcohol).

TOLYLENE-DI-OXAMIC ACID $C_{11}H_{10}N_2O_6$ *i.e.* $C_6H_3Me(NH.CO.CO_2H)_2$ [1:2:4]. Formed, together with the amide, by the action of alcoholic NH_3 on the ether. Crystalline. Very sweet. Decomposed by warm KOHAq into oxalic acid and tolylene-diamine.—Ag_2A''.—PbA''.—BaA'' 2aq.

Di-amide $C_6H_3Me(NH.CO.CONH_2)_2$[1:2:4]. Formed from the ether and alcoholic ammonia (Schiff, *A.* 268, 333). White powder, m. sol. alcohol.

Ethyl ether [1:2:4] $C_6H_3Me(NH.CO.CO_2Et)_2$. [130°]. Formed by boiling $C_6H_3Me(NH_2).NH.CO.CO_2Et$ with alcohol and oxalic ether (Schiff a. Vanni, *A.* 268, 340). Small needles (from ether).

Amide - ether $C_6H_3Me<\begin{array}{l}NH.CO.CO_2Et\\NH.CO.CO.NH_2\end{array}\left[1{:}\begin{smallmatrix}2\\4\end{smallmatrix}\right]$ [210°]. Formed from $C_6H_3Me(NH_2).NH.CO.CO.NH_2$ by boiling with alcohol and oxalic ether (Schiff, *A.* 268, 341).

Amide ether $C_6H_3Me{<}\begin{smallmatrix}NH.CO.CONH_2\\NH.CO.CO_2Et\end{smallmatrix}\left[1\begin{smallmatrix}2\\4\end{smallmatrix}\right]$ [c. 220°]. Got by fusing $C_6H_3Me(NH_2).NH.CO.CO_2Et$ with oxamic ether.

TOLYLENE-OXAMIDE $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C_2O_2$. [c. 260°]. Formed from (1,2,4)-tolylene-diamine and chloro-glyoxylic ether, and also by heating tolylene-diamine oxalate to 160° (Schiff a. Vanni, *A.* 268, 312).

TOLYLENE-PENTENYL-DIAMINE $\left[1\begin{smallmatrix}3\\4\end{smallmatrix}\right]$ $C_6H_3Me{<}\begin{smallmatrix}N\\NH\end{smallmatrix}{\gg}C.C_4H_9$. [116°]. Formed by reducing the valeryl derivative of nitro-*p*-toluidine (Friederici, *B.* 11, 1974; Hübner, *A.* 209, 365). Prisms (from ligroïn), v. e. sol. alcohol.

TOLYLENE - DI - PHENYL - DI - AMIDO-METHYLENE-DIAMINE $C_{20}H_{20}N_4$ *i.e.* $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C(NHPh)_2$. [161°]. Formed from $C(NPh)_2$ and (1,3,4)-tolylene-diamine at 130°-149° (Dahm a. Gasiorowski, *B.* 19, 3057). Needles (from benzene), v. sol. alcohol.—B'_23HCl. [171°].—$B'H_2SO_4$. Plates, v. sol. water and alcohol.

TOLYLENE-PROPENYL-DIAMINE $C_6H_3Me{<}\begin{smallmatrix}NH\\N\end{smallmatrix}{\gg}CEt$. [166°]. Formed by distilling the dipropionyl derivative of tolylene-*o*-diamine (Bistrzycki, *B.* 23, 1879). Needles, m. sol. water, almost insol. ligroïn.

TOLYLENE RED *v.* TOLYLENE BLUE.

DI-TOLYLENE DISULPHIDE $\begin{array}{l}CMe{:}CH.C.S.C.CH{:}CH\\ CH\ {:}CH.C.S.C.CH{:}CMe\end{array}$. [116°]. Formed by the action of heat at 200°-250° on tolylene diazo-sulphide $C_6H_3Me{<}\begin{smallmatrix}N\\S\end{smallmatrix}{\gg}N$ [43°], obtained from ethenyl-amido-tolyl mercaptan and HNO_2 (Jacobson a. Ney, *B.* 22, 911). Conc. H_2SO_4 gives an intense blue colour.

TOLYLENE - DI - THIO - DI - CARBAMIC ETHER [1:3:4] $C_6H_3Me(N{:}C(SH).OEt)_2$ [120°]. Formed by boiling tolylene-di-thiocarbimide with alcohol (Billeter a. Steiner, *B.* 20, 230). Plates (from benzene). Yields a yellowish-white silver salt.

TOLYLENE - DI - THIOCARBIMIDE [1:2:4] $C_6H_3Me(N.CS)_2$. [56°]. (c. 300°). Formed from tolylene-*m*-diamine and $CSCl_2$, and also by heating tolylene-di-thio-di-urea with conc. HClAq (Billeter a. Steiner, *B.* 18, 3292; 20, 230). Needles. Converted by NH_4Aq into tolylene-di-thio-di-urea [206°], by aniline into di-phenyl-tolylene-di-thio-di-urea [168°]. Copper at 250° produces $C_6H_3MeCy_2$ [141°].

Tolylene-di-thiocarbimide [1:3:4] $C_6H_3Me(N.CS)_2$. [42°]. Formed from an aqueous solution of tolylene-*o*-diamine hydrochloride and $CSCl_2$ in $CHCl_3$ (B. a. S.). Plates. Converted by HCl at 200° into *o*-tolylene-thio-urea.

TOLYLENE-DI-THIO-DIGLYCOLLIC ACID $C_6H_3Me(S.CH_2.CO_2H)_2$. [152°]. Formed from thio-orcin $C_6H_3Me(SH)_2$ [35°], chloro-acetic acid, and NaOHAq (Gabriel, *B.* 12, 1640). Needles, m. sol. hot Aq.

TOLYLENE THIO-UREA $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}CS$. Formed from $C_6H_3Me(NH_2HCl)_2$ [1:2:3] and excess of NH_4SCN by boiling with water, evaporating, and heating to 120° (Lellmann, *A.* 228, 245). Small red crystals (from alcohol). Does not melt below 326°; may be sublimed. Insol. water, sl. sol. alcohol, dissolved by warm NaOH; re-ppd. by HCl. When boiled with lead acetate and excess of NaOH, no PbS is formed.

Tolylene - thio - urea $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}CS$. [284°]. Formed by heating (1,3,4)-tolylene-*o*-diamine sulphocyanide at 130° (Lellmann, *A.* 221, 10]. Formed also by the action of alcoholic NH_3 on *o*-tolylene di-thiocarbimide (Billeter a. Steiner, *B.* 20, 231). Silvery plates, sol. alcohol, HOAc, and cold NaOHAq, sl. sol. water and $CHCl_3$.

m-**Tolylene - thio - urea** $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}CS$. [119°]. Formed from (1,2,4)-tolylene-diamine and alcoholic CS_2 (Lussy, *B.* 8, 293). Crystalline powder, v. e. sol. alcohol.

m-**Tolylene-di-thio-di-urea** [1:2:4] $C_6H_3Me(NH.CS.NH_2)_2$. [218°] (L.); [200°] (B. a. S.). Formed by heating tolylene-*m*-diamine sulphocyanide (Lussy, *B.* 7, 1265; Gebhardt, *B.* 17, 3046; Billeter a. Steiner, *B.* 18, 3293; 20, 228). Crystalline powder, insol. water and ether, nearly insol. alcohol, m. sol. hot HOAc.

TOLYLENE-TOLENYL-AMIDINE $C_{15}H_{14}N_2$ *i.e.* $C_6H_3Me{<}\begin{smallmatrix}NH\\N\end{smallmatrix}{\gg}C.C_6H_4Me$. Formed by reducing [1:4] $C_6H_4Me.CO.NH.C_6H_3(NO_2)Me$ [4:3:1] (Hübner, *A.* 210, 331). Needles, sl. sol. water.—$B'HCl$.—$B'HNO_3$.—$B'_2H_2SO_4$. Crystals, sl. sol. water.

TOLYLENE - DI - *p* - TOLYL - DI - AMIDO-METHYLENE-DIAMINE $C_{22}H_{24}N_4$ *i.e.* $C_6H_3Me{<}\begin{smallmatrix}NH\\NH\end{smallmatrix}{>}C(NH.C_6H_4Me)_2$. [196°]. Formed by heating $C(NC_6H_4Me)_2$ with (1,3,4)-tolylene-diamine (Dahm a. Gasiorowski, *B.* 19, 3059). Needles (from alcohol).—B'_23HCl. [143°]. Deliquescent needles, v. sol. water.

TOLYLENE-TOLYL-DIAMINE $C_{14}H_{16}N_2$ *i.e.* [1:3:4] $C_6H_3Me(NH_2)NHC_6H_4Me$ [1:4]. *Amido-di-p-tolyl-amine.* [109°]. Formed by reducing nitro-di-*p*-tolylamine (O. Fischer, *B.* 23, 3798; 26, 187). Prisms (from ligroïn), turning brownish-red in air. H_2SO_4 forms a blue solution changing to green. $FeCl_3$ forms $C_{28}H_{27}N_5O$ [188°] crystallising in red plates, yielding $B'_2H_2PtCl_6$. Boiling with acetic anhydride and sodium acetate produces $C_7H_6{<}\begin{smallmatrix}N(C_7H_7)\\N\end{smallmatrix}{\gg}CMe$ [95°], which forms $B'_2H_2PtCl_6$. Benzoic aldehyde forms $C_7H_6{<}\begin{smallmatrix}N(C_7H_7)\\NH\end{smallmatrix}{>}CHPh$ [156°], which yields $(C_{21}H_{20}N_2)_2H_2PtCl_6$ and $C_{21}H_{20}N_2HAuCl_4$.

Salts.—$B'H_2C_2O_4$. Nearly insol. cold Aq.—$B'C_6H_3N_3O_7$. Brownish-red crystals.

Acetyl derivative [126°]. Prisms.

Tolylene-*p*-tolyl-diamine [1:4:3] $C_6H_3Me(NH_2).NHC_6H_4Me$ [1:4]. [107°]. Formed from toluene-azo-toluene or *s*-di-*p*-tolyl-hydrazine (hydrazo-toluene) in alcoholic solution by the action of $SnCl_2$ and HCl (Täuber, *B.* 25, 1022; *cf.* Melms, *B.* 8, 554; Goldschmidt, *B.* 11, 1626). Plates, v. e. sol. alcohol. $NaNO_2$ colours its solution in H_2SO_4 deep blue (?). Benzoic aldehyde reacts, forming

$C_7H_6\left<\begin{matrix}N(C_7H_7)\\N\end{matrix}\right>CPh$ [165°] (*cf.* Lellmann, *B.* 15, 832). Benzil in alcohol and HCl forms $C_{28}H_{24}N_2O$ [173°]. Ethyl nitrite and H_2SO_4 added to its alcoholic solution form the azimide $C_7H_6\left<\begin{matrix}N(C_7H_7)\\N\end{matrix}\right>N$ [93°]. On oxidation together with *p*-toluidine it forms the ditoluide of amido-toluquinone (Green, *C. J.* 63, 1408).

Tolylene-di-*p*-tolyl-diamine [1:2:5] $C_6H_3Me(NHC_7H_7)_2$. [113°]. Formed by heating hydrotoluquinone (40 g.) with *p*-toluidine (160 g.) and $ZnCl_2$ (80 g.) to 200°–280° for 5 hours (Green, *C. J.* 63, 1408). Plates, sol. HOAc, insol. water.

TOLYLENE-*p*-TOLYL-GUANIDINE $C_6H_3Me\left<\begin{matrix}NH\\NH\end{matrix}\right>C:NC_7H_7$. [198°]. Formed from tolylene-*o*-diamine and $C(NC_7H_7)_2$ (Keller, *B.* 24, 2518). Prisms (from alcohol), or tables (from benzene). Phenyl cyanate forms the compound $C_7H_6\left<\begin{matrix}N\\N\end{matrix}\right>C:NC_7H_7\left<\begin{matrix}CO\\CO\end{matrix}\right>NPh$ [233°], crystallising from hot alcohol in needles.—B'HCl.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$ 5aq. Needles, sl. sol. cold water.

Acetyl derivative $C_7H_6\left<\begin{matrix}NAc\\NH\end{matrix}\right>C:NC_7H_7$. [149°]. Needles, v. sol. alcohol.

Di-benzoyl derivative [201°]. Needles.

Nitrosamine $C_7H_6:N_2H(NO):C:NC_7H_7$. [c. 140°]. Decomposed on fusion.

TOLYLENE-*p*-TOLYL-THIO-UREA $\left.\begin{array}{l}CH:CH.C.N(C_7H_7)\\CMe:CH.C.NH\end{array}\right>CS$. [270°]. Formed from tolylene-tolyl-diamine and CS_2 in alcohol (Fischer a. Sieder, *B.* 23, 3799). Prisms, insol. water, sl. sol. ligroïn. Conc. H_2SO_4 forms a green solution.

TOLYLENE-UREA $C_8H_8N_2O$ *i.e.* $\left[1:\begin{matrix}3\\4\end{matrix}\right]C_6H_3Me\left<\begin{matrix}NH\\NH\end{matrix}\right>CO$. [292°]. Formed by heating tolylene-*o*-diamine with urea and got also by the action of HClAq at 140° on $C_6H_3Me\left<\begin{matrix}NH\\N\end{matrix}\right>C.OEt$ [163°], which is formed by the action of $HN:C(OEt)_2$ on tolylene-*o*-diamine hydrochloride (Sandmeyer, *B.* 19, 2651). Formed also by heating $C_7H_6(NH_2).NH.CO.NPh_2$ (Lellmann a. Bonhöffer, *B.* 20, 2124) or the compound $C_7H_6(NH_2).NH.CO.NHPh$ (Leuckart, *J. pr.* [2] 41, 324, who states that it melts above 300°), and by heating tolylene-*o*-diamine in benzene with $COCl_2$ in toluene in sealed tubes at 100° (Hartmann, *B.* 23, 1048). Needles, sl. sol. hot water.—B'HCl: prisms.

TOLYLENE-DI-UREA $C_9H_{12}N_4O_2$ *i.e.* [1:3:4] $C_6H_3Me(NH.CO.NH_2)_2$. [282°]. Got from tolylene-diamine hydrochloride and potassium cyanate in aqueous solution (Lellmann, *A.* 228, 14). Needles, sl. sol. water and chloroform, sol. alcohol and hot conc. HCl; v. sol. HOAc.

Tolylene-di-urea $C_9H_{12}N_4O_2$ *i.e.* [1:2:4] $C_6H_3Me(NH.CO.NH_2)_2$. [220°]. Formed from tolylene-*m*-diamine sulphate and KCyO (Strauss, *A.* 148, 157). Formed also from tolylene cyanate and ammonia (Lussy, *B.* 8, 291). Scales, sl. sol. alcohol and hot water.—B''2HCl.

TOLYLENE-VIOLET *v.* TOLYLENE BLUE.

***s*-DI-TOLYL-ETHANE** $C_6H_4Me.CH_2.CH_2.C_6H_4Me$. (296°). Formed from $C_6H_4Me.CH_2Cl$ and sodium (Vollrath, *Z.* 1866, 489). Oil.

***u*-Di-*p*-tolyl-ethane** $CH_3.CH(C_6H_4Me)_2$. (295°). S.G. $\frac{20}{4}$ ·974. Formed by shaking paraldehyde with toluene and H_2SO_4 at 0° (O. Fischer, *B.* 7, 1191). Formed also by heating di-α-tolyl-propionic acid with lime (Haiss, *B.* 15, 1476) and by the action of ethylidene chloride and $AlCl_3$ on toluene (Anschütz, *B.* 18, 664; *A.* 235, 315). Oil. Yields toluyl-benzoic acid and di-tolyl ketone on oxidation.

***s-mp*-Di-tolyl-ethane** $C_2H_4(C_7H_7)_2$. (297°–300°). Formed from ethylene bromide, toluene, and $AlCl_3$ (Friedel a. Balsohn, *Bl.* [2] 35, 52; *A. Ch.* [6] 1, 487). Yields isophthalic and terephthalic acids on oxidation.

References.—AMIDO-, CHLORO-, TRI-CHLORO-, DI-NITRO-, and OXY-TOLYL-, ETHANES.

TOLYL ETHER *v.* DI-TOLYL OXIDE.

***o*-TOLYL-ETHYL ALCOHOL.** *Hexahydride* $CH_2\left<\begin{matrix}CH_2.CHMe\\CH_2.CH_2\end{matrix}\right>CH.CHMe.OH$. (195°–200°). Formed, together with the tetrahydride $CH_2\left<\begin{matrix}CH_2.CMe\\CH_2.CH_2\end{matrix}\right>C.CHMe.OH$ (142° at 50 mm.) by reducing $C_6H_8Me.CO.CH_3$ in moist ethereal solution by sodium (Kipping a. Perkin, jun., *C. J.* 57, 22). Oil. Yields an acetyl derivative (204°–208°).

***p*-TOLYL-ETHYL-*m*-AMIDO-PHENOL.** *Ethyl derivative* $C_7H_7.NEt.C_6H_4.OEt$. Formed from $C_7H_7.NH.C_6H_4.OH$, potash, and EtI (Hatschek a. Zega, *J. pr.* [2] 33, 217). Oil.

***p*-Tolyl-ethyl-*p*-amido-phenol.** *Ethyl derivative* $C_{17}H_{21}NO$ *i.e.* $C_7H_7.NEt.C_6H_4.OEt$. (c. 340°). From $C_7H_7.NH.C_6H_4.OH$, potash, and EtI (H. a. Z.). Oil.

TOLYL-ETHYL-AMINE *v.* ETHYL-TOLUIDINE.

Di-tolyl-ethyl-amine $(C_6H_4Me)_2NEt$. (255°–260° at 20 mm.). Formed by heating di-*p*-tolyl-amine with EtOH and HCl at 250°–280° (Girard, *Bl.* [2] 24, 120). Oil.

***o*-TOLYL ETHYL CARBONATE** $C_{10}H_{12}O_3$ *i.e.* [1:2] $C_6H_4Me.O.CO.OEt$. (236°). Formed from sodium *o*-cresol and $ClCO_2Et$ (Bender, *B.* 13, 700). Oil.

***m*-Tolyl ethyl carbonate.** (246°). Formed in like manner from *m*-cresol. Oil.

***p*-Tolyl ethyl carbonate.** (245°). Oil. By long heating at 300° it yields di-*p*-tolyl carbonate and di-ethyl carbonate (Bender, *B.* 19, 2268).

DI-*p*-TOLYL-ETHYLENE $C_{16}H_{16}$ *i.e.* $C_6H_4Me.CH:CH.C_6H_4Me$. *Di-methyl-stilbene.* [179°]. (above 300°). Formed by distilling $(C_6H_4Me)_2CH.CCl_3$ with zinc-dust (Goldschmiedt a. Hepp, *B.* 6, 1504; Elbs a. Förster, *J. pr.* [2] 39, 300), and by heating di-*p*-tolyl fumarate, CO_2 being evolved (Anschütz, *B.* 18, 1948). Plates, v. sol. $CHCl_3$. Yields a dibromide [204°].

***u*-Di-tolyl-ethylene** $CH_2:C(C_6H_4Me)_2$. (305°). Formed by the action of alcoholic potash on $CH_2Cl.CH(C_7H_7)_2$ (Hepp, *B.* 7, 1413). Oil. Yields di-tolyl-ketone [94°] on oxidation.

Tetra-tolyl-ethylene $C_{30}H_{28}$ *i.e.* $(C_7H_7)_2C:C(C_7H_7)_2$. [215°]. A product of the action of chloroform and $AlCl_3$ on toluene (Schwarz, *B.* 14, 1529). Plates, with greenish-yellow fluorescence, sol. benzene.

References.—BROMO- and DI-CHLORO- TOLYL-ETHYLENE.

o-TOLYL-ETHYLENE-DIAMINE $C_7H_7NH.C_2H_4.NH_2$. (c. 267°). Formed from o-tolylamido-ethyl-phthalimide and HCl (Newman, *B.* 24, 2194). Sol. water and alcohol.—$B''2HCl$. [168°–173°].—$B''2C_6H_3N_3O_7$. [148°]. Green needles.

Di-benzoyl derivative [164·5°]. Needles.

p-Tolyl-ethylene-diamine. Formed in like manner (N.). Liquid.—$B''2HCl$. [218°].—$B''H_2PtCl_6$. Yellowish plates.

Di-acetyl derivative [107°]. Needles.

Di-benzoyl derivative [161°]. Cubes.

Di-o-tolyl-ethylene-diamine $C_{16}H_{20}N_2$ *i.e.* $C_7H_7NH.CH_2.CH_2.NHC_7H_7$. [71°]. S. ·3 at 100°. S. (cold alcohol) 9. S. (ether) 14. Formed by the action of o-toluidine on ethylene bromide in presence of Na_2CO_3 (Bischoff, *B.* 23, 1982, 2031; 25, 3257; *cf.* Mauthner a. Suida, *M.* 7, 230; Colson, *Bl.* [2] 48, 799). Plates (from ligroïn), v. sol. alcohol. Yields indole on heating with zinc-dust. $CH_2Cl.CO_2H$ and NaOAc from di-tolyl-pyrazine hexahydride [154°].—$B''2HCl$.—$B''H_2PtCl_6$.—$B''H_2SO_4$ (dried at 100°).—$B''2HBr$. [222°]. S. 3 at 100°.

Acetyl derivative $C_2H_4(NAc.C_7H_7)_2$. [153°].

Bromo-acetyl derivative $C_2H_4(NC_7H_7.CO.CH_2Br)_2$. [205°]. Sl. sol. cold HOAc and ligroïn.

Bromo-propionyl derivative $C_{22}H_{26}N_2Br_2O_2$. [181°].

Bromo-n-butyryl derivative $(C_{24}H_{30}N_2Br_2O_2)C_6H_6$ (from benzene). [190°].

Bromo-isobutyryl derivatives $C_7H_7NH.C_2H_4.NC_7H_7.CO.CBrMe_2$ [137°] and $C_{24}H_{30}N_2Br_2O_2$ [173°].

Di-p-tolyl-ethylene-diamine [97·5°]. Formed by heating p-toluidine with ethylene bromide at 150° (Gretillat, *M. S.* [3] 3, 383; Bischoff, *B.* 25, 3260). Crystals, v. e. sol. alcohol.—*Hydrobromide* [255°].

Acetyl derivative $C_2H_4(NAc.C_7H_7)_2$. [139°].

Bromo-acetyl derivative $C_{20}H_{22}N_2Br_2O_2$. [196°].

Bromo-propionyl derivative. [182°].

Bromo-n-butyryl derivative $C_{24}H_{30}N_2Br_2O_2$. [125°].

Bromo-isobutyryl derivative $C_{24}H_{30}N_2Br_2O_2$. [175°].

Di-o-tolyl-di-ethylene-diamine $C_{18}H_{22}N_2$. [171°]. Formed, together with di-o-tolyl-ethylene-diamine, by heating o-toluidine with $C_2H_4Br_2$ (M. a. S.). Needles, sl. sol. alcohol. Forms indole when distilled with zinc-dust.

Di-p-tolyl-di-ethylene-diamine [190°]. (360°). Formed by heating $C_2H_4Cl.OH$ with p-toluidine at 220° (Wurtz, *A. Suppl.* 7, 94; Demole, *A.* 173, 138). Prisms, v. sl. sol. alcohol.—$B''H_2PtCl_6$.

Tri-p-tolyl-tri-ethylene-triamine $N_3(C_7H_7)_3(C_2H_4)_3$. [186°]. Formed by heating p-toluidine with $C_2H_4Br_2$ (G.). Needles, v. sl. sol. alcohol. Is perhaps identical with the preceding body. Its hydrochloride melts at 189°.

Reference.—NITRO-DI-TOLYL-ETHYLENE-DIAMINE.

p-TOLYL ETHYLENE ETHYL DIOXIDE $C_6H_4Me.O.CH_2.CH_2.OEt$. (244°). Formed from $C_7H_7.O.C_2H_4Br$ and alcoholic potash (Schreiber, *B.* 24, 195).

DI-p-TOLYL ETHYLENE DIKETONE $C_{18}H_{18}O_2$ *i.e.* $C_2H_4(CO.C_6H_4Me)_2$. *Di-toluyl-ethane.* [159°]. Formed by the action of succinyl chloride and $AlCl_3$ on toluene (Hollemann, *R. T. C.* 6, 70; Claus, *B.* 20, 1877). Needles, v. sl. sol. cold alcohol, insol. alkalis. AcCl converts it into di-p-tolyl-furfurane $C_{18}H_{16}O$ [164°]. Ammonium acetate and HOAc on boiling form di-p-tolyl-pyrrole [197°]. P_2S_5 forms di-p-tolyl-thiophene [171°].

DI-p-TOLYL-ETHYLENE-DI-METHYL-DI-AMINE $C_{18}H_{24}N_2$ *i.e.* $C_2H_4(NMe.C_6H_4Me)_2$. [80°]. Formed by boiling its di-methylo-di-bromide with NH_3Aq (Hübner, *A.* 224, 337). Tables or prisms (from alcohol), v. sl. sol. water.—$B''H_2HgCl_4$. [190°].—$B''H_2PtCl_6$. Orange-yellow powder.

Methylo-iodide $B''MeI$. Needles. Decomposed at 100°. M. sol. hot water.

Methylo-bromide $B''2MeBr$. Formed by heating di-methyl-p-toluidine with $C_2H_4Br_2$ at 105° for some days. Yields $B''Me_2Hg_2Cl_6$ [159°–162°], $B''Me_2SnCl_6$, $B''Me_2PtCl_6$, and $B''2C_6H_2MeN_3O_7$ [197°], which crystallises from alcohol.

TOLYL ETHYLENE OXIDE *v.* ETHYLENE ETHER OF CRESOL.

DI-p-TOLYL ETHYLENE DISULPHONE $(C_7H_7.SO_2)_2C_2H_4$. [201°]. Made by boiling sodium toluene p-sulphinate with $C_2H_4Br_2$ and alcohol (Otto, *J. pr.* [2] 30, 351; 40, 534). Got also by boiling the same salt with $CH_3.CCl_2.CO_2Na$. Needles or plates. Dilute KOHAq converts it into toluene sulphinic acid and $C_7H_7.SO_2.C_2H_4.OH$ [55°], which yields $C_7H_7.SO_2.C_2H_4Cl$ [79°], $C_7H_7.SO_2.C_2H_4I$ [100°], $C_7H_7.SO_2.C_2H_4OBz$ [176°] and $(C_7H_7.SO_2.C_2H_4)_2S$ [150°–160°]. Ammonia forms $(C_7H_7.SO_2.C_2H_4)_2NH$, which yields a hydrochloride [201°].

DI-p-TOLYL-ETHYLENE-UREA $\begin{matrix}CH_2.N(C_7H_7)\\CH_2.N(C_7H_7)\end{matrix}\Big>CO$. [228°]. Formed from di-p-tolyl-ethylene-diamine and $COCl_2$ (Michler a. Keller, *B.* 14, 2181). Needles.

p-TOLYL-DI-ETHYL-PHOSPHINE $C_7H_7.PEt_2$. (240°). Formed from $C_7H_7PCl_2$ and $ZnEt_2$ (Czimatis, *B.* 15, 2016). Liquid.—$B'MeI$. [137°].—$B'_2Me_2PtCl_6$. Yellow plates.

p-TOLYL ETHYL SULPHONE $C_7H_7.SO_2.C_2H_5$. [56°]. Formed by oxidation of $C_7H_7.SEt$ and by the action of EtBr on sodium toluene p-sulphinate (Otto, *B.* 13, 1276; 18, 161). Formed also by warming the acid $C_7H_7.SO_2.CHMe.CO_2H$ with KOHAq. Trimetric plates; $a:b:c$ = ·526:1:·721. Sol. alcohol and ether.

p-TOLYL ETHYL SULPHONE α-CARBOXYLIC ACID $C_7H_7.SO_2.CHMe.CO_2H$. *Tolyl-sulphono-propionic acid.* [37°]. Formed by heating $C_7H_7.SO_2Na$ with $CH_3.CHBr.CO_2Et$ and alcohol at 150° and saponifying the product (Otto, *J. pr.* [2] 40, 555). Crystals (from alcohol), converted by Cl into $CH_3.CHCl.SO_2.C_7H_7$.

TOLYL ETHYL DISULPHOXIDE *v.* *Ethyl ether* of TOLUENE THIOSULPHONIC ACID.

TOLYL ETHYL THIOBIURET $C_{11}H_{15}N_3S_2$. [134°]. Formed from tolyl-thiobiuret, alcohol, aqueous NH_3, and EtI (Tursini, *B.* 17, 585). Needles (from alcohol).

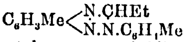
o-TOLYL-ETHYL-THIOSEMICARBAZIDE $C_7H_7NH.NH.CS.NHEt$. [180°]. Formed o-tolyl-hydrazine and an alcoholic solution of ethyl-thiocarbimide (Dixon, *C. J.* 57, 262). Needles, v. sl. sol. cold water. $CuSO_4$ colours its alcoholic solution deep blue.

TOLYL ETHYL DI-THIO-CARBONATES $CS(OEt).S.C_6H_4Me$. The *o*-, *m*-, and *p*- compounds formed by the action of potassium xanthate on cold solutions of *o*-, *m*-, and *p*-diazotoluene chloride are oils (Leuckart, *J. pr.* [2] 41, 188). They are converted into tolyl mercaptans by boiling with alcoholic potash.

***o*-TOLYL-ETHYL-THIO-UREA** $CS(NHEt).NHC_6H_4Me$. [84°]. Formed from *o*-tolyl-thiocarbimide and ethylamine (Staats, *B.* 13, 136). Prisms, insol. water, sol. alcohol and ether.

***p*-Tolyl-ethyl-thio-urea** [96°]. Formed in like manner (Weith, *B.* 8, 1530). Tables, v. sol. hot water.

***o*-Tolyl-di-ethyl-thio-urea** $CS(NEt_2).NHC_7H_7$. [102°]. Formed from *o*-tolyl-thiocarbimide and $NHEt_2$ (Gebhardt, *B.* 17, 3038). Needles or prisms.

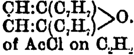
***p*-TOLYL-ETHYL-TOLUTRIAZINE DIHYDRIDE** $C_{17}H_{19}N_3$ *i.e.*  $C_6H_3Me<\begin{smallmatrix}N.CHEt\\N.N.C_6H_4Me\end{smallmatrix}$. [168°]. Formed by heating toluene-azo-toluidine with propionic aldehyde at 140° (Goldschmidt a. Poltzer, *B.* 24, 1009). Needles (from hot benzene).—B'HCl. [96°].—Platinochloride [221°]. Small yellow needles.

***p*-TOLYL-ETHYL-UREA** $C_{10}H_{14}N_2O$ *i.e.* $NHC_7H_7.CO.NHEt$. Formed from *p*-toluidine and ethyl cyanate (Sell, *A.* 126, 162). Crystals, insol. water, v. e. sol. alcohol.

DI-*o*-TOLYL-FORMAMIDINE $C_{15}H_{16}N_2$ *i.e.* $NHC_7H_7.CH:NC_7H_7$. [151°]. Formed by boiling the formyl derivative of *o*-toluidine for a long time, or by heating it with *o*-toluidine and PCl_3 (Ladenburg, *B.* 10, 1260). Formed also by distilling the thioformyl derivative of *o*-toluidine *in vacuo* (Senier, *C. J.* 47, 762). Prisms (from alcohol), insol. dilute NaOHAq. Yields crystalline $C_{15}C_{16}N_2Br_2$.—$B'_2H_2PtCl_6$.

Di-*m*-tolyl-formamidine $NHC_7H_7.CH:NC_7H_7$. [123°]. Formed by boiling *m*-toluidine with formic acid (Niementowski, *B.* 20, 1893). Needles or plates, insol. water. Br in CS_2 yields crystalline $NHC_7H_7.CHBr.NBrC_7H_7$.—B'HCl. [214°].—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. Yellow needles.

Di-*p*-tolyl-formamidine [141°]. Formed by distilling $C_7H_7NH.CHS$ *in vacuo* (Senier, *C. J.* 47, 767; *B.* 18, 2296). Prisms.—$B'_2H_2PtCl_6$.

DI-*p*-TOLYL-FURFURANE $C_{18}H_{16}O$ *i.e.*  $\begin{smallmatrix}CH:C(C_7H_7)\\CH:C(C_7H_7)\end{smallmatrix}>O$. [164°]. Formed by the action of AcCl on $C_2H_2(CO.C_7H_7)_2$ (Holleman, *R. T. C.* 6, 72). Small plates, converted by P_2S_5 into di-tolyl-thiophene, and by ammonium acetate into di-tolyl-pyrrole.

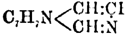
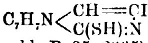
***p*-TOLYL-GLYOXAL** $C_6H_4Me.CO.CHO$. [102°]. Formed from the oxim by dissolving in aqueous $NaHSO_3$, stirring the crystalline mass with alcohol and a little HOAc, filtering, and boiling with dilute H_2SO_4 (Müller a. Pechmann, *B.* 22, 2556). Needles (from hot water), v. sol. alcohol. Reduces cold ammoniacal $AgNO_3$, but not Fehling's solution. When shaken with benzene (containing thiophene) and H_2SO_4 it colours the benzene green. Yields *p*-tolyl-glyoxylic acid and *p*-toluic acid on oxidation.

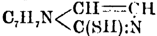
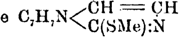
Phenyl hydrazide $C_7H_7.C(N_2HPh).CH(N_2HPh)$. [145°]. Yellow needles (from dilute alcohol).

Oxim $C_7H_7.CO.CH:NOH$. *Tolyl nitroso-methyl ketone.* [100°]. Formed from tolyl methyl ketone, amyl nitrite and NaOEt. Needles (from benzene).

Acetyl derivative of the syn-oxim $C_7H_7.CO.CH:NOAc$ [68°]. From the oxim and Ac_2O (Söderbaum, *B.* 25, 3461). Tables (from MeOH). Cold NaOHAq splits it up into NaCy and *p*-toluic acid. Conc. H_2SO_4 acts in like manner. Ac_2O at 100° forms $C_7H_7.CO.CN$ [52°], whence boiling NaOHAq forms *p*-toluic acid.

Acetyl derivative of the anti-oxim $C_7H_7.C(OH)_2.CH:NOAc$. [148°]. From the oxim and AcCl at 0°, followed by water. Cold NaOHAq forms $C_7H_7.CH(OH).CO_2H$ [146°], v. sol. ether. Conc. H_2SO_4 converts this acetyl *anti*-oxim into the oxim. Converted by KCy dissolved in dilute alcohol into *p*-toluyl-formoïn $C_7H_7.CO.CH(OH).CO.CO.C_7H_7$ [161°] (Söderbaum, *B.* 25, 3473).

***p*-TOLYL-GLYOXALINE** $C_{10}H_{10}N_2$ *i.e.*  $C_7H_7N<\begin{smallmatrix}CH:CH\\CH:N\end{smallmatrix}$. (285°). Got by warming  $C_7H_7N<\begin{smallmatrix}CH=CH\\C(SH):N\end{smallmatrix}$ with dilute HNO_3 (Marckwald, *B.* 25, 2365). Pale-yellow crystals, sl. sol. water. Smells like mushrooms.—$B'_2H_2PtCl_6$.—$B'AgNO_3$.—Picrate. [179°]. Golden needles.

***p*-TOLYL-GLYOXALYL MERCAPTAN**  $C_7H_7N<\begin{smallmatrix}CH=CH\\C(SH):N\end{smallmatrix}$. [205°]. Got by action of boiling HClAq on the product of the action of amido-acetal on *p*-tolyl thiocarbimide (Marckwald, *B.* 25, 2363). Silvery leaflets, m. sol. hot water. Yields $(C_{10}H_{10}N_2S)_2PtCl_4$. MeI in alcohol forms $(C_{10}H_9MeN_2S)HI$ [95°], which yields the base  $C_7H_7N<\begin{smallmatrix}CH=CH\\C(SMe):N\end{smallmatrix}$ [90°], which forms a picrate [140°].

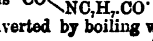
***p*-TOLYL-GLYOXYLIC ACID** $C_9H_8O_3$ *i.e.* $C_6H_4Me.CO.CO_2H$. [97°]. Formed by the action of $AlCl_3$ on a mixture of toluene and $Cl.CO.CO_2C_5H_{11}$ (Roser, *B.* 14, 1750). Formed also by oxidising *p*-tolyl methyl ketone with cold alkaline K_3FeCy_6 (Buchka a. Irish, *B.* 20, 1762, 2213). Needles (from ligroïn), sl. sol. hot water, v. sol. alcohol and ether. Yields *p*-toluic and terephthalic acids on oxidation. Benzene (containing thiophene) when shaken with tolyl-glyoxylic acid and H_2SO_4 is turned red, and finally bluish-violet.

Salts.—KA'.—NaA' ½aq (Claus a. Kroseberg, *B.* 20, 2018).—BaA'_2.—$BaA'_2$8aq.—CaA'_2aq.—AgA'. Needles, v. sol. hot water.

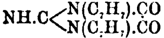
Ethyl ether EtA'. (260°–270°).

Amide $C_9H_9NO_2$. [160°]. Prisms.

Phenyl hydrazide [144°].

DI-*o*-TOLYL-GUANIDINE $C_{15}H_{17}N_3$ *i.e.* $C(NH)(NHC_7H_7)_2$. [179°]. Formed by the action of NH_3, lead acetate, and KOHAq on di-*o*-tolyl-thio-urea (Berger, *B.* 12, 1855). Crystals, sol. ether. Cyanogen passed into its alcoholic solution forms the dicyanide $C_{17}H_{17}N_5$ [174°] which is converted by HCl into the oxalyl derivative $C_{17}H_{15}N_3O_2$ [207°], whence boiling with alcoholic HCl forms  $CO<\begin{smallmatrix}NC_7H_7.CO\\NC_7H_7.CO\end{smallmatrix}$. [214°]. The dicyanide is converted by boiling with ani-

line into $C_{22}H_{21}N_5$, which yields crystalline $B'HCl$ aq.—$B'_2H_2PtCl_6$: yellow pp.

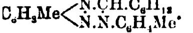
Di-*p*-tolyl-guanidine $NH.C(NHC_7H_7)_2$. [168°]. Formed by passing cyanogen chloride into fused *p*-toluidine (W. Wilson, *C. J.* 8, 154; A. G. Perkin, *C. J.* 37, 696). Formed also by desulphuration of di-tolyl-thio-urea in presence of NH_3 (Hofmann, *B.* 7, 1739). Needles (from ligroïn). Nitric acid (S.G. 1·5) gives a di-nitro-derivative [197°], which forms crystalline $B'HNO_3$. Alcohol and HNO_3 (S.G. 1·4) produce di-nitro-*p*-tolyl-urea. Cyanogen passed into its ethereal solution forms $C_{15}H_{17}N_3Cy_2$, crystallising from ether in prisms, converted by dilute HClAq into  $NH.C{<}\begin{matrix}N(C_7H_7).CO\\N(C_7H_7).CO\end{matrix}$ [188·5°] (Landgrebe, *B.* 10, 1587). The cyanide is converted by boiling in alcoholic solution with aniline hydrochloride into $C_{23}H_{21}N_5\frac{1}{2}$aq [110°–115°].—**Salt** $B'_2H_2PtCl_6$.

Tri-*o*-tolyl-guanidine $C_{22}H_{23}N_3$ *i.e.* $C(NC_7H_7)(NHC_7H_7)_2$. [131°]. Formed by the action of *o*-toluidine in alcoholic solution in presence of lead oxide on di-*o*-tolyl-thiourea (Berger, *B.* 12, 1857; *cf.* Girard, *B.* 6, 445). Formed also when di-*o*-tolyl-thiourea is boiled for a long time (Barr, *B.* 19, 1769). Minute prisms. Yields a dicyanide $C_{24}H_{23}N_5$ [141°], converted by conc. HClAq in alcoholic solution into $C_{24}H_{21}N_3O_2$ [179°].—$B'_2H_2PtCl_6$: yellow prisms.

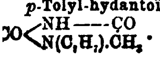
Tri-*p*-tolyl-guanidine $C_{22}H_{23}N_3$. [123°]. S. (alcohol) 7·4 at 0°. Formed by heating di-*p*-tolyl-thio-urea with copper (Merz a. Weith, *Z.* 1868, 610), or, in alcoholic solution, with *p*-toluidine and PbO (Hofmann, *B.* 2, 459). Got by heating *p*-toluidine with PCl_3 and *p*-tolyl cyanate (Weith, *B.* 9, 820). Formed also when di-*p*-tolyl-urea is boiled for a long time (Barr, *B.* 19, 1768), and likewise by the action of *p*-toluidine on the product of the action of chlorine on tolyl cyanate (Nef, *A.* 270, 322). Needles (from ligroïn). Yields a dicyanide $C_{24}H_{21}N_5$ [184°], which forms $B'HCl3$aq and $B'_2H_2PtCl_6$ and is converted by boiling with alcoholic HCl into di-tolyl-parabanic acid.

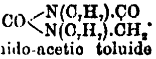
Salts.—$B'HCl$ aq. S. ·6 at 0°.—$B'_2H_2PtCl_6$. S. ·045 at 0°.—$B'HNO_3$. S. ·07 at 0°.—$B'_2H_2SO_4$. Plates (from hot water). Neutral in reaction.

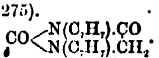
***p*-TOLYL HEPTADECYL KETONE** [1:4]$C_6H_4Me.CO.C_{17}H_{35}$. [67°]. (278° at 15 mm.). Formed from toluene, stearyl chloride, and $AlCl_3$ (Krafft, *B.* 21, 2268). Oxidised by HNO_3 (S.G. 1·12) to *p*-toluic acid.

***p*-TOLYL-HEXYL-TOLUTRIAZINE DIHYDRIDE** $C_{21}H_{27}N_3$ *i.e.*  $C_6H_3Me{<}\begin{matrix}N.CH.C_6H_{13}\\N.N.C_6H_4Me\end{matrix}$. [165°]. Formed by heating œnanthol with toluene-*o*-azo-toluidine at 175° (Goldschmidt a. Poltzer, *B.* 24, 1010). Needles, sol. hot benzene.—BHCl. [96°].—$B'_2H_2PtCl_6$. [171°]. Yellow crystalline pp.

***o*-TOLYL-HYDANTOÏN** $C_{10}H_{10}N_2O_2$. [176°]. Formed by heating *o*-tolyl-amido-acetic acid with urea at 180° (Ehrlich, *B.* 16, 742). Light-yellow plates, sol. alcohol and hot water. On boiling with baryta-water it gives *o*-tolyl-hydantoïc acid, which, when set free from its salts, at once splits up into water and *o*-tolyl-hydantoïn.

***p*-Tolyl-hydantoïn** $C_{10}H_{10}N_2O_2$ *i.e.*  $CO{<}\begin{matrix}NH\text{——}CO\\N(C_7H_7).CH_2\end{matrix}$. [210°]. Formed, together with *p*-tolyl-hydantoic acid $CO(NH_2).N(C_7H_7).CH_2.CO_2H$, by fusing *p*-tolyl-amido-acetic acid with urea (Schwebel, *B.* 11, 1128). Needles (from water), v. sol. alcohol. ***p*-Tolyl-hydantoic acid** is crystalline, sl. sol. hot alcohol and hot water.

Di-*o*-tolyl-hydantoïn  $CO{<}\begin{matrix}N(C_7H_7).CO\\N(C_7H_7).CH_2\end{matrix}$. [275°]. Got from *o*-tolyl-amido-acetic toluide and $COCl_2$ (Bischoff, *B.* 25, 2275).

Di-*p*-tolyl-hydantoïn  $CO{<}\begin{matrix}N(C_7H_7).CO\\N(C_7H_7).CH_2\end{matrix}$. [175°]. Formed from *p*-tolyl-amido-acetic toluide and $COCl_2$ (Bischoff, *B.* 25, 2280). Plates (from alcohol), sl. sol. ligroïn.

TOLYL-HYDRAZIDO-METHYL-THIAZOLE DIHYDRIDE $\begin{matrix}CHMe.S\\CH_2\text{—}N\end{matrix}{>}C.NH.NHC_7H_7$. Formed by heating tolyl-allyl-thio-semicarbazide with conc. HClAq at 100° (Avenarius, *B.* 24, 270). The *p*- compound melts at 133°. Both the *o*- and the *p*- compounds form crystalline hydrochlorides.

***o*-TOLYL-HYDRAZIDO-PROPIONIC ACID** $C_6H_4Me.NH.NH.CHMe.CO_2H$. [143°]. Formed by the action of sodium-amalgam on the *o*-tolyl-hydrazide of pyruvic acid (Japp a. Klingemann, *C. J.* 53, 519). Small needles (from MeOH).

***o*-TOLYL-HYDRAZINE** $C_7H_7NH.NH_2$. [53°] (P.); [56°] (F.); [59°] (Gallinek a. Richter, *B.* 18, 3175). Prepared from *o*-toluidine in the same manner as phenyl-hydrazine is obtained from aniline (Fischer a. Bösler, *A.* 212, 338; Freund, *B.* 24, 4200). Glittering plates, slowly oxidised by air, forming a brown oil.—$B'HCl$ aq: needles.—$B'HNO_3$: plates. With $SOCl_2$ and ether it forms $C_7H_7NH.N{:}SO$, a yellow oil smelling like geraniums (Michaelis, *A.* 270, 119). Glucose yields *o*-tolyl-glucosazone $C_{20}H_{26}N_4O_4$ [201°] (Raschen, *A.* 239, 229). Di-methyl di-ketone forms $CH_3.C(N_2HC_7H_7).C(N_2HC_7H_7).CH_3$ [198°] (Japp a. Klingemann, *A.* 247, 221).

Formyl derivative $C_6H_4Me.NH.NHCHO$. [121°]. Formed from *o*-tolyl hydrazine and formamide. Needles (Gattermann, *B.* 25, 1078).

Acetyl derivative $C_7H_7.NH.NHAc$. [104°]. Formed from *o*-tolyl-hydrazine and Ac_2O (G.).

Propionyl derivative $C_7H_7.NH.NH.C_3H_5O$. [84°]. Formed from *o*-tolyl-hydrazine and propionic acid (G.). Colourless tables.

Benzoyl derivative $C_7H_7.NH.NHBz$. [180°]. Got from the hydrazine and BzCl in Et_2O (G.). Needles. Gives off all its nitrogen in the free state on boiling with Fehling's solution (Strache a. Iritzer, *M.* 14, 38).

***m*-Tolyl-hydrazine** $C_7H_7.NH.NH_2$. (242°) (Buchka a. Schachtebek, *B.* 22, 841; *cf.* V. Meyer a. Lecco, *B.* 16, 2976). Oil.—$B'HCl$. Needles, v. sol. water and alcohol.

***p*-Tolyl-hydrazine** $C_7H_7NH.NH_2$. [61°]. (242°). Obtained from *p*-toluidine (Fischer, *B.* 8, 589; 9, 890). White plates (from ether), sl. sol. water.

Reactions.—1. With $SOCl_2$ and ether it forms $C_7H_7NH.N{:}SO$ [112°], crystallising in yellow needles (Michaelis a. Ruhl, *A.* 270, 118).—2. $C_6H_5PCl_2$ forms $C_7H_7NH.N{:}PC_6H_5$ [162°], crystallising in prisms.—3. $POCl_3$ forms $(C_7H_7NH.NH)_3PO$ [189°].—4. *Acetone* forms $CMe_2(N_2HC_7H_7)$ [52°].—5. *Acetoacetic ether* forms $C_{13}H_{18}N_2O_2$ [93°] (Knorr, *B.* 17, 550).—6. *Oxalic ether* forms $NHC_7H_7.NH.CO.CO_2Et$. [133°] (Preund, *B.* 24, 4198).—7. *Di-methyl diketone* yields $CH_3.C(N_2HC_7H_7).C(N_2HC_7H_7).CH_3$ [230°], and $CH_3.C(N_2HC_7H_7)Ac$ [161°] (Japp, *C. J.* 53, 544).

Salt.—$B'C_6H_5PH_2O_2$. [148°] (Michaelis, *A.* 270, 134).

Toluene-*p*-phosphinate $B'C_7H_7PH_2O_2$. [161°].

Formyl derivative $C_6H_4Me.NH.NH.CHO$. [164°]. Formed by heating the alcoholic solution of *p*-tolyl-hydrazine with chloroform and potash. Formed also by heating *p*-tolyl-hydrazine with formamide at 130° (Ruhemann, *C. J.* 55, 248). Plates (from water), v. sol. alcohol.

Acetyl derivative $C_6H_4Me.NH.NHAc$. [121°]. Formed from *p*-tolyl-hydrazine and AcOH (Gattermann, *B.* 25, 1080). Plates.

Propionyl derivative [170°]. Needles.

Dibenzoyl derivative [188°] (Fischer).

Di-*o*-tolyl-hydrazine.

Formyl derivative $(C_7H_7)_2N.NH.CHO$. [139°]. Formed from $C_7H_7NH.NH.CHO$ and $CuSO_4$ (Gattermann, *B.* 25, 1078). Plates.

Acetyl derivative $(C_7H_7)_2N.NHAc$. [191°]. Formed in like manner from acetyl-*o*-tolyl-hydrazine and $CuSO_4$. Needles.

Propionyl derivative [167°]. Needles.

Benzoyl derivative [209°]. Needles.

***u*-Di-*p*-tolyl-hydrazine** $(C_7H_7)_2N.NH_2$. [172°]. Formed by reduction of di-tolyl-nitrosamine with zinc-dust and HOAc (Lehne, *B.* 13, 1546). Plates, v. sol. alcohol and benzene.—B'HCl.

Formyl derivative $(C_7H_7)_2N.NH.CHO$. [146°]. Formed from formyl-*p*-tolyl-hydrazine and $CuSO_4$ (Gattermann, *B.* 25, 1079). Plates.

Acetyl derivative. [176°]. Needles.

Propionyl derivative [171·5°]. Needles.

Benzoyl derivative. [187°]. Needles.

***s*-Di-*o*-tolyl-hydrazine** $C_7H_7NH.NHC_7H_7$. *o-Hydrazo-toluene.* [165°] (P.); [146°] (S.). Formed by reduction of *o*-toluene-azo-toluene by sodium amalgam (Petrieff, *B.* 6, 557; Schultz, *B.* 17, 467). Converted into di-amido-ditolyl $[3:4:1]C_6H_3Me(NH_2).C_6H_3Me(NH_2)[1:3:4]$ [128°] by heating with HCl. The diamido-derivative $C_7H_6(NH_2).NH.NH.C_7H_6(NH_2)$ [180°] is a product of the action of sodium-amalgam on nitro-*p*-toluidine (Buckney, *B.* 11, 1453).

***s*-Di-*m*-tolyl-hydrazine** $C_7H_7NH.NHC_7H_7$. Formed by reducing *m*-toluene-*m*-azo-toluene by alcoholic ammonium sulphide (Goldschmidt, *B.* 11, 1626; Barsilowsky, *A.* 207, 116). Liquid, converted by H_2SO_4 into di-amido-ditolyl.

***s*-Di-*p*-tolyl-hydrazine** $C_7H_7NH.NHC_7H_7$. [126°]. Formed in like manner from *p*-toluene-*p*-azo-toluene (Melms, *B.* 3, 553) and by the action of zinc-dust and NaOHAq on *p*-nitro-toluene (Janovsky, *M.* 9, 829). Tables or needles, v. e. sol. alcohol. In alcoholic solution it is readily oxidised by air to $C_7H_7.N_2.C_7H_7$. Dilute H_2SO_4 converts it into toluidine and toluene-azo-toluene. On treatment in alcoholic solution with hydrochloric acid it changes to tolylene-tolyl-diamine. The di-amido-derivative $[1:2:4]C_6H_3Me(NH_2).NH.NH.C_6H_3Me(NH_2)[4:1:2]$ obtained from $C_6H_3Me(NH_2).N_2.C_6H_3Me(NH_2)$ by reducing with sodium-amalgam, is crystalline and yields $B''H_2SO_4$, $B''2HCl$, $B''2HBr$, and $B''H_2PtCl_6$ (Graeff, *A.* 229, 352).

Reference.—OXY-TOLYL-HYDRAZINE.

***o*-TOLYL-HYDRAZINE SULPHONIC ACID** $C_6H_3Me(N_2H_3).SO_3H$ [1:2:4]. Formed by adding *o*-diazo-toluene *p*-sulphonic acid to a cold solution of $SnCl_2$ (Limpricht, *B.* 18, 2193). Colourless needles, v. sol. hot water, nearly insol. alcohol.—KA′ 2aq: orange-red prisms.—BaA'_2: yellow crystalline powder.

***o*-Tolyl-hydrazine sulphonic acid** $C_6H_3Me(N_2H_3).SO_3H$ [1:*x*:2]. Formed by heating *o*-tolyl-hydrazine (1 pt.) with conc. H_2SO_4 (5 pts.) at 100° (Gallinck a. Richter, *B.* 18, 3175). Thin needles (containing ½aq). By boiling with aqueous $CuSO_4$ it is quantitatively decomposed into a toluene sulphonic acid and nitrogen.—NaA′ 3½aq.—BaA'_2 4aq.—ZnA'_2 3aq.—PbA'_2 6aq.—$Pb_3A'_2(OH)_4$. Sparingly soluble needles.

***p*-Tolyl-hydrazine-*o*-sulphonic acid** $C_6H_3Me(N_2H_3).SO_3H$ [1:4:2]. [274°]. Formed by reducing *p*-diazo-toluene *o*-sulphonic acid with Na_2SO_3 (Brackett a. Hayes, *Am.* 9, 401) or HCl and $SnCl_2$ (Pasche, *B.* 21, 3416). Tables, sl. sol. cold water. Decomposed by fusion. Not attacked by warm H_2SO_4.

***p*-Tolyl-hydrazine *m*-sulphonic acid** $C_6H_3Me(N_2H_3).SO_3H$ [1:3:4]. Obtained by reducing *p*-diazotoluene *m*-sulphonic acid by cooled $SnCl_2$ (Limpricht, *B.* 18, 2193). Slender prisms, sol. hot water. $FeCl_3$ evolves nitrogen in the cold. Conc. H_2SO_4 at 80° forms a red amorphous substance (Schneider, *Am.* 8, 271).

***p*-Tolyl-hydrazine disulphonic acid** $C_6H_2Me(N_2H_3)(SO_3H)_2$. Formed by adding *p*-diazo-toluene disulphonic acid to a cold solution of $SnCl_2$ (Limpricht, *B.* 18, 2193). Nodules, v. sol. water.—$BaH_2A''_2$ 2½aq: tables.

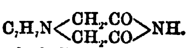
Di-tolyl-hydrazine disulphonic acid $C_6H_3Me(SO_3H).NH.NH.C_6H_3Me(SO_3H)$. A product of the reduction of the corresponding azo-compound by $SnCl_2$ (Neale, *A.* 203, 72). Crystalline powder (containing 2½aq), sl. sol. water.—BaA″ 5aq.—CaA″ 3½aq: monoclinic efflorescent prisms.

Reference.—NITRO-TOLYL-HYDRAZINE SULPHONIC ACID.

***o*-TOLYL-IMIDO-DIACETIC ACID** $[1:2]C_6H_4Me.N(CH_2.CO_2H)_2$. [c. 160°]. Formed by heating *o*-tolyl-amido-acetic acid (1 mol.) with chloro-acetic acid (1 mol.), Na_2CO_3 (1½ mols.) and a little water at 140° (Bischoff, *B.* 23, 1994; 25, 2270). White crystals, insol. ligroïn, sl. sol. ether, m. sol. alcohol.—NH_4A'. [160°]. V. sol. Aq.

Amide $C_7H_7N(CH_2.CO.NH_2)_2$. [164°]. Plates.

Di-o-toluide $C_7H_7N(CH_2.CO.NHC_7H_7)_2$. [150°].

Imide 

$C_7H_7N\left<\begin{matrix}CH_2.CO\\CH_2.CO\end{matrix}\right>NH$. [146°]. Prisms (from alcohol), sl. sol. water.

o-Tolylamic acid $C_7H_7N(CH_2.CO_2H).CH_2.CO.NHC_7H_7$. [148°]. Crystals (from alcohol).

***p*-Tolylimido-diacetic acid** $[1:4]C_6H_4Me.N(CH_2.CO_2H)_2$. *Diglycotolylamic acid.* [c. 140°]. Formed by the action of $CH_2Cl.CO_2H$ on *p*-tolyl-glycocoll (Meyer, *B.* 14, 1323; Bischoff, *B.* 23, 2000). Needles (from water). Very unstable. — CuA'_2 aq: green needles.—$Ag_2A'(NO_3)$: needles.—*p*-Toluidine

salt $(C_7H_7NH_2)HA'$. [119°]. Crystals, sol. hot water.

Mono-amide. [222°]. A product of the action of Ac_2O on the compound [168°] got from chloro-acetic acid and *p*-toluidine (Bischoff, *B.* 25, 2280).

Di-amide $C_7H_7N(CH_2.CO.NH_2)_2$. [250°].

Di-p-toluide $C_7H_7N(CH_2.CO.NHC_7H_7)_2$. [251°]. Long needles (from alcohol).

Amide p-toluide $C_7H_7N(CH_2.CO.NH_2)CH_2.CO.NHC_7H_7$. [210°].

p-Tolylamic acid $C_7H_7N(CH_2.CO_2H).CH_2.CONHC_7H_7$. [222°]. Needles, insol. water, sol. hot alcohol.

***p*-TOLYL-IMIDO-DIACRYLIC ETHER** $C_6H_4MeN(CH:CH.CO_2Et)_2$. [73°]. Formed from *p*-toluidine and formyl-acetic ether (Von Pechmann, *B.* 25, 1053). Yellow needles (from dilute alcohol).

***o*-TOLYL-β-IMIDO-BENZYL-MALONIC ETHER** $C_{21}H_{23}NO_4$ *i.e.* $C_6H_5.C(NC_7H_7).CH(CO_2Et)_2$. [95°]. Formed by the action of ω-chloro-benzylidene-*o*-toluidine upon sodium-malonic ether (Just, *B.* 19, 985). Crystals, v. sol. ether. Split up by dilute HClAq at 120° into acetophenone and *o*-toluidine. The *p*-isomeride is liquid.

***o*-TOLYL-β-IMIDO-BUTYRIC ACID** $C_6H_4Me.N:CMe.CH_2.CO_2H$. [112°]. Formed by heating acetoacetic ether with *o*-toluidine at 150° (Knorr, *B.* 17, 542; Pawlewski, *B.* 22, 2203). Needles (from hot water), converted by conc. H_2SO_4 into (*Py.* 1)-oxy-(*B.* 4, *Py.* 3)-di-methyl-quinoline.

p-**Tolyl-β-imido-butyric acid.** Formed in like manner from *p*-toluidine. Crystals. Converted by H_2SO_4 into (*Py.* 1)-oxy-(*B.* 2, *Py.* 3)-di-methyl-quinoline.

***p*-TOLYL IODO-ETHYL SULPHONE** $C_7H_7.SO_2.CH_2.CH_2I$. [100°]. Formed from tolyl oxy-ethyl sulphone and HIAq at 160° (Otto, *J. pr.* [2] 30, 357). Crystals, v. sol. hot alcohol.

TOLYL IODO-METHYL SULPHONE $C_7H_7.SO_2.CH_2I$. [126°]. Formed by heating sodium toluene sulphinate with CH_2I_2 and alcohol (Otto, *B.* 21, 655). Small needles, v. e. sol. hot alcohol.

DI-*p*-TOLYL KETONE $CO(C_6H_4Me)_2$. [92°]. (333°) at 725 mm. Formed by oxidation of di-tolyl-methane (Weiler, *B.* 7, 1183), of *u*-di-tolyl-ethane (O. Fischer, *B.* 7, 1195), and of *u*-di-tolyl-ethylene (Hepp, *B.* 7, 1414) by chromic acid mixture.

Preparation.—50 g. $AlCl_3$, 65 c.c. toluene, 50 c.c. CS_2, and 11 c.c. of a solution of $COCl_2$ in CS_2 saturated at 0° are put into a corked half-litre flask and gently warmed. After 20 minutes HCl is allowed to escape and a second 11 c.c. of CS_2 saturated with phosgene is added. The operation is repeated 2 or 3 times; the yield is 50 p.c. of the calculated (Elbs, *J. pr.* [2] 35, 467; *cf.* Ador a. Crafts, *B.* 10, 2174).

Properties.—Crystals (from alcohol). Converted by HNO_3 at 250° into benzoyl-terephthalic acid. Reduced by HI and P to di-tolyl-methane (Ador a. Rilliet, *B.* 12, 2303).

Oxim $(C_7H_7)_2C:NOH$. [163°]. Prisms (Goldschmidt, *B.* 23, 2746). Decomposes on keeping with sudden evolution of nitrous fumes. Conc. H_2SO_4 at 100° forms the *p*-toluide of *p*-toluic acid.

Di-*p*-tolyl diketone $C_7H_7.CO.CO.C_7H_7$. *p-Tolil.* [105°]. Formed by boiling toluoïn (1 pt.) with HNO_3 (2 pts.) (Stierlin, *B.* 22, 381). Yellow plates (from warm alcohol). Gives a violet colour when boiled with alcoholic potash.

(α)-*Oxim* $C_7H_7.C(NOH).C(NOH).C_7H_7$. [217°]. Plates or needles, sl. sol. alcohol. Yields a diacetyl derivative [134°].

(β)-*Oxim* [225°]. Formed, together with the (α)-oxim, by the action of hydroxylamine hydrochloride on the ketone. Needles, v. sol. alcohol. Yields a di-acetyl derivative [144°].

Di-*p*-tolyl tetraketone $C_7H_7.CO.C(OH)_2.CO.CO.C_7H_7$. [88°]. Formed by the action of nitric acid (S.G. 1·3) on $C_7H_7.CO.CH(OH).CO.CO.C_7H_7$ (Söderbaum, *B.* 25, 3474). Prisms (containing $(C_{18}H_{16}O_5)_2CS_2$) (when crystallised from CS_2).

Di-oxim $C_7H_7.C(NOH).CO.CO.C(NOH).C_7H_7$. [181°]. Plates (containing EtOH) (from alcohol).

Bi-oxim $C_7H_7.CO.C(NOH).C(NOH).CO.C_7H_7$. So called '(β)-nitro-cymene.' [125°]. Mol. w. 324 (by Raoult's method). Formed by the action of nitric acid on cymene and on *p*-tolyl methyl ketone (Holleman, *R. T. C.* 6, 60; *cf.* Landolph, *B.* 6, 937; Fittica, *A.* 172, 311). Needles, v. sol. warm alcohol. Converted by NaOHAq into *p*-toluic acid. Zinc-dust and HOAc reduce it to $C_7H_7.CO.CH_2.CH_2.CO.C_7H_7$ [159°]. Alcoholic NH_3 forms *p*-toluic amide and $C_{16}H_9N_3O_2$ [162°]. Boiling Ac_2O forms $C_{18}H_{18}N_2O_4Ac_2O$ [167°].

Reference.—Oxy-di-tolyl ketone.

TOLYL-MALONAMIC ACID *v.* Malonic acid.

TOLYL-MELAMINE *v.* *Cyanuramide* in the article on Cyanic acids.

***o*-TOLYL-MERCAPTAN** $[1:2]C_6H_4Me.SH$. [15°]. (188°) (H.); (193°) (V.). Formed by reducing (4,1,2)-bromo-tolyl mercaptan (Hübner, *A.* 169, 30; Vallin, *B.* 19, 2953). Prepared by boiling *o*-tolyl ethyl dithiocarbonate with alcoholic potash, the yield being 70 p.c. of the theoretical amount (Leuckart, *J. pr.* [2] 41, 188). Plates.—$Pb(SC_7H_7)_2$. Brick-red pp., turning white in air.

m-**Tolyl mercaptan** $[1:3]C_6H_4Me.SH$. [c. 200°]. Formed by reducing toluene *m*-sulphonic chloride with tin and HCl (Hübner, *A.* 169, 51) and by boiling *m*-tolyl ethyl xanthate with alcoholic potash (L.). Colourless liquid with intense odour of mercaptan. Volatile with steam. In ammoniacal alcoholic solution it is oxidised by air to *m*-tolyl disulphide.

p-**Tolyl mercaptan** $[1:4]C_6H_4Me.SH$. [43°]. (188°) (J.); (191°) (Crafts, *B.* 19, 3130; Otto, *B.* 19, 3129); (194°) (Vallin, *B.* 19, 2953). Formed by reducing toluene *p*-sulphonic chloride with tin and HCl (Märcker, *A.* 136, 79; Javorsky, *Z.* 1865, 222). Formed also by heating *p*-tolyl ethyl xanthate with alcoholic potash (L.). Formed also from di-*p*-tolyl disulphide, alcohol, and H_2S (Otto a. Rössing, *B.* 19, 3130). Unctuous lamina (from ether), volatile with steam. Conc. H_2SO_4 forms a blue solution. Readily oxidised to di-*p*-tolyl disulphide [46°]. Chloro-acetone forms $C_7H_7.S.CH_2.CO.CH_3$ (151° at 15 mm.); S.G. $\frac{15}{15}$ 1·0986 which yields a phenyl-hydrazide

[62°] (Delisle, *A.* 260, 268).—$Hg(SC_7H_7)_2$.—$C_7H_7S.HgCl$. Plates.

Ethyl ether C_7H_7SEt. (221°). S.G. 11 1·0016. Colourless oil (Otto, *B.* 13, 1277).

References.—Amido- and Bromo- tolyl mercaptan.

o-TOLYL-MESITYL-THIO-UREA $C_7H_7.NH.CS.NHC_6H_2Me_3$. [167°]. Formed from *o*-toluidine and mesityl thiocarbimide (Eisenberg, *B.* 15, 1014). Needles, insol. Aq.

DI-TOLYL-METHANE $CH_2(C_7H_7)_2$. [23°]. (286°).

Formation.—1. From formic aldehyde (or methylal), toluene, and H_2SO_4 (Weiler, *B.* 7, 1181).—2. By reducing di-tolyl ketone with HI and P (Ador a. Rilliet, *B.* 12, 2302).—3. A product of the action of $AlCl_3$ and toluene on CH_2Cl_2, on CH_3Cl, or on $CCl_3.NO_2$ (Friedel a. Crafts, *A. Ch.* [6] 11, 266; *Bl.* [2] 43, 50; Elbs a. Wittich, *B.* 18, 347).

Properties.—Prisms, v. sol. ether. Oxidised by chromic acid mixture to di-tolyl ketone, toluyl-benzoic acid, and $CO(C_6H_4.CO_2H)_2$. Yields a di-nitro- derivative [164°].

Tri-tolyl-methane $CH(C_7H_7)_3$. [73°]. (377°). Obtained from tri-amido-tri-tolyl-carbinol (Rosenstiehl a. Gerber, *A. Ch.* [6] 2, 353). Crystalline.

References.—Di-bromo- and Di-chloro-, di-tolyl-methane.

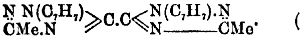
o-TOLYL METHYL-p-AMIDO-PHENOL

Methyl derivative $C_7H_7NMe.C_6H_4OMe$. (336° cor.). From $C_7H_7NH.C_6H_4OH$, KOH, and MeI (Philip, *J. pr.* [2] 34, 59). Oil.

TOLYL-METHYL-AMINE *v.* Methyl-toluidine, Methyl-benzyl-amine, and Amido-xylene.

Di-p-tolyl-methyl-amine $(C_7H_7)_2NMe$. (235°–240° at 20 mm.). Formed from ditolylamine, MeOH, and HCl at 250°-280° (Girard, *Bl.* [2] 24, 120). Does not combine with acids.

DI-TOLYL-DI-METHYL-DI-TRIAZYL


$\begin{matrix}N\;N(C_7H_7)\\CMe.N\end{matrix}\!\!>C.C<\!\!\begin{matrix}N(C_7H_7).N\\N\text{———}CMe\end{matrix}$ (259°–260°). Formed by boiling *p*-tolyl-hydrazine cyanide $(C_7H_7NH.NH_2)_2Cy_2$ with Ac_2O (Bladin, *B.* 22, 3114). Crystals (from alcohol), m. sol. alcohol.

p-TOLYL-METHYL-BENZYL KETONE $C_6H_4Me.COCH_2.C_6H_4Me$. [102°]. Got by reducing *p*-toluoïn with zinc and alcoholic HCl (Stierlin, *B.* 22, 383). Needles, insol. water, v. sol. benzene.

o-TOLYL-METHYLENE-AMINE $C_7H_7N:CH_2$ (?). Formed by adding *o*-toluidine to a solution of formic aldehyde (Wellington a. Tollens, *B.* 18, 3307). Colourless syrup.

p-Tolyl-methylene-amine $C_7H_7N:CH_2$ (?). [c. 122°]. Formed, together with a polymeride sl. sol. benzene and alcohol, by adding *p*-toluidine to a solution of formic aldehyde (W. a. T.). Crystals, v. sol. benzene.

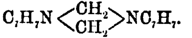
Di-o-tolyl-methylene-diamine $(C_7H_7NH)_2CH_2$. (over 350°). Formed, together with the following solid isomeride, by heating *o*-toluidine with CH_2Cl_2 at 110°–115° (Grünhagen, *A.* 256, 305). Liquid, v. sol. ether and alcohol.—$B'_2H_2PtCl_6$: brown amorphous powder.

Isomeride [c. 135°]. Crystalline powder, sl. sol. cold alcohol.—Salts: $B''2HCl$.—$B''2HBr$.—$B''H_2SO_4$.—$B''2H_3PO_4$.—$B''3H_2C_2O_4$.—$B''2H_2C_2O_4$. Radiating aggregates.

Di-p-tolyl-methylene-diamine $(C_7H_7.NH)_2CH_2$. (above 350°). Formed, together with the solid isomeride, by heating *p*-toluidine with CH_2Cl_2 (G.). Oil, v. sol. ether.—$B''HCl$.—$B''_2H_2PtCl_6$.—$B''HAuCl_4$.

Isomeride $C_{15}H_{18}N_2$. [c. 156°]. (over 350°). Amorphous, sl. sol. ether.—$B''2HCl$ (?).—$B''H_2PtCl_6$.—$B''2HAuCl_4$.—$B''2H_2C_2O_4$. Crystalline crusts.

Di-p-tolyl-di-methylene-diamine

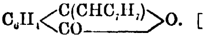

$C_7H_7N\left<\begin{matrix}CH_2\\CH_2\end{matrix}\right>NC_7H_7$. [90°]. A product of the action of CH_2Cl_2 on *p*-toluidine at 100° (Grünhagen, *A.* 256, 296). Granules, sol. hot alcohol. Converted by nitrous acid into a crystalline nitroso- derivative $(C_7H_7N)_2C_2H_2(NOH)$ (?)—$B''2HCl$.—$B''2HAuCl_4$.—$B''2HBr$.—$B''H_2SO_4$.

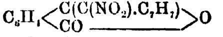
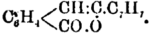
o-Tolyl-trimethylene-diamine $C_3H_6(NH_2).NHC_7H_7$. (281°). Formed by reducing *o*-tolyl-pyrazole dihydride in alcoholic solution by sodium (Balbiano, *G.* 18, 354). Oil.

p-Tolyl-trimethylene-diamine $C_3H_6(NH_2).NHC_7H_7$. [c. −15°]. (287°). A product of the action of Na on an alcoholic solution of *p*-tolyl-pyrazole (Balbiano). Liquid. Oxalate. [208°]. Spherical groups of minute needles.

p-TOLYL METHYLENE METHYL SULPHONE KETONE $C_7H_7.SO_2.CH_2.CO.CH_3$. [51°]. Formed from chloro-acetone and sodium toluene *p*-sulphinate (Otto, *J. pr.* [2] 36, 401). Silky needles. Yields a bromo- derivative [130°].

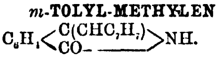
m-TOLYL-METHYLENE-PHTHALIDE

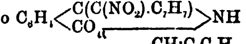

$C_6H_4\left<\begin{matrix}C(CHC_7H_7)\\CO\text{———}\end{matrix}\right>O$. [153°]. Formed by heating *m*-tolyl-acetic acid with phthalic anhydride and a little NaOAc (Heilmann, *B.* 23, 3157). Needles (from ligroïn), sl. sol. ether.

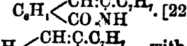
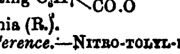
p-Tolyl-methylene-phthalide $C_{16}H_{12}O_2$. *p-Xylal-phthalide.* [151°]. Formed in like manner from *p*-tolyl-acetic acid (Ruhemann, *B.* 24, 3965). Yellow needles (from alcohol), sl. sol. ether. Nitrous acid passed into its solution in chloroform forms 
$C_6H_4\left<\begin{matrix}C(C(NO_2).C_7H_7)\\CO\text{————}\end{matrix}\right>O$ [140°], which may be reduced to the compound 
$C_6H_4\left<\begin{matrix}CH:C.C_7H_7\\CO.O\end{matrix}\right.$. [116°].

Reference.—Nitro-tolyl-methylene-phthalide.

m-TOLYL-METHYLENE-PHTHALIMIDINE


$C_6H_4\left<\begin{matrix}C(CHC_7H_7)\\CO\text{———}\end{matrix}\right>NH$. [165°]. Formed by heating *m*-tolyl-methylene-phthalide with alcoholic ammonia (Heilmann, *B.* 23, 3161). Yellowish needles.

p-Tolyl-methylene-phthalimidine $C_{16}H_{13}NO$. [204°]. Formed by heating *p*-tolyl-methylene-phthalide with alcoholic NH_3, the compound $NH_2.CO.C_6H_4.CO.CH_2C_7H_7$ being first formed (Ruhemann, *B.* 24, 3968). Converted by passing nitrous acid through its solution in chloroform into 
$C_6H_4\left<\begin{matrix}C(C(NO_2).C_7H_7)\\CO\text{————}\end{matrix}\right>NH$ [227°].

Isomeride 
$C_6H_4\left<\begin{matrix}CH:C.C_7H_7\\CO.NH\end{matrix}\right.$. [228°]. Formed by heating 
$C_6H_4\left<\begin{matrix}CH:C.C_7H_7\\CO.O\end{matrix}\right.$ with alcoholic ammonia (R.).

Reference.—Nitro-tolyl-methylene-phthalimidine.

DI-*p*-TOLYL TRIMETHYLENE DISULPHONE $C_3H_6(SO_2C_7H_7)_2$. [125°]. Formed from trimethylene bromide and sodium toluene *p*-sulphinate (Otto, *B.* 24, 1834). Plates. Converted by alcoholic potash at 120° into the compound $O(CH_2.CH_2.CH_2.SO.C_7H_7)_2$ [80°].

TOLYL-METHYL-IMESATIN *v.* *Toluide* of *Methyl*-ISATIN.

***m*-TOLYL METHYL KETONE** $C_7H_7.CO.CH_3$ *Methyl-acetophenone.* (219°). Formed by distilling calcium *m*-toluate with calcium formate (Buchka a. Irish, *B.* 20, 1766).

Tolyl methyl ketone. (225°). S.G. ^{22} ·9891. V.D. 4·58. Formed, together with the *p*-compound, by the action of AcCl on toluene and $AlCl_3$ (Essner a. Gossin, *Bl.* [2] 42, 95). This is perhaps the *o*-compound.

***p*-Tolyl methyl ketone.** (217°) (M.); (230° cor.) (W.). Formed by the action of $AlCl_3$ on a mixture of toluene and Ac_2O or AcCl (Michaelis, *B.* 15, 185; Claus, *B.* 19, 234). Formed also by heating toluene with HOAc, $ZnCl_2$, and $POCl_3$ (Frey, *J. pr.* [2] 43, 114) and as a by-product in the oxidation of (*a*)-nitro-cymene (Widman, *B.* 19, 587). Oil. Yields a dibromide $C_9H_8Br_2O$ [100°]. $KMnO_4$ forms terephthalic acid. Alkaline K_3FeCy_6 forms *p*-toluic and *p*-tolyl-glyoxylic acids (B. a. K.). HNO_3 forms $C_{18}H_{14}N_2O_4$ [125°], which is reduced by zinc-dust and HOAc to $C_2H_4(CO.C_7H_7)_2$ (Hollemann, *R. T. C.* 10, 211).

Oxim [88°]. Crystals (from ligroïn).

Phenyl-hydrazide [97°]. Prisms.

Reference.—AMIDO-, IODO-, and OXY-, TOLYL METHYL KETONE.

***o*-TOLYL METHYL KETONE TETRAHYDRIDE** $CH_2\left<\begin{matrix}CH_2.CMe\\CH_2.CH_2\end{matrix}\right>C.CO.CH_3$. (206°). Formed from *aω*-di-acetyl-pentane by treatment with conc. H_2SO_4 (Kipping a. Perkin, jun., *C. J.* 57, 18). Oil, smelling like peppermint. Does not combine with $NaHSO_3$. In moist ether it is reduced by Na to the hexahydride.

Oxim $C_9H_{15}NO$. Liquid.

Phenyl hydrazide $C_{15}H_{20}N_2$. Oil.

Tolyl methyl ketone hexahydride *v.* METHYL-HEXAMETHYLENYL METHYL KETONE.

***m*-TOLYL-METHYL-MALONIC ACID** $[1:3]C_6H_4Me.CH_2.CH(CO_2H)_2$. [133°]. Formed by saponification of the ether (Poppe, *B.* 23, 110). Rhombohedra, sl. sol. water.—K_2A'': needles.

Methyl ether Me_2A''. (c. 300°).

Ethyl ether Et_2A''. (320°). Formed from *ω*-bromo-*m*-xylene and sodium malonic ether. Oil. Converted by alcoholic NH_3 at 150° into $C_6H_4Me.CH_2.CH(CO_2Et).CO.NH_2$ [186°], which on warming with water forms the ammonium salt $C_6H_4Me.CH_2.CH(CO_2Et).CO_2NH_4$ [77°]. Et_2A'' is converted by methylamine into the methylamide $C_6H_4Me.CH_2.CH(CO_2Et).CONHMe$ [120°], and by aniline into $C_6H_4Me.CH_2.CH(CO.NHPh)_2$ [188°].

Di-*m*-tolyl-di-methyl-malonic ether $(C_6H_4Me.CH_2)_2C(CO_2Et)_2$. [122°]. A product of the action of *ω*-bromo-*m*-xylene on sodium malonic ether (Poppe, *B.* 23, 109).

***o*-TOLYL-METHYL-OXAZOLINE** $C_{11}H_{13}NO$ *i.e.* $\begin{matrix}CHMe.O\\CH_2—N\end{matrix}\!\!>C.C_7H_7$. (258°). Formed by boiling $C_7H_7.CO.NH.CH_2.CHMeBr$ with alcoholic potash (Salomon, *B.* 26, 1323). Oil.—$B'C_6H_3N_3O_7$. [129°].—$B'_2H_2PtCl_6$.

***p*-Tolyl-methyl-oxazoline** $C_{11}H_{13}NO$. (265°). Formed from the bromopropyl-amide of *p*-toluic acid (Salomon, *B.* 26, 1326). Oil.—Picrate $B'C_6H_3N_3O_7$. [183°].—$B'_2H_2PtCl_6$. [184°].

***p*-TOLYL-DI-METHYL-PHOSPHINE** $C_7H_7PMe_2$. (210°). Formed from $C_7H_7PCl_2$ and $ZnMe_2$ (Czimatis, *B.* 15, 2014). Oil, oxidised by HgO to $C_7H_7PMe_2O$. CS_2 forms $C_7H_7PMe_2CS_2$ [110°] crystallising in red plates.

Methylo-iodide B'MeI. [255°]. Needles. Yields $B'MeI_3$ and $B'_2Me_2PtCl_6$.

Benzylo-chloride. Yields $B'_2(C_7H_7)_2PtCl_6$ [226°], a yellow crystalline pp.

***p*-TOLYL-METHYLPHTHALIMIDE** $[4:2:1]C_6H_3Me:C_2O_2:N.C_6H_4Me$. [180°]. Formed by distilling (4,2,1)-methyl-phthalic acid with *p*-toluidine (Niementowski, *M.* 12, 630). Crystalline mass, v. e. sol. chloroform, insol. water.

***p*-TOLYL-METHYL-PHTHALIMIDINE** $C_6H_4\left<\begin{matrix}CH(CH_2.C_6H_4Me)\\CO\end{matrix}\right>NH$. [149°]. Formed from *p*-tolyl-methylene-phthalimidine, HI and P (Ruhemann, *B.* 24, 39[illegible]). Needles.

DI-*p*-TOLYL-METHYL-PIPERAZINE $C_{19}H_{21}N_2$. [105°]. Formed from di-*p*-tolyl-propylene-diamine, ethylene bromide, and Na_2CO_3. Needles (from alcohol) (Bischoff, *B.* 25, 3278).

***o*-TOLYL-METHYL-PROPYLENE-*ψ*-THIO-UREA** $\begin{matrix}CHMe.S\\CH_2—N\end{matrix}\!\!>C.NMe.C_7H_7$. (c. 295°). Formed from *o*-tolyl-propylene-*ψ*-thio-urea and MeI (Prager, *B.* 22, 2999). Yields (*β*)-methyl-taurine on oxidation.—$B'C_6H_3N_3O_7$. [138°].—B'HI. [166°].—$B'_2H_2PtCl_6$. Decomposes over 200°.

***p*-TOLYL-DI-METHYL-PYRROLE** $(C_7H_7)N\left<\begin{matrix}CMe:CH\\CMe:CH\end{matrix}\right.$. [46°]. (255°). Got by heating the di-carboxylic acid (Knorr, *B.* 18, 308). Crystals, volatile with steam.

Reference.—AMIDO-TOLYL-DI-METHYL-PYRROLE.

***p*-TOLYL-DI-METHYL-PYRROLE DICARBOXYLIC ACID** $(C_7H_7)N\left<\begin{matrix}CMe:C.CO_2H\\CMe:C.CO_2H\end{matrix}\right.$. Got by saponifying its ether, which is formed by mixing acetic acid solutions of di-acetyl-succinic ether and *p*-toluidine (Knorr, *B.* 18, 304). Needles, decomposes at about 250°, with evolution of CO_2.—K_2A''.—$AgHA''$.

Ethyl ether Et_2A''. [67°]. Tables.

Reference.—AMIDO-TOLYL-DI-METHYL-PYRROLE DICARBOXYLIC ACID.

***p*-TOLYL-DI-METHYL-SULPHAMIDE** $SO_2(NMe_2).NHC_7H_7$. [91°]. Formed from $NMe_2.SO_2Cl$ and *p*-toluidine (Behrend, *A.* 222, 129). Crystals, v. sol. alcohol and ether.

***p*-TOLYL METHYL SULPHONE** $C_7H_7.SO_2.CH_3$. [87°]. Formed by the action of conc. KOHAq on *p*-tolyl-sulphono-acetic acid (Otto, *B.* 18, 161). Got also from $C_7H_7.SO_2Na$ and MeI (Otto). Needles (from very dilute alcohol), v. sol. hot water.

***o*-TOLYL-METHYL-THIAZOLINE** $\begin{matrix}CHMe.S\\CH_2—N\end{matrix}\!\!>C.C_7H_7$. (284°-295°). Formed by heating *o*-toluic bromo-propylamide with P_2S_5 at 150° (Salomon, *B.* 26, 1328). Oil.—$B'C_6H_3N_3O_7$. [136°].

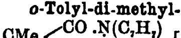
***p*-Tolyl-methyl-thiazoline** $C_{11}H_{13}NS$. (295°). Oil.—$B'C_6H_3N_3O_7$. [141°].—$B'_2H_2PtCl_6$.

o-TOLYL-METHYL-THIOHYDANTOÏN

$\mathrm{HMe}<\begin{matrix}\mathrm{CO.N(C_7H_7)}\\ \mathrm{NH.CS}\end{matrix}$. [198°]. Formed from *o*-tolyl-thiocarbimide and alanine (Marckwald, *B.* 24, 3281). Crystals.

p - Tolyl-methyl - thiohydantoïn. [197°]. Formed in like manner from *p*-tolyl-thiocarbimide and alanine (Aschan, *B.* 17, 427). Minute prisms. On heating with alcoholic potash it is converted by hydrolysis into a salt of the oily $NHC_7H_7.CS.NH.CHMe.CO_2H$, which slowly changes, in the free state, back into the hydantoïn.

o-Tolyl-di-methyl-thiohydantoïn



$\mathrm{CMe_2}<\begin{matrix}\mathrm{CO.N(C_7H_7)}\\ \mathrm{NH.CS}\end{matrix}$. [175°]. Formed from *o*-tolyl-thiocarbimide and *α*-amido-isobutyric acid (Marckwald, *B.* 24, 3284). Needles, v. sol. hot alcohol.

p-Tolyl-di-methyl-thiohydantoïn. [85°]. Formed in like manner from *p*-tolyl-thiocarbimide. Crystals, v. sol. most solvents.

o-TOLYL-METHYL-THIO-UREA $NHMe.CS.NHC_7H_7$. [153°]. Formed from methyl-thiocarbimide and *o*-toluidine in alcohol (Dixon, *C. J.* 55, 622). Pearly crystals, m. sol. hot water, sol. alcohol.

p-Tolyl-methyl-thio-urea. [126°]. Formed in like manner from *p*-toluidine. Vitreous prisms, v. sol. hot water.

Reference.—Tolyl-thio-urea.

o-TOLYL-(α)-NAPHTHYLAMINE $C_{17}H_{15}N$ *i.e.* $C_{10}H_7.NH.C_6H_4Me$. [95°]. Formed by heating (*α*)-naphthol (1 mol.) with *o*-toluidine (2 mols.) and $CaCl_2$ (1 mol.) in sealed tubes at 290°, the yield being 37 p.c. of the theoretical amount (Friedländer, *B.* 16, 2084). Flat needles, v. sol. alcohol and ether.

o-Tolyl-(β)-naphthylamine $C_{10}H_7NH.C_6H_4Me$. [96°]. Formed by heating a mixture of (*β*)-naphthol with *o*-toluidine and $CaCl_2$ at 280°. Silvery plates (from ligroïn), v. sol. alcohol.—$B'2C_6H_3N_3O_7$. [110°]. Reddish-brown needles.

Benzoyl derivative [118°]. Plates.

p-Tolyl-(α)-naphthylamine $C_{17}H_{15}N$. [79°]. (360° at 528 mm.). Formed by heating (*α*)-naphthol with *p*-toluidine and $CaCl_2$ at 280°, the yield being 50 p.c. Short prisms (from alcohol). Its solutions exhibit blue fluorescence.

p-Tolyl-(β)-naphthylamine. [104°]. Formed by heating *p*-toluidine hydrochloride with (*β*)-naphthol for 8 hours at 200° (Witt, *B.* 20, 578; *cf.* Friedländer, *B.* 16, 2078). Plates (from alcohol). Its solutions have violet-blue fluorescence. Dissolved in isoamyl alcohol it is reduced by Na to a hydride [44°] (Bamberger a. Müller, *B.* 22, 1309). With nitroso-dimethyl-aniline hydrochloride and HOAc it yields a saffranine $C_{10}H_6N_2Cl(C_7H_7):C_6H_3NMe_2$ (Witt, *B.* 21, 724). *p*-Tolyl-naphthyl-amine (10 g.), heated with nitroso-dimethylaniline hydrochloride (4 g.), $ZnCl_2$ (10 g.), and HOAc (100 c.c.), forms $C_{20}H_{12}(NH.C_6H_4Me)_2$ [225°], which yields an acetyl derivative [225°].

Acetyl derivative [85°]. Needles.

Benzoyl derivative [139°]. Needles.

Reference. — Tetra-bromo-tolyl-naphthylamine.

DI-p-TOLYL-NAPHTHYLENE-DIAMINE $C_{10}H_6(NHC_7H_7)_2$. [237°]. Formed by heating di-oxy-naphthalene with *p*-toluidine and *p*-toluidine hydrochloride (Annaheim, *B.* 20, 137 Needles (from xylene). Gives a red colour o heating with solid $ZnCl_2$.

o-TOLYL-(α)-NAPHTHYL-THIO-UREA $CS(NHC_{10}H_7)(NHC_7H_7)$. [168°]. Formed b the action of *o*-tolyl thiocarbimide on (*α*)-naph thylamine or of (*α*)-naphthyl thiocarbimide o *o*-toluidine (Mainzer, *B.* 15, 1416). Sho needles, sol. alcohol. Split up by conc. HClA at 150° into *o*-toluidine, (*α*)-naphthylamin *o*-tolyl-thiocarbimide, and (*α*)-naphthyl thi carbimide.

o - Tolyl - (β) - naphthyl - thio - urea [194° Formed from *o*-tolyl thiocarbimide and (*β*)-nap thylamine (M.).

p - Tolyl - (α) - naphthyl - thio - urea [168° Formed from *p*-tolyl thiocarbimide and (*α*)-naph thylamine (M.). Slender white needles.

p - Tolyl - (β) - naphthyl - thio - urea [164° Formed from *p*-tolyl thiocarbimide and (*β*) naphthylamine (M.). Decomposed by HClAq a 150° into *p*-toluidine, (*β*)-naphthylamine, *p*-toly thiocarbimide, and (*β*)-naphthyl thiocarbimide.

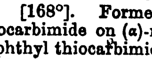
p-TOLYL p-NITRO-BENZYL OXIDE $C_6H_4Me.O.CH_2.C_6H_4.NO_2$. [91°]. Formed fro *p*-nitro-benzyl chloride and alcoholic C_7H_7ON (Frische, *A.* 224, 144). Yellowish plates, so ether.

TOLYL NITROSO-METHYL KETONE v *Oxim* of Tolyl-glyoxal.

TOLYL-OXAMIC ACID *v.* vol. iii. p. 654.

TOLYL-OXAMIDE *v.* Oxalic acid.

o-TOLYL-OXAZOLINE



$\begin{matrix}\mathrm{CH_2.O}\\ \mathrm{CH_2.N}\end{matrix}\!\!>\!\mathrm{C.C_7H_7}$. (255°). Formed by dissolving *o*-toluic bromo ethyl-amide in hot water and adding alkal (Salomon, *B.* 26, 1322). Oil. Evaporating wit aqueous HCl (1 mol.) forms the compoun $C_7H_7.CO.O.CH_2.CH_2.NH_2$, while excess of HC gives $C_7H_7.CO.NH.CH_2.CH_2Cl$. — $B'C_6H_3N_3O$ [145°].—$B'_2H_2PtCl_6$. [189°].

p-Tolyl-oxazoline $C_{10}H_{11}NO$. [66°]. (265°) Formed by decomposing $C_7H_7.CO.NH.CH_2.CH_2B$ with alkali. Needles.—$B'C_6H_3N_3O_7$. [188°].—$B'_2H_2PtCl_6$. [186°].

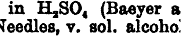
DI-o-TOLYL OXIDE $(C_6H_4Me)_2O$. *Cresy ether.* (272°–278°). S.G. ${}^{24.8}$ 1·047. A produc of the distillation of $Al(OC_6H_4Me)_3$ (Gladstone a Tribe, *C. J.* 49, 27). Oil, smelling like geraniu leaves.

Di-m-tolyl oxide $(C_7H_7)_2O$. (284°–288°) μ_a 1·5576 at 16°. V.D. 193·9. A product o distillation of aluminium thymol $Al(OC_{10}H_{13})$ (Gladstone a. Tribe, *C. J.* 41, 13). Oil.

Di-p-tolyl oxide $(C_7H_7)_2O$. [50°]. (270°–300°) Formed by distilling aluminium *p*-cresol (C. a T.). Prisms (from alcohol).

Isomeride [165°]. Formed by heatin *p*-cresol with $ZnCl_2$ (Busch, *B.* 17, 2638). Crystals, volatile with steam.

DI-TOLYL-OXINDOLE

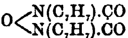


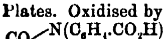
$\mathrm{C_6H_4}<\begin{matrix}\mathrm{C(C_7H_7)_2}\\ \mathrm{NH}\end{matrix}>\mathrm{CO}$ *Toluisatin.* [200°]. Formed by adding toluen to a solution of isatin in H_2SO_4 (Baeyer a Lazarus, *B.* 18, 2638). Needles, v. sol. alcoho and ether, sol. aqueous alkalis. Yields an acety derivative $C_{22}H_{18}O(NAc)$ [143°] and an ethy derivative $C_{22}H_{18}O(NEt)$ [108°], both being crystalline.

TOLYL-OXY-ACETIC ACID *v. Tolyl derivative* of GLYCOLLIC ACID and OXY-TOLYL-ACETIC ACID.

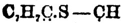
***p*-TOLYL OXY-ETHYL SULPHONE** $C_7H_7.SO_2.CH_2.CH_2OH$. [55°]. Got from sodium toluene *p*-sulphinate and glycol chlorhydrin (Otto, *J. pr.* [2] 30, 355). Needles (from alcohol) with bitter taste. Heating with KOHAq gives $C_{18}H_{22}S_2O_4$ [84°].

Benzoyl derivative $C_7H_7.SO_2.C_2H_4.OBz$. [176°]. Needles, sl. sol. hot alcohol.

DI-*o*-TOLYL-PARABANIC ACID $C_{17}H_{14}N_2O_3$ *i.e.*  $CO<\begin{matrix}N(C_7H_7).CO\\N(C_7H_7).CO\end{matrix}$ [203°]. Formed by boiling an alcoholic solution of oxalyl-di-tolyl-guanidine with conc. HClAq (Berger, *B.* 12, 1856). Small needles.

Di-*p*-tolyl-parabanic acid [144°]. Formed by boiling di- (or tri-) *p*-tolyl-guanidine dicyanide with alcohol and HCl (Landgrebe, *B.* 11, 978). Plates. Oxidised by potassium permanganate to  $CO<\begin{matrix}N(C_6H_4.CO_2H).CO\\N(C_6H_4.CO_2H).CO\end{matrix}$ [159° ?].

***p*-TOLYL PENTADECYL KETONE** $C_{15}H_{31}.CO.C_6H_4Me$. [60°]. (262° at 15 mm.). Formed from palmityl chloride, toluene, and $AlCl_3$ (Krafft, *B.* 21, 2266). Needles (from alcohol). Yields *p*-toluic acid on oxidation.

***o*-TOLYL-PENTHIAZOLINE** $C_{11}H_{13}NS$ *i.e.*  $\begin{matrix}C_7H_7C.S-CH_2\\N.CH_2.CH_2\end{matrix}$. Got by heating trimethylene chlorobromide with thio-*o*-toluic amide (Pinkus, *B.* 26, 1081). Oil, volatile with steam. Its hydrochloride gives a white compound with $HgCl_2$.

***p*-Tolyl-penthiazoline** [53°].

***p*-TOLYL-PHENTLIAZINE.** *Dihydride* $C_6H_4<\begin{matrix}N=N\\CH_2.N.C_7H_7\end{matrix}$ [151°]. Formed by the action of HNO_2 on *o*-amido-benzyl-*p*-toluidine hydrochloride (Busch, *B.* 25, 450). Yellow plates (from alcohol).—B'HCl.—$B'_2H_2PtCl_6$. [190°].—$B'C_6H_3N_3O_7$. [132°]. Dark-yellow needles.

***p*-TOLYL-PHENYL-ACETAMIDINE** $C_{15}H_{16}N_2$ *i.e.* $C_6H_5.CH_2.C(N.C_6H_4Me).NH_2$. [119°]. Formed by heating phenyl-acetonitrile with *p*-toluidine hydrochloride (Bernthsen, *A.* 184, 342). Crystals (from alcohol).—$B'_2H_2PtCl_6$: yellow prisms.

DI-*p*-TOLYL-DIPHENYLACETYLENE-DIAMINE $C_{28}H_{24}N_2$ *i.e.* $C_7H_7N:CPh.CPh:NC_7H_7$. [161°]. Formed, together with $Bz.CPh:NC_7H_7$ [116°], by heating benzil (1 mol.) with *p*-toluidine (2 mols.) at 130° (Bandrowski, *M.* 9, 690). Triclinic plates.

DI-TOLYL-PHENYLENE-DIAMINE *v.* PHENYLENE-DI-TOLYL-DIAMINE.

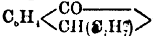
TOLYL PHOSPHATES.

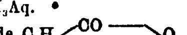
Tri-*o*-tolyl-phosphate $(C_7H_7O)_3PO$. Formed by heating *o*-cresol with $POCl_3$, the yield being 95 p.c. (Heim, *B.* 16, 1767; Rapp, *A.* 224, 173). Oil, sol. alcohol and ether.

***p*-Tolyl phosphate** $PO(OC_7H_7)(OH)_2$. [116°]. Formed by the action of water on $PO(OC_7H_7)Cl_2$, which is a product of the action of $POCl_3$ on *p*-cresol (Rapp, *A.* 224, 168). Plates, sol. alcohol, ether, and water.

Tri-*p*-tolyl phosphate $PO(OC_7H_7)_3$. [78°]. Formed by heating *p*-cresol with $POCl_3$, the yield being 95 p.c. Colourless tables, insol. Aq.

***p*-TOLYL-PHOSPHINE** $C_7H_7NH_2$. [4°]. (178°). Formed by the action of $AlCl_3$ on a mixture of toluene and PCl_3, the resulting $C_7H_7PCl_2$ [20°] (245°), being converted by water into $C_7H_7P(OH)_2$, which splits up on heating into tolyl-phosphine and toluene phosphonic acid $C_7H_7PO_3H_2$ (Michaelis, *B.* 12, 1009; 13, 653; *A.* 212, 230). Oil with strong odour. Rapidly oxidised by air to $C_7H_7P(OH)_2$. HI forms $C_7H_7PH_3I$, crystallising in colourless needles.

***p*-TOLYL-PHTHALIDE** $C_{15}H_{12}O_2$ *i.e.*  $C_6H_4<\begin{matrix}CO\text{———}\\CH(C_7H_7)\end{matrix}>O$. [129°]. Formed by reducing $C_7H_7.CO.C_6H_4.CO_2H$ in alcoholic solution with Zn and HCl (Gresly, *A.* 234, 235). Needles, sol. hot alcohol, insol. NH_3Aq.

Di-*p*-tolyl-phthalide  $C_6H_4<\begin{matrix}CO\text{———}\\C(C_7H_7)_2\end{matrix}>O$. [116°]. Formed by heating phthalyl chloride (100 g.) with toluene (450 g.) and $AlCl_3$ (Berchem, *Bl.* [2] 42, 168; *cf.* Friedel a. Crafts, *Bl.* [2] 35, 505). Prisms, sol. alcohol and ether.

TOLYL-PHTHALIMIDE *v. Tolylimide* of PHTHALIC ACID.

***m*-TOLYL-PROPIOLIC ACID** $C_7H_7.C:C.CO_2H$. [109·5°]. Formed by boiling di-bromo-tolyl-propionic acid $C_7H_7.CHBr.CHBr.CO_2H$ with alcoholic potash (Müller, *B.* 20, 1215). $AgNO_3$ gives an explosive white pp.

o-TOLYL-PROPIONIC ACID $C_7H_7.C_2H_4O_2$. Monoclinic prisms (Young, *B.* 25, 3102).

***m*-Tolyl-propionic acid** $C_7H_7.CH_2.CH_2.CO_2H$. [43°]. Formed by reducing *m*-tolyl-acrylic acid with sodium-amalgam (Müller, *B.* 20, 1214; von Miller, *B.* 23, 1899). Needles (from ligroïn), sol. water, alcohol, and ether. Volatile with steam.

***m*-Tolyl-propionic acid** [125°]. Formed by oxidation of *m*-isobutyl-toluene by HNO_3 (Effront, *B.* 17, 2330). Needles, sl. sol. hot water.—AgA': crystals, sol. hot water.

***p*-Tolyl-propionic acid.** [116°] (Von Miller, *B.* 23, 1898); [120°] (Kröber, *B.* 23, 1033). Formed by reducing *p*-tolyl-acrylic acid. Condensed by hot H_2SO_4 to oxy-methyl-indonaphthene.

Di-*a*-tolyl-propionic acid $CH_3.C(C_7H_7)_2.CO_2H$. [152°]. Prepared by adding toluene to a solution of pyruvic acid in H_2SO_4 at −10° (Böttinger, *B.* 14, 1596; 15, 1474). Monoclinic crystals, sol. hot alcohol. Give *a*-di-tolyl-ethane on distillation with lime. Oxidised by $KMnO_4$ to di-phenyl-ethane tri-carboxylic acid.—AgA'.

Ethyl ether EtA'. [145°]. Prisms.

References. — BROMO-, NITRO-, and OXY-, TOLYL-PROPIONIC ACIDS.

***p*-TOLYL-PROPIONIC ALDEHYDE** $C_7H_7.CH_2.CH_2.CHO$. (223°). S.G. ^{13} ·9941. Formed by the action of water on the compound of CrO_2Cl_2 with the cymene got from camphor and P_2O_5 (Richter a. Schüchner, *B.* 17, 1931). Got also by distilling calcium *p*-tolyl-propionate with calcium formate (Miller, *B.* 23, 1082). Oil, smelling like peppermint. Volatile with steam. Yields *p*-toluic and terephthalic acids on oxidation.

DI-*o*-TOLYL-PROPYLENE-DIAMINE $CHMe(NHC_7H_7).CH_2.NHC_7H_7$. (280° at 120 mm.). Got by heating *o*-toluidine with propylene bromide (Bischoff, *B.* 25, 3276).

Acetyl derivative $C_{21}H_{28}N_2O_2$. [120°].

Di-*p*-tolyl-propylene-diamine $C_3H_6(NHC_7H_7)_2$. (277° at 48 mm.) (Bischoff, *B.* 25, 3277). Got from *p*-toluidine and $C_3H_6Br_2$. Oil.

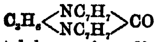
Acetyl derivative $C_{21}H_{28}N_2O_2$. [114°].

Benzoyl derivative $C_{31}H_{30}N_2O_2$. [152°].

o-TOLYL-PROPYLENE-ψ-THIO-UREA

$C_7H_7NH.C<\genfrac{}{}{0pt}{}{S.CHMe}{N.CH_2}$. [126°]. Formed from s-o-tolyl-allyl-thio-urea and HCl (Prager, *B.* 22, 2999). Tables, sl. sol. hot water.—$B'_2H_2PtCl_6$. [178°]. Prisms.—$B'C_6H_3N_3O_7$. [176°]. Cubes.

DI-o-TOLYL-PROPYLENE UREA

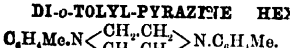

$C_3H_6<\genfrac{}{}{0pt}{}{NC_7H_7}{NC_7H_7}>CO$. [93°]. Formed from di-o-tolyl-propylene-diamine and $COCl_2$ (Bischoff, *B.* 25, 3276). Prisms (from dilute alcohol).

Di-p-tolyl-propylene-urea. [130°].

d-TOLYL ISOPROPYL KETONE

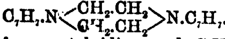
$C_6H_4Me.CO.Pr$. (236°). Formed from toluene, isobutyryl chloride and $AlCl_3$ (Claus, *J. pr.* [2] 46, 480). Oil, with bitter taste and aromatic odour. Yields p-toluic and terephthalic acids on oxidation. Yields an oxim [92°]. May be reduced to p-tolyl-isopropyl-carbinol; an oil boiling above 300°.

DI-o-TOLYL-PYRAZINE HEXAHYDRIDE


$C_6H_4Me.N<\genfrac{}{}{0pt}{}{CH_2.CH_2}{CH_2.CH_2}>N.C_6H_4Me$. *Di-o-tolyl-piperazine.* [171°]. Formed from ethylene bromide, o-toluidine, and Na_2CO_3 at 160° (Bischoff, *B.* 22, 1781; 23, 1982; *cf.* Mauthner a. Suida, *M.* 7, 233). Crystals (from ether).

Isomeride. [154°]. Formed by heating di-o-tolyl-ethylene-diamine with chloro-acetic acid and NaOAc (Bischoff, *B.* 23, 2031). Thin needles (from alcohol).

Di-p-tolyl-pyrazine hexahydride


$C_7H_7.N<\genfrac{}{}{0pt}{}{CH_2.CH_2}{CH_2.CH_2}>N.C_7H_7$. [188°]. Formed from p-toluidine and $C_2H_4Br_2$ in presence of NaOAc or Na_2CO_3. Prisms, sl. sol. alcohol. With $NaNO_2$ and HOAc it yields a di-nitroso-derivative [167°].

o-TOLYL-PYRAZOLE

$CH<\genfrac{}{}{0pt}{}{CH.N.C_7H_4Me}{CH:N}$ (246·5° cor.). S.G. $\frac{0}{0}$ 1·0868; $\frac{13}{0}$ 1·0753. Formed by boiling epichlorhydrin (1 mol.) with o-tolyl-hydrazine (2 mols.) and benzene, boiling off the benzene, and heating the residue at 150° (Balbiano, *G.* 18, 368). Not reduced by boiling with alcohol and Na.—$B'_2H_2PtCl_6$. [201°].—B'EtI. [100°]. Needles, v. e. sol. water.

Dihydride $C_3H_5N_2.C_7H_7$. (271°). S.G. $\frac{0}{0}$ 1·084. Formed from acroleïn tolyl-hydrazide and dilute (2 p.c.) H_2SO_4. Oil. Sol. fuming HClAq, but reppd. by water. $K_2Cr_2O_7$ and H_2SO_4 give an indigo-blue colour.

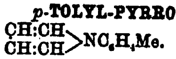
p-Tolyl-pyrazole. [33°]. (259° cor.). Formed, in like manner, from epichlorhydrin and p-tolyl-hydrazine. Yellowish plates, sl. sol. hot water.—$B'_2H_2PtCl_6$2aq: needles. [184°].—B'EtI. [105°]. Prisms, v. sol. water.

Dihydride. [60·5°]. (282° i.V.). Formed from acroleïn p-tolyl-hydrazide and dilute H_2SO_4. Got also by reducing p-tolyl-pyrazole in alcoholic solution by Na. Iridescent plates, sl. sol. hot water. Its acidified solution is coloured violet-red by $K_2Cr_2O_7$.

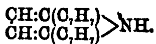
p-TOLYL-PYRIDINE HEXAHYDRIDE

$C_6H_4Me.N.C_5H_{10}$. (262°). Formed by heating piperidine with p-bromo-toluene at 270° (Lellmann a. Just, *B.* 24, 2099). V. sol. alcohol and benzene.

p-TOLYL-PYRROLE $C_{11}H_{11}N$ *i.e.*


$\genfrac{}{}{0pt}{}{CH:CH}{CH:CH}>NC_6H_4Me$. Got by dry distillation of p-toluidine mucate (Lichtenstein, *B.* 14, 933). Converted by AcCl into crystalline $C_7H_7NC_4Ac_4$.—B'_2HgCl_2.

Di-p-tolyl-pyrrole


$\genfrac{}{}{0pt}{}{CH:C(C_7H_7)}{CH:C(C_7H_7)}>NH$. [197°]. Formed by treating di-p-tolyl-furfurane or $(C_7H_7.CO)_2C_2H_4$ with NH_4OAc (Hollemann, *R. T. C.* 6, 73). Small plates with bluish lustre. Does not form a K derivative. Boiling HClAq gives a red resin. With isatin, after several days, it gives an intense red colour.

o-TOLYL-QUINAZOLINE DIHYDRIDE

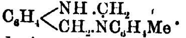
$C_{15}H_{14}N_2$ *i.e.*

$C_6H_4<\genfrac{}{}{0pt}{}{N=CH}{CH_2.N.C_6H_4Me}$. Formed by reducing the formyl derivative of o-nitro-benzyl-o-toluidine with tin and HClAq (Paal a. Busch, *B.* 22, 2701). Oil.—$B'HSnCl_3$.—B'HCl: amorphous.—$B'_2H_2PtCl_6$. [210°]. Needles (from alcohol containing HCl).

p-Tolyl-quinazoline dihydride. [120°]. Formed in like manner. Plates, v. sol. alcohol.—$B'HSnCl_3$. [165°].—B'HCl 2aq. [85°].—B'HCl. [251°].—$B'_2H_2PtCl_6$. [216°]. Yellow needles.

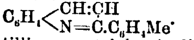
Methylo-iodide B'MeI. [186°]. Needles.

p-Tolyl-quinazoline tetrahydride

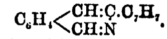

$C_6H_4<\genfrac{}{}{0pt}{}{NH.CH_2}{CH_2.NC_6H_4Me}$. [127°]. Formed by reducing the dihydride in alcoholic solution by sodium. Needles, m. sol. alcohol. Yields a nitrosamine [100°]. Yields a crystalline hydrochloride.

Reference.—Oxy-tolyl-quinazoline.

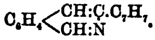
(*Py.* 3)-**o-TOLYL-QUINOLINE** $C_{16}H_{13}N$ *i.e.*


$C_6H_4<\genfrac{}{}{0pt}{}{CH:CH}{N=C.C_6H_4Me}$. [77°]. Formed by distilling oxy-tolyl-quinoline (pseudoflavenol) with zinc-dust (Weidel a. Bamberger, *M.* 9, 108). Silky needles (from benzene).—$B'_2H_2PtCl_6$ (dried at 105°). Orange tables.

m-Tolyl-isoquinoline


$C_6H_4<\genfrac{}{}{0pt}{}{CH:C.C_7H_7}{CH:N}$. [52°]. Formed by heating (1)-chloro-(3)-m-tolyl-isoquinoline with HI and P for three hours at 170° (Heilmann, *B.* 23, 3168). Needles (from MeOH).

p-Tolyl-isoquinoline


$C_6H_4<\genfrac{}{}{0pt}{}{CH:C.C_7H_7}{CH:N}$. [78°]. Formed in like manner (Ruhemann, *B.* 24, 3975). Needles.—B'HI.—$B'H_2CrO_4$.—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. Yellow needles.

Reference.—Oxy-tolyl-quinoline.

TETRA-m-TOLYL-SILICANE $Si(C_7H_7)_4$. [151°]. (above 550°). S.G. ^{20} 1·1188. Formed from m-bromo-toluene, $SiCl_4$, and sodium (Polis, *B.* 19, 1021). Prisms (from ether), v. sol. benzene.

Tetra-p-tolyl-silicane $Si(C_7H_7)_4$. [228°]. (above 450°). S.G. ^{20} 1·0793. Formed from $SiCl_4$, p-bromo-toluene, ether, Na, and a little EtOAc (Polis, *B.* 18, 1542; 19, 1019). Monoclinic crystals (from chloroform). Decomposed by conc. HNO_3, forming silica and di-p-nitro-toluene [72°].

TETRA-o-TOLYL SILICATE $Si(OC_7H_7)_4$. (c. 437°). Formed by heating o-cresol with $SiCl_4$, the yield being 90 p.c. of the theoretical quantity (Hertkorn, *B.* 18, 1686). Oil, v. sol.

alcohol. Decomposed by hot water into silica and *o*-cresol.

Tetra-*m*-tolyl silicate $Si(OC_7H_7)_4$. (445°) at 720 mm. Syrup (H.).

Tetra-*p*-tolyl silicate $Si(OC_7H_7)_4$. [70°]. (444°). Tables or prisms, v. sol. benzene (H.).

***p*-TOLYL SILICO-CHLORIDE** $C_7H_7SiCl_3$. (219°). Formed from $Hg(C_7H_7)_2$ and $SiCl_4$ at 310° (Ladenburg, *A.* 173, 165). Liquid, converted by dilute aqueous ammonia into $C_7H_7.SiO.OH$ [c. 150°], which is converted at 200° into solid $(C_7H_7.SiO)_2O$.

TOLYL SULPHATES.

***o*-Tolyl sulphuric acid** [1:2] $C_6H_4Me.O.SO_2.OH$. Occurs in small quantity in the urine of horses (Preusse, *H.* 2, 355). Prepared from $C_6H_4Me.OK$ and $K_2S_2O_7$ (Baumann, *B.* 11, 1911). The K salt crystallises in plates, m. sol. water.

***m*-Tolyl sulphuric acid** $C_6H_4Me.O.SO_2.OH$. Occurs in very small quantity in horses' urine (P.).

***p*-Tolyl sulphuric acid** $C_6H_4Me.O.SO_2.OH$. Occurs in the urine of horses and cows (Baumann, *B.* 9, 1389, 1716; Städeler, *A.* 77, 18). Formed by boiling potassium *p*-cresol with $K_2S_2O_7$. The K salt is sl. sol. cold alcohol.

DI-*o*-TOLYL-SULPHAZIDE $C_{14}H_{16}N_2SO_2$ *i.e.* [2:1] $C_6H_4Me.NH.NH.SO_2.C_6H_4Me$ [1:2]. *Tolyl-toluene-sulphazide.* [142°]. Obtained by the action of SO_2 upon *o*-diazo-toluene in alcoholic solution. White glistening needles (Limpricht, *B.* 20, 1241). When boiled with baryta-water it decomposes into *o*-toluene-sulphinic acid, toluene, and nitrogen.

Di-*p*-tolyl-sulphazide $C_{14}H_{16}N_2SO_2$ *i.e.* [4:1] $C_6H_4Me.NH.NH.SO_2.C_6H_4Me$ [1:4]. *Tolyl-toluene-sulphazide.* [140°]. Formed in like manner from *p*-diazo-toluene (L.). Small needles. By boiling with baryta-water it is decomposed into *p*-toluene-sulphinic acid, toluene, and nitrogen.

Reference.—Nitro-di-tolyl-sulphazide.

DI-*p*-TOLYL SULPHIDE $S(C_6H_4Me)_2$. [57°]. (above 300°). Formed by distillation of lead *p*-tolyl-mercaptide (Otto, *B.* 12, 1175). Small needles, insol. water, sol. alcohol. Yields di-*p*-tolyl sulphone on oxidation by $KMnO_4$.

Di-*m*-tolyl disulphide $C_{14}H_{14}S_2$ *i.e.* $(C_6H_4Me)_2S_2$. Formed from *m*-tolyl mercaptan by treatment with dilute HNO_3 (Hübner a. Post, *A.* 169, 51). Liquid at −22°. Decomposed on boiling or by atmospheric oxidation of its ammoniacal alcoholic solution (Leuckart, *J. pr.* [2] 41, 189).

Di-*p*-tolyl disulphide $(C_6H_4Me)_2S_2$. [43°]. Formed from *p*-tolyl mercaptan by atmospheric oxidation (Märcker, *A.* 136, 88) or by the action of $ClSO_3H$ (Beckurts a. Otto, *B.* 11, 2066), or by treatment with ICy (Thurnauer, *B.* 23, 769). Formed also by the action of H_2S on a warm dilute solution of toluene *p*-sulphinic acid in alcohol (Otto, *J. pr.* [2] 37, 211). Crystals, v. e. sol. ether. Begins to boil at 307° i.V. but decomposes on distillation. Alcoholic K_2S forms *p*-tolyl mercaptan (Otto a. Rössing, *B.* 19, 3129).

Di-*p*-tolyl tetrasulphide $(C_6H_4Me)_2SO_4$. [75°]. Formed by the action of H_2S on a conc. solution of toluene *p*-sulphinic acid (Otto, *J. pr.* [2] 37, 211). Small plates, insol. water, v. sol. ether.

References.—Di-amido-, Di-bromo-, and Oxy-di-tolyl-sulphide.

***o*-TOLYL SULPHOCYANIDE** $C_6H_4Me.S.CN$. (c. 245°). Formed by adding cuprous sulphocyanide in KSCy to a solution of *o*-diazo-toluene (Thurnauer, *B.* 23, 770). Yellowish-red oil with unpleasant odour.

***p*-Tolyl sulphocyanide.** (c. 248°). Formed in like manner, and also by passing CyCl through alcohol containing lead *p*-tolyl mercaptide. Liquid, solidifying below 0°.

DI-*p*-TOLYL SULPHONE $(C_6H_4Me)_2SO_2$. [158°]. (405°) at 714 mm. Prepared by the action of $AlCl_3$ on a mixture of toluene and toluene *p*-sulphonic chloride (Beckurts a. Otto, *B.* 11, 2068; 12, 1177; *cf.* Michael, *B.* 10, 584). Formed by the action of fuming H_2SO_4 or SO_3 on toluene (Deville, *A.* 44, 306; Otto a. Grüber, *A.* 154, 193) and by the action of $KMnO_4$ and HOAc on di-*p*-tolyl sulphide. Prisms (from benzene), sl. sol. cold alcohol and ether. Potash-fusion yields *p*-cresol and diphenyl (Otto, *B.* 19, 2426).

DITOLYL DISULPHONIC ACID [1:4:5] $C_6H_3Me(SO_3H).C_6H_3Me(SO_4H)$ [5:1:4]. Formed from di-amido-ditolyl disulphonic acid by diazotisation followed by boiling with alcohol (Halle, *A.* 270, 363). Crystals, v. e. sol. water, m. sol. alcohol, insol. ether.—K_2A''. Hexagonal plates.—KHA'': prisms.—BaA'' 5aq.

Chloride $C_{14}H_{12}S_2O_4Cl_2$. [229°].

Amide $C_{14}H_{12}S_2O_4(NH_2)_2$. Needles.

***p*-TOLYL-SULPHONO-ACETIC ACID.** $C_6H_4Me.SO_2.CH_2.CO_2H$. [118°]. Formed from sodium benzene sulphinate and chloro-acetic acid (Gabriel, *B.* 14, 834). Crystals (from benzene), sl. sol. hot water. Cl passed into its aqueous solution forms $C_7H_7SO_2.CHCl_2$ [114°]. Br forms $C_7H_7.SO_2.CHBr_2$ and $C_7H_7.SO_2.CH_2Br$ (Otto, *J. pr.* [2] 40, 542).—AgA': trimetric tables.

Ethyl ether EtA'. Converted by bromine (2 mols.) at 90° into $C_7H_7.SO_2.CBr_2.CO_2Et$ which on saponification by cold NaOHAq yields $C_7H_7.SO_2.CHBr_2$ [117°].

***p*-TOLYL-SULPHONO-ACETONE** $CH_3.CO.CH_2.SO_2.C_6H_4Me$. [51°]. Formed by heating sodium toluene *p*-sulphinate with chloro-acetone in alcohol (Otto, *J. pr.* [2] 36, 425). Needles, v. sol. alcohol. Bromine forms $CH_2Br.CO.CH_2.SO_2C_7H_7$ [130°], m. sol. alcohol.

Di-*p*-tolyl-di-sulphono-acetone $CO(CH_2.SO_2.C_6H_4Me)_2$. Formed by heating $CH_2Br.CO.CH_2.SO_2C_7H_7$ with sodium toluene *p*-sulphinate in alcoholic solution. Plates, v. sol. hot HOAc and chloroform.

DI-TOLYL DI-SULPHONO-DI-ETHYL-AMINE $NH(C_2H_4.SO_2.C_7H_7)_2$. Formed by heating di-tolyl ethylene disulphone with NH_3Aq (Otto, *J. pr.* [2] 30, 359).—B'HCl. [201°].—$B'HAuCl_4$: dark-yellow needles.

DI-TOLYL-DI-SULPHONO-DI-ETHYL OXIDE $O(C_2H_4.SO_2.C_7H_7)_2$. [84°]. Formed by the action of conc. KOHAq on $C_2H_4(SO_2C_7H_7)_2$ and as a by-product in the preparation of $C_7H_7.SO_2.C_2H_4OH$ [55°] by the action of dilute KOHAq on the same body (Otto a. Tröger, *B.* 26, 944; *cf. J. pr.* [2] 30, 171, 321).

TOLYL DISULPHOXIDE *v. Tolyl ether of* Toluene thiosulphonic acid.

Di-*p*-tolyl sulphoxide $SO(C_6H_4Me)_2$. [92°]. Formed from toluene, $SOCl_2$, and $AlCl_3$ (Parker, *B.* 23, 1844). Flat needles (from ligroïn), v. e. sol. benzene. Reduced by sodium and alcohol to di-tolyl sulphide [56°]. $KMnO_4$ in HOAc forms di-tolyl sulphone [158°].

DI-*o*-TOLYL-TETRAZINE $C_{16}H_{16}N_4$ *i.e.* $C_7H_7N<\begin{smallmatrix}N:CH\\CH:N\end{smallmatrix}>NC_7H_7$. [141°]. Formed from *o*-tolyl-hydrazine, chloroform, and alcoholic potash (Ruhemann, *C. J.* 57, 52). Crystals. Yields crystalline $C_{16}H_{15}(SO_3H)N_4$ and $C_{16}H_{15}(NO_2)N_4$ [207°].—B'HCl: needles.

Methylo-iodide B'MeI. [198°]. Nodules.

Di-*p*-tolyl-tetrazine $C_{16}H_{16}N_4$. Formed in like manner. B'HCl: very unstable white needles.

Methylo-iodide B'MeI. [242°]. Needles.

***o*-TOLYL-THIAZOLE DIHYDRIDE** $C_6H_4Me.C<\begin{smallmatrix}N.CH_2\\S.CH_2\end{smallmatrix}$. (282°). Formed from thio-*o*-toluic amide and ethylene bromide (Gabriel a. Heymann, *B.* 24, 786). Got also by heating *o*-toluic bromo-ethyl-amide with P_2S_5 (Salomon, *B.* 26, 1329). Converted by bromine-water into taurine and *o*-toluic acid. — $B'_2H_2PtCl_6$. [199°].—$B'C_6H_3N_3O_7$. [132°].

***p*-Tolyl-thiazole dihydride.** [81°]. Prepared in like manner. Tables.

***p*-TOLYL-THIOBIURET** $C_9H_{11}N_3S_2$. [158°]. Formed by fusing *p*-toluidine (2 pts.) with persulphocyanic acid (1 pt.) (Tursini, *B.* 17, 584). Minute needles, sol. NaOHAq. Yields $C_9H_{10}N_3S_2Et$ [134°], crystallising from alcohol in needles, and $C_9H_{10}AcN_3S_2$ [166°], crystallising in needles.

***o*-TOLYL-β-THIOCARBAMIC ACID** [1:2]$C_6H_4Me.NH.CS.OH$.

Ethyl ether $C_7H_7N:C(SH).OEt$. *Tolyl-thiourethane.* Formed by heating *o*-tolyl-thiocarbimide with alcohol at 130° (Liebermann a. Natanson, *B.* 13, 1576; *A.* 207, 161). Oil, sol. alkalis.—$C_{10}H_{12}AgNSO$: white pp. insol. NH_3Aq. Converted by MeI into $C_7H_7N(OEt).SMe$, and by EtI into $C_7H_7N(OEt).SEt$, both being oils boiling above 250°.

***m*-Tolyl-β-thiocarbamic acid** [1:3]$C_6H_4Me.NH.CS.OH$.

Ethyl ether $C_7H_7N:C(SH).OEt$. [68°]. Formed in like manner (L. a. N.). Yields $C_{10}H_{12}AgNSO$ and oily $C_{10}H_{12}EtNSO$.

***p*-Tolyl-β-thiocarbamic acid.** *Ethyl ether* $C_7H_7NC(SH).OEt$. [87°]. Formed in the same way (L. a. N.). Triclinic crystals. Ammoniacal $AgNO_3$ added to its alcoholic solution ppts. $C_7H_7NC(OEt).SAg$, which is converted by MeI into $C_7H_7NC(OEt).SMe$, and by EtI into $C_7H_7NC(OEt).SEt$, both being oils boiling above 250°. $C_7H_7NC(OEt).SEt$ is decomposed by dilute H_2SO_4 at 180° into *p*-toluidine and thiocarbonic ether.

***o*-Tolyl-α-thiocarbamic acid** $C_7H_7NH.CO.SH$.

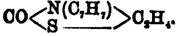
Methyl ether MeA'. [70°]. Formed by heating $C_7H_7NH.C(NC_7H_7).SMe$ with dilute H_2SO_4 at 140° (Will a. Bielschowski, *B.* 15 1317). Plates.

Ethyl ether EtA'. [60°]. Tables.

***p*-Tolyl-α-thiocarbamic acid** $NHC_7H_7.CO.SH$.

Methyl ether MeA'. [107°]. Formed by heating $C_7H_7NH.C(NC_7H_7).SMe$ with dilute H_2SO_4 at 170°. Needles, v. sol. alcohol and ether.

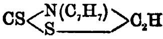
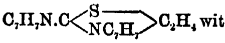
Ethyl ether EtA'. [79°]. Formed from *p*-toluidine and Cl.CO.SEt. Needles. Yields EtSH and tolyl cyanate on distillation.

Ethylene derivative  $CO<\begin{smallmatrix}N(C_7H_7)\\S\end{smallmatrix}>C_2H_4$. [88°]. Long slender needles.

***o*-Tolyl-di-thio-carbamic acid** $C_7H_7NH.CS.SH$.—NiA'_2. Brown needles, insol. water.—BaA'_2. Plates (Losanitsch, *B.* 24, 3027). Forms di-*o*-tolyl-thio-urea on heating.

Methyl ether MeA'. [132°]. Formed from the Ba salt and MeI. White needles.

Ethyl ether EtA'. [72°]. Formed by heating $C_7H_7NH.C(NC_7H_7).SEt$ with CS_2 at 160° (Will a. Bielschowski, *B.* 15, 1317). Prisms.

Ethylene derivative $C_{10}H_{11}NS_2$ *i.e.*  $CS<\begin{smallmatrix}N(C_7H_7)\\S\end{smallmatrix}>C_2H_4$. [129°]. Formed by heating  $C_7H_7N.C<\begin{smallmatrix}S\\NC_7H_7\end{smallmatrix}>C_2H_4$ with CS_2 at 200°. Yields $C_{10}H_{11}NS_2MeI$, crystallising in prisms [151°].

***m*-Tolyl-di-thio-carbamic acid** $C_7H_7NH.CS.SH$.

Salts.—BaA'_2. Formed from *m*-toluidine, CS_2, and $Ba(OH)_2$ in alcohol (Losanitsch, *B.* 24, 3027). Needles, sol. water, insol. cold alcohol.—NiA'_2. Yellowish-brown plates.

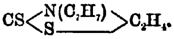
Methyl ether MeA'. [89°]. Needles.

***p*-Tolyl-di-thio-carbamic acid** $C_7H_7NH.CS_2H$.

Salts.—NH_4A'. Formed from *p*-toluidine, CS_2, alcohol, and NH_3Aq (Losanitsch, *B.* 24, 3026). Yellowish prisms, sol. water, insol. alcohol.—BaA'_2. Needles.—NiA'_2. Formed from *p*-toluidine, CS_2, ammoniacal $NiSO_4$, and alcohol. Brown needles, sol. alcohol, insol. water.

Methyl ether MeA'. [84°]. Prisms.

Ethyl ether EtA'. [74°]. Formed by heating $NHC_7H_7.C(NC_7H_7).SEt$ with CS_2 at 160° (W. a. B.). Needles, split up by heat into *p*-tolyl thiocarbimide and EtSH.

Ethylene ether  $CS<\begin{smallmatrix}N(C_7H_7)\\S\end{smallmatrix}>C_2H_4$. [126°]. Crystals. Yields a methylo-iodide [107°], which is converted by aniline into $C_{16}H_{18}N_2S$ [128°], and by *o*-toluidine into $C_{17}H_{18}N_2S$ [82°].

Reference. — NITRO-TOLYL-THIOCARBAMIC ETHER.

***o*-TOLYL-THIOCARBAZIC ACID** *o-Tolyl hydrazide* $C_7H_7NH.NH.CS.SNH_3.NHC_7H_7$. Formed from *o*-tolyl-hydrazine, ether, and CS_2 (Freund, *B.* 24, 4200). Prismatic tables, insol. ether, decomposed by water and alcohol. The *p*-isomeride melts at 109°.

DI-*o*-TOLYL-THIOCARBAZIDE $C_{15}H_{18}N_4S$ *i.e.* $CS(NH.NHC_6H_4Me)_2$. [130°]. Formed from *o*-tolyl-thiocarbazic acid and *o*-tolyl-hydrazine at 90° (Freund, *B.* 24, 4201). Needles, sol. alcohol, insol. Aq.

Di-*p*-tolyl-thiocarbazide. [121°]. Formed in like manner at 110° (Freund, *B.* 24, 4194). Plates, v. sol. hot alcohol.

Di-*o*-tolyl-thiosemicarbazide $C_{15}H_{17}N_3S$ *i.e.* $NHC_7H_7.CS.NH.NHC_7H_7$. [149°]. Formed by heating *o*-tolyl-thiocarbimide (1 mol.) with *o*-tolyl-hydrazine (1 mol.) in alcohol (Dixon, *C. J.* 61, 1017). Octahedra, m. sol. hot alcohol, insol. Aq.

Di-*p*-tolyl-thiosemicarbazide. [154°]. Formed in like manner (D.). Prisms, v. e. sol. hot alcohol.

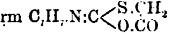
_op_-Di-tolyl-thiosemicarbazide [4:1]$C_6H_4Me.NH.CS.NH.NHC_6H_4Me$[1:2]. [142°]. Formed from _p_-tolyl-thiocarbimide and _o_-tolylhydrazine (D.). Prisms, sl. sol. hot alcohol.

Isomeride [2:1]$C_6H_4Me.NH.CS.NH.NHC_6H_4Me$[1:4]. [163°]. Formed from _o_-tolyl-thiocarbimide and _p_-tolylhydrazine (Dixon, _C. J._ 61, 1015). Prisms, m. sol. hot alcohol.

DI-_o_-TOLYL-THIOCARBAZONE $C_{15}H_{16}N_4S$ _i.e._ $C_7H_7N:N.CS.NH.NHC_7H_7$. [168°]. Formed from di-_o_-tolyl-thiocarbazide and alcoholic potash (Preund, _B._ 24, 4201). Blue-black needles, v. sol. chloroform, sl. sol. alcohol. Conc. H_2SO_4 forms a bluish-green solution.

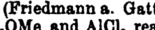
Di-_p_-tolyl-thiocarbazone. [105°]. Formed in like manner. Dark-blue amorphous flakes.

_o_-TOLYL-THIOCARBIMIDE C_8H_7NS _i.e._ [1:2]$C_6H_4Me.N:CS$. (239°). Formed from di-_o_-tolyl-thio-urea by distilling with P_2O_5 (Staats, _B._ 13, 136), by heating with aqueous H_3PO_4 (Hofmann, _B._ 15, 986; Mainzer, _B._ 16, 2017), or by boiling with fuming HClAq (Girard, _B._ 6, 445). Oil.

Reactions.—1. _Chlorine_ forms $C_7H_7.NCl.CSCl$ (218°), which is converted by alcohol into a mixture of di-_o_-tolyl-urea and _o_-tolyl-carbamic ether (Lachmann, _B._ 12, 1349).—2. _Chloro-acetic acid_ and alcohol at 150° form  $C_7H_7.N:C<\begin{matrix}S.CH_2\\O.CO\end{matrix}$ crystallising in needles [120°], decomposed by boiling baryta-water into _o_-toluidine, CO_2, and thioglycollic acid (Völtzkoff, _B._ 13, 1580).—3. PhOMe and $AlCl_3$ on warming form $C_7H_7NH.CS.C_6H_4OMe$ [95°] (Tust a. Gattermann, _B._ 25, 3528). PhOEt and $AlCl_3$ give $C_{16}H_{17}NSC$ [116°].

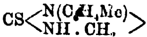
_m_-Tolyl-thiocarbimide $C_7H_7.N:CS$. (244°) at 732 mm. Formed by boiling di-_m_-tolyl urea with conc. HClAq (Weith a. Landolt, _B._ 8, 719). Heavy oil. Converted by copper-powder at 220° into _m_-toluic nitrile.

_p_-Tolyl-thiocarbimide [1:4] $C_6H_4Me.N:CS$. [26°]. (237°). Formed by heating di-_p_-tolyl-thio-urea with P_2O_5 or aqueous H_3PO_4 of S.G. 1·7 (Hofmann, _B._ 1, 173; 15, 986; Staats, _B._ 13, 135). Formed also, together with phenyl-thiocarbimide, by heating $PhN:C:NC_7H_7$ with CS_2 at 190° (Huhn, _B._ 19, 2409). Needles (from ether), v. sol. alcohol.

Reactions.—1. _Ammonia_ forms tolyl-thio-urea, and other bases act in like manner.—2. _Bromine_ forms $C_7H_7NBr.CSBr$, which readily gives off Br_2 leaving $(C_7H_7NCS)_2Br_2$ crystallising in plates decomposing at 210° (Helmers, _B._ 20, 790).—2. _Chlorine_ forms $(C_7H_7NCS)_2Cl_2$, whence dilute alcohol gives $(C_7H_7NCS)_2O$ [139°], crystallising in needles.—3. $CH_2Cl.CO_2H$ and alcohol at 150° form  $C_7H_7N:C<\begin{matrix}S.CH_2\\O.CO\end{matrix}$ [162°] (Völtzkoff, _B._ 13, 1579).—4. Warmed with toluene and $AlCl_3$ it gives $C_7H_7NH.CS.C_7H_7$ [166°].—5. Heated with $AlCl_3$ it yields $(C_7H_7N.CS)_2S$ [176°] (Friedmann a. Gattermann, _B._ 25, 3525). 6. C_6H_5OMe and $AlCl_3$ react, with formation of $C_7H_7NH.CS.C_6H_4.OMe$ [157°].—7. C_6H_5OEt and $AlCl_3$ give $C_{16}H_{17}NOS$ [151°], which may be oxidised to $C_{16}H_{15}NOS$ [170°].

DI-_p_-TOLYL DI-THIO-CARBONATE $CO(SC_6H_4Me)_2$. [91°]. Formed from _p_-tolyl mercaptan and $COCl_2$. It is also a by-product in the action of _p_-diazo-toluene chloride on potassium xanthate (Leuckart, _J. pr._ [2] 41, 190). Needles (from alcohol).

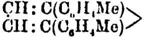
TRI-TOLYL TRI-THIOCYANURATE $(C_6H_4Me.SCy)_3$. [114°]. Formed from sodium _p_-tolyl mercaptan and cyanuric chloride (Klason, _J. pr._ [2] 33, 120). Crystals (from HOAc).

_o_-TOLYL-THIOHYDANTOÏN $C_9H_{10}NSO$ _i.e._  $CS<\begin{matrix}N(C_6H_4Me)\\NH.CH_2\end{matrix}>CO$. [136°]. Formed from _o_-tolyl-thiocarbimide and amido-acetic acid (Marckwald, _B._ 24, 3281). Plates, v. sol. alcohol, sl. sol. ligroïn.

_p_-Tolyl-thiohydantoïn [210°] (M.). Formed as above (M.; _cf._ Aschan, _B._ 17, 426). Flat prisms, sol. alkalis.

Isomeride [183°]. Formed by fusing $CH_2Cl.CO.NHC_7H_7$ with thio-urea (P. Meyer, _B._ 10, 1966). Small crystals.

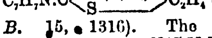
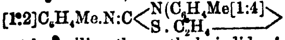
_p_-Tolyl-ψ-thiohydantoic acid $C_7H_7N:C(NH_2).S.CH_2.CO_2H$. [176° – 182°]. Formed by boiling chloro-acetic acid with ammonium sulphocyanide, _p_-toluidine, and alcohol (Jäger, _J. pr._ [2] 16, 21). Prisms, not attacked by Ac_2O and Br.

DI-_p_-TOLYL-THIOPHENE $C_{18}H_{16}S$ _i.e._  $\begin{matrix}CH:C(C_6H_4Me)\\CH:C(C_6H_4Me)\end{matrix}>S$. [171°]. Formed by heating di-_p_-tolyl-furfurane with P_2S_5 (Hollemann, _R. T. C._ 6, 74). Small plates (from alcohol). Gives an intense dark-green colour with isatin and H_2SO_4.

_o_-TOLYL-THIO-UREA $NH_2.CS.NHC_6H_4Me$. [155°]. Formed from _o_-tolyl thiocarbimide and NH_3Aq (Staats, _B._ 13, 136). V. sol. hot water and alcohol, sl. sol. ether.

Acetyl derivative $NHAc.CS.NHC_6H_4Me$. [184°]. Formed from acetyl thiocarbimide and _o_-toluidine in alcohol (Dixon, _C. J._ 55, 804). Pale lemon-yellow prisms, insol. water, sol. alcohol.

Benzoyl derivative $NHBz.CS.NHC_6H_4Me$. [119°]. Formed in like manner (Dixon, _C. J._ 55, 623). Pale-yellow prisms, blackened by $AgNO_3$.

Di-_o_-tolyl-thio-urea $CS(NH.C_6H_4Me)_2$. [158°]. Formed from _o_-toluidine and CS_2 (Girard, _B._ 4, 985; Berger, _B._ 12, 1854; Ador a. Rilliet, _B._ 12, 2301). Long needles, v. sol. hot alcohol. Converted by heating with MeI into the hydroiodide of di-tolyl-methyl-thiourea $C_{16}H_{18}N_2S$, which may be represented as 'methyl di-_o_-tolyl-imido-thiocarbamate' $C_7H_7N:C(SMe).NHC_7H_7$. This body melts at 60°, while the corresponding ethyl derivative melts at 51°. The ethylene derivative [91°] may be represented by the formula  $C_7H_7N:C<\begin{matrix}N(C_7H_7)\\S\end{matrix}>C_2H_4$ (Will a. Bielschowski, _B._ 15, 1316). The isomeric compound  [1:2]$C_6H_4Me.N:C<\begin{matrix}N(C_6H_4Me[1:4])\\S.C_2H_4\end{matrix}>$ [82°] is got by boiling the methylo-iodide of the ethylene derivative of _p_-tolyl-di-thio-carbamic acid with _o_-toluidine.

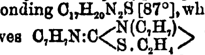
_m_-Tolyl-thio-urea $NHC_7H_7.CS.NH_2$. [103°]. Formed from _m_-tolyl thiocarbimide and ammonia (Weith a. Landolt, _B._ 8, 719). Prisms, m. sol. hot water, v. sol. alcohol and ether.

Di-_m_-tolyl-thio-urea $CS(NHC_7H_7)_2$. [122°]. Formed from _m_-toluidine, CS_2, and alcohol (W.

a. L.). Needles, v. sol. alcohol, nearly insol. hot water.

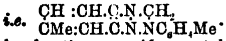
p-Tolyl-thio-urea $NHC_7H_7.CS.NH_2$. [188°]. (C. a. W.); [182°] (S.). Formed by heating *p*-toluidine hydrochloride with ammonium sulphocyanide (De Clermont a. Wehrlin, *C. R.* 83, 347). Formed also from *p*-tolyl-thiocarbimide ammonia (Staats, *B.* 18, 136). Plates (from alcohol) with bitter taste, sl. sol. cold water, m. sol. alcohol.

Acetyl derivative $NHC_7H_7.CS.NHAc$. [176°]. Formed from acetyl sulphocyanide and *p*-toluidine (Miguel, *Bl.* [2] 28, 103). Needles, v. e. sol. hot alcohol, v. sol. ether.

Di-*p*-tolyl-thio-urea $CS(NHC_6H_4Me)_2$. [176°]. Formed by boiling *p*-toluidine with CS_2 and alcohol (Sell, *A.* 126, 160). It is also a product of the action of allyl-thiocarbimide on an alcoholic solution of *p*-toluidine (Maly, *Z.* [2] 5, 258). Trimetric prisms (Levin, *J.* 1882, 384), insol. water, nearly insol. cold alcohol. In alcoholic solution it is converted by HgO into di-*p*-tolyl-urea. In benzene solution $COCl_2$ forms $C_{16}H_{14}N_2SO$ [116°] (Will, *B.* 14, 1487). $CSCl_2$ forms $C_{16}H_{14}N_2S_2$ [109°] (Freund a. Wolf, *B.* 25, 1465). MeI forms $C_7H_7N{:}C(NHC_7H_7).SMe$ [128°], crystallising in needles, split up by heat into $C(NC_7H_7)_2$ [60°] and HSMe, converted by heating with acids or alkalis into di-*o*-tolyl-urea and MeSH, and forming the salts B'HCl [173°] and $B'H_2SO_4$ [156°]. EtI forms the corresponding $C_{17}H_{20}N_2S$ [87°], while ethylene bromide gives  $C_7H_7N{:}C\left\langle\begin{matrix}N(C_7H_7)\\S.C_2H_4\end{matrix}\right\rangle$ [112°], which yields $B'H_2SO_4$ [194°] and a hydrochloride [219°] (Will a. Bielschowski, *B.* 14, 1492; 15, 1309).

References.—NITRO- and OXY- TOLYL-THIO-UREA.

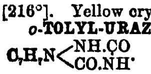
p-TOLYL - TOLUTRIAZINE DIHYDRIDE $C_{15}H_{15}N_3$ *i.e.*



$$\begin{matrix}CH:CH.C.N.CH_2\\CMe:CH.C.N.NC_6H_4Me\end{matrix}$$

[178°]. Formed by heating *o*-amido-azo-toluene with formic paraldehyde and alcohol at 140° (Goldschmidt a. Poltzer, *B.* 24, 1008). Prisms, v. sol. hot alcohol.—B'HCl. [220°].—$B'_2H_2PtCl_6$. [216°]. Yellow crystalline pp.

***o*-TOLYL-URAZOLE** $C_9H_9N_3O_2$ *i.e.*



$$C_7H_7N\left\langle\begin{matrix}NH.CO\\CO.NH\end{matrix}\right.$$

[170°]. Got by heating *o*-tolyl-hydrazine hydrochloride with urea (Pinner, *B.* 21, 1219). White leaflets, v. sol. hot water.

***p*-Tolyl-urazole.** [274°]. Yellowish needles, v. sl. sol. hot water.

***o*-TOLYL-UREA** $C_8H_{10}N_2O$ *i.e.* $NH_2.CO.NH.C_6H_4Me$ [1:2]. [185°]. Formed from *o*-toluidine hydrochloride and potassium cyanate (Cosack, *B.* 18, 1089). Plates, sol. alcohol, ether, and hot water.

Benzoyl derivative $CO(NHBz).NHC_7H_7$. [210°]. Formed from *o*-tolyl cyanate and benzamide at 125° (Gattermann a. Cantzler, *B.* 25, 1088). Needles.

***m*-Tolyl-urea** $NH_2.CO.NHC_6H_4Me$ [1:3]. [142°]. Formed from *m*-toluidine hydrochloride and potassium cyanate (Cosack, *B.* 12, 1450; 18, 1089). Needles or tables (from alcohol) or plates (from water).

***p*-Tolyl-urea** $NH_2.CO.NHC_6H_4Me$ [1:4]. [172°] (C.); [180°] (St.; P.). Formed in like manner (C.; *cf.* Sell, *C. J.* 16, 190). Formed also by the action of *p*-toluidine on mercuric fulminate (Steiner, *B.* 8, 519), and also from *p*-toluamidoxim, benzene sulphonic acid, NaOH, and $CHCl_3$ (Pinnow, *B.* 24, 4167). Needles, sol. hot water, v. sl. sol. ligroïn.

Di-*o*-tolyl-urea $CO(NHC_7H_7)_2$. [246°] (B.); [254°] (W.); [256°] (Barr, *B.* 19, 1769).

Formation.—1. By the action of alcohol or water at 100° on the dichloride of *o*-toluic nitrile (Lachmann, *B.* 12, 1349).—2. From *o*-toluidine hydrochloride and cyanamide (Berger, *B.* 12, 1859).—3. From tolyl cyanate and water (Nevile a. Winther, *B.* 12, 2325).—4. From *o*-toluidine and $COCl_2$ (Girard, *B.* 6, 444).—5. By heating *o*-toluidine with urea (G.).—6. A product of the distillation of *o*-tolyl-amido-acetic acid (Widman, *J. pr.* [2] 38, 303).—7. By the action of Ac_2O and benzene on the *o*-toluide of *o*-tolyl-imido-diacetic acid (Bischoff, *B.* 23, 1995).

Properties.—Needles (from HOAc), insol. ether, sl. sol. alcohol. Not volatile with steam.

Di-*m*-tolyl-urea $CO(NH.C_6H_4Me)_2$. [203°] (G. a. C.); [217°] (C.). Formed from *m*-tolyl cyanate and *m*-toluidine (Gattermann a. Cantzler, 25, 1089), by the action of $ClCO_2Et$ on *m*-toluidine, by heating *m*-tolyl-carbamic ether with water, and by heating *m*-tolyl-urea with *m*-toluidine at 160° (Cosack, *B.* 12, 1450; 13, 1090). Needles (from alcohol), insol. water.

Di-*p*-tolyl-urea $CO(NH.C_6H_4Me)_2$. [255°].

Formation.—1. By boiling an alcoholic solution of di-*p*-tolyl-thio-urea with HgO as long as HgS is formed (Sell, *C. J.* 16, 190; *A.* 126, 161).—2. By passing $COCl_2$ into *p*-toluidine dissolved in chloroform (Michler, *B.* 9, 710; Kühn, a. Henschel, *B.* 21, 505).—3. By heating tolyl-urea with *p*-toluidine at 160° (Weith, *B.* 9, 821). 4. From *p*-tolyl-cyanate and *p*-toluidine (Gattermann a. Cantzler, *B.* 25, 1089).

Properties.—Needles, insol. water, sl. sol. cold alcohol.

Tri-*p*-tolyl-urea $C_{22}H_{22}N_2O$. [189°]. Got from $(C_7H_7)_2N.COCl$ and *p*-toluidine (Hammerich, *B.* 25, 1822). Needles, sol. warm benzene, insol. ether. Gives a benzoyl derivative [137°].

Tetra-*p*-tolyl-urea $C_{29}H_{28}N_2O$. [80°]. Got from $(C_7H_7)_2N.COCl$ and di-*p*-tolyl-amine. Needles, v. e. sol. alcohol.

References.—AMIDO-, NITRO-, and OXY-TOLYL-UREA.

TOLYL-XYLIDINE $C_{15}H_{17}N$ *i.e.* $C_6H_4Me.NH.C_6H_3Me_2$. [70°]. (c. 300° at 487 mm.). Silky needles (from alcohol) (Girard a. Vogt, *Bl.* [2] 18, 69).

***o*-TOLYL *m*-XYLYL KETONE** $C_{16}H_{16}O$ *i.e.* [1:2] $C_6H_4Me.CO.C_6H_3Me_2$ [1:2:3]. (330°) at 728 mm. Formed from *o*-toluic chloride and *m*-xylene (Smith, *B.* 24, 4050). Oil. Converted by hydroxylamine at 120° into a mixture of anilides.

TONKA BEANS, the fruit of *Dipterix odorata*, contains coumarin (*q. v.*) (Boullay a. Boutron-Charlard, *J. Ph.* 11, 426; [3] 7, 160).

TRAGACANTH GUM. Exudes from *Astragalus verus*, a tree growing in Armenia and the north of Persia. It swells up in water, about one-half of it dissolving. It contains arabin, bassorin, starch, and water.

TRANSPIRATION. Graham, in 1846 and 1849, applied the term 'transpiration' to the passage of gases through capillary tubes into a

vacuum (*v. T.* 1846. 573; 1849. 349). The rates of transpiration of different gases bear constant relations to each other; but these rates have not been connected in any definite ways with the compositions of the gases. M. M. P. M.

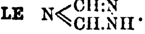
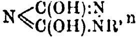
TREE GUM *v.* XYLAN.

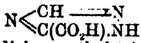
TREHALOSE *v.* SUGAR.

TREHALUM $C_{24}H_{42}O_{21}$. S. ·06 at 17°; 1·8 at 100°. $[\alpha]_D = +179°$. Occurs in *Trehala manna* (Scheibler a. Mittelmeier, *B.* 26, 133[illegible]). Tasteless, minute prisms. Very hygroscopic. Does not reduce Fehling's solution. Does not react with phenyl-hydrazine. Boiling dilute H_2SO_4 forms glucose. At 180° it slowly forms trehalin, which is v. sol. water and ppd. by alcohol. Trehalin dissolves in phenyl-hydrazine. Iodine colours trehalum and trehalin violet. Diastase, yeast, and invertin have no action. Ac_2O and NaOAc yield an acetyl derivative [above 240°].

TRI-. In the alphabetical arrangement of this dictionary the prefix 'tri,' when indicating the presence of three radicles, is treated as if it did not form part of a name, except where the entire name is numerical, as in 'tridecane.'

TRIANOSPERMIN. A crystalline substance occurring in *Trianosperma ficifolia*, a climbing plant of Brazil (Peckholt, *Ar. Ph.* [2] 113, 104; Parodi, *Ph.* [3] 10, 667). It has a pungent taste, is alkaline in reaction, sol. water, alcohol, and ether, and is ppd. by $Pb(OAc)_2$ and $PtCl_4$.

TRIAZOLE  $N{<}\begin{matrix}CH{:}N\\ CH.NH\end{matrix}$. *Pyrrodiazole.* [120·5°]. (260°). V.D. 2·39 (calc. 2·49). Formed by heating its carboxylic acid alone or with boiling water (Andreocci, *B.* 25, 229; Bladin, *B.* 25, 745). Needles (from ether), v. sol. water and alcohol, may be sublimed. The di-oxy- derivatives of alkyl-triazoles  $N{<}\begin{matrix}C(OH){:}N\\ C(OH).NR'\end{matrix}$, named by Pinner 'urazoles,' are obtained by heating hydrazines with urea (Pinner, *B.* 20, 2358).

TRIAZOLE CARBOXYLIC ACID  $N{<}\begin{matrix}CH{=\!=}N\\ C(CO_2H).NH\end{matrix}$. [137°]. Obtained by oxidising methyl-triazole (Andreocci, *B*, 25, 229) or amido-phenyl-triazole carboxylic acid and alkaline $KMnO_4$ (Bladin, *B.* 25, 744). Amorphous powder.—CuA'_2aq. Green crystalline powder.

TRICARBALLYLIC ACID *v.* vol. i. p. 679.

TRICOSANE *v.* TRI-ICOSANE.

TRIDECANE $C_{13}H_{28}$. [−6°]. (234°). S.G. $\frac{0}{4}$ ·771; $\frac{15}{4}$ ·761. Formed by reduction of methyl dodecyl ketone or of tridecoic acid by HI and P (Krafft, *B.* 15, 1699). Formed also by distilling barium myristate with NaOMe (Mai, *B.* 22, 2184).

TRIDECOIC ACID $C_{12}H_{25}.CO_2H$. [41°]. (236° at 100 mm.). Formed by oxidation of methyl tridecyl ketone (Krafft, *B.* 12, 1669). Crystals. —AgA'.

Amide $C_{12}H_{25}.CO.NH_2$. [98·5°]. Formed by digesting the nitrile with conc. H_2SO_4 and pouring into water (Lutz, *B.* 19, 1439). Plates (from alcohol).

Nitrile $C_{12}H_{25}CN$. (275°). Formed from tridecylamine, Br, and NaOH. Oil, v. sol. alcohol and ether.

TRIDECYL ALCOHOL $(C_6H_{13})_2CH.OH$. [42°]. Formed by reducing di-hexyl ketone (Kipping, *C. J.* 57, 536). Plates (from dilute alcohol), insol. water. May be distilled. HBr forms $(C_6H_{13})_2CHBr$ [39°].

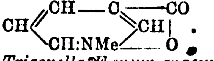
TRIDECYLAMINE $C_{13}H_{27}NH_2$. [27°]. (265°). Formed by boiling myristyl-tridecyl-urea with KOHAq (Lutz, *B.* 19, 1437). Unctuous mass, v. sol. alcohol and ether. Absorbs water and CO_2 from the air.—B'HCl: needles, decomposing at 100°.—$B'_2H_2PtCl_6$.—$B'_2H_2SO_4$: needles, insol. cold water.

TRIDECYLENE $C_{13}H_{26}$. (233° cor.). S.G. ^{0} ·8445. Occurs in petroleum from Burmah (Warren a. Storer, *Z.* 1868, 232).

TRIDECYL-UREA. *Myristyl derivative* $C_{28}H_{56}N_2O_2$ *i.e.* $C_{13}H_{27}NH.CO.NHC_{11}H_{27}O$. [103°]. Formed by the action of Br and KOHAq on the amide of myristic acid (Reimer a. Will, *B.* 18, 2016). Crystals (from alcohol), almost insol. cold water, sol. ether.

TRIGENIC ACID *v.* ETHYLIDENE-BIURET.

TRIGONELLIN $C_7H_7NO_2$ *i.e.*



. Occurs in the seeds of *Trigonella Fœnum-græcum* (Jahns, *B.* 18, 2518; 20, 2840). It is also produced by saponification of the product of the reaction of MeI on potassium pyridine (β)-carboxylate (Hantzsch, *B.* 19, 31). Colourless prisms (containing aq), converted by HClAq at 265° into pyridine (β)-carboxylic acid (*q. v., Reaction* 4).—B'HCl.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$ [198°].—$B'_4 3HAuCl_4$. [186°]. Slender needles.

***n*-TRI-ICOSANE** $C_{23}H_{48}$. [48]. (234° at 15 mm.). S.G. $\frac{48}{4}$ ·7785; $\frac{81}{4}$ ·7570. Formed from laurone $(C_{11}H_{23})_2CO$ by treatment with PCl_5 and reduction of the resulting $(C_{11}H_{23})_2CCl_2$ with HI and P at 240° (Krafft, *B.* 15, 1712). Obtained also by fractional distillation of paraffin oil from brown coal (Krafft, *B.* 21, 2263). Glittering plates (from ether-alcohol), sl. sol. alcohol.

TRI-ICOSANE DICARBOXYLIC ACID $C_{23}H_{46}(CO_2H)_2$. [102·5°]. Formed by heating di-oxy-penta-icosylene with soda-lime (Stärcke, *A.* 223, 300). Flocculent pp. (from ligroïn-ether). —PbA''.

TRI-ICOSYL ALCOHOL $(C_{11}H_{23})_2CH.OH$. [76°]. Formed by reducing laurone with Na and water (Kipping, *C. J.* 57, 983). Plates (from ether), insol. water. Yields an acetyl derivative $(C_{11}H_{23})_2CH.OH$ [35°].

TRI-ICOSYL ALCOHOL $C_{23}H_{47}.OH$. [82°]. A wax-like body extracted by hot alcohol from flax fibres (Cross a. Bevan, *C. N.* 59, 135). Yields an acetyl derivative [65°].

TRIMELLITIC ACID *v.* vol. iii. p. 201.

TRIMESIC ACID *v.* vol. iii. p. 230.

TRIMESITIC ACID *v.* PYRIDINE TRICARBOXYLIC ACID.

TRIMETHYLENE *v.* vol. iii. p. 304.

TRITICIN $C_{12}H_{22}O_{11}$. $[\alpha]_D = -43·6°$ (Reidemeister, *J. Th.* 1881, 69). Extracted by dilute alcohol from the root of couch-grass (*Triticum repens*) (H. Müller, *Ar. Ph.* [3] 2, 500; 3, 1). Tasteless hygroscopic powder, v. sol. water, insol. alcohol and ether. Lævorotatory. On boiling with water, especially in presence of acids, it changes into lævulose. Its solutions are not ppd. by metallic salts, nor coloured by iodine.

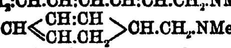
TROPÆOLINES *v.* AZO- COMPOUNDS.

TROPEÏNES. A name given by Ladenburg to alkoyl derivatives of tropine (*q. v.*).

TROPIC ACID *v.* OXY-PHENYL-PROPIONIC ACID.

TROPIDINE *v.* METHYL-ETHYLENE PYRIDINE TETRAHYDRIDE.

(α)-Methyl-tropidine $C_9H_{15}N$ *i.e.* $CH_2{:}CH.CH{:}CH.CH{:}CH.CH_2.NMe_2$ (Ladenburg) or



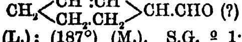
$CH{<}\begin{matrix}CH{:}CH\\CH.CH_2\end{matrix}{>}CH.CH_2.NMe_2$ (Merling). Formed by distilling tropidine methylo-hydroxide with water (Roth, *B.* 17, 157; Merling, *B.* 24, 3118). Oil. HClAq forms 'hydrochloro-(α)-methyl-tropidine' which gradually changes into the isomeric tropidine methylo-chloride. — $B'_2H_2PtCl_6$. [174°].—$B'HAuCl_4$: golden-yellow pp.

Methylo-iodide B'MeI. [162°]. Needles.

(β)-Methyl-tropidine $C_9H_{15}N$. (205°). S.G. 15 ·922. Formed by heating (α)-methyl-tropidine at 150°–200°. Oil. Converted by HCl into tropilene.

TROPIGENIN $C_7H_{13}NO$. [161°]. Got by oxidation of tropine by alkaline $KMnO_4$ (Merling, *B.* 15, 287). Got also by boiling 'homohydro-apotropine' with baryta-water (Pesci, *G.* 12, 329). Needles, sol. water and alcohol. Reconverted by MeI into tropine. Oxidised by chromic acid mixture to ecgonic acid and a small quantity of tropic acid (Liebermann, *B.* 24, 615).—B'HI.—B'_2CO_2: crystalline pp. — $B'_2H_2PtCl_6$ aq. — $B'HAuCl_4$: golden-yellow plates, sol. alcohol.

TROPILENE $C_7H_{10}O$ *i.e.*

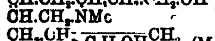


$CH_2{<}\begin{matrix}CH{:}CH\\CH_2.CH_2\end{matrix}{>}CH.CHO$ (?) (Merling) (182°) (L.); (187°) (M.). S.G. $\frac{0}{}$ 1·0091. V.D. 102·3 (calc. 110). Formed by distilling tropidine methylo-iodide with KOH (Ladenburg, *B.* 14, 2403; 15, 1028; *A.* 217, 138). Formed also from (β)-methyl-tropidine and cold HClAq (Merling, *B.* 24, 3123). Oil, smelling like oil of bitter almonds and acetone, sol. dilute HClAq, v. sol. alcohol and ether. Reduces warm ammoniacal $AgNO_3$, forming a mirror. Reduces Fehling's solution and $KMnO_4$ in the cold. Not attacked by AcCl. Combines with $NaHSO_3$ (M.). Nitric acid forms an adipic acid $C_6H_{10}O_4$. Slowly combines with methylamine, forming (β)-methyl-tropine.

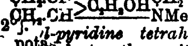
TROPILIDENE C_7H_8 *i.e.*

$CH{<}\begin{matrix}CH{:}CH\\CH.CH_2\end{matrix}{>}C{:}CH_2$. (114°). S.G. $\frac{0}{4}$ ·9129. Formed by distilling methyl-tropine methylo-iodide with KOH (Ladenburg, *A.* 217, 133; *B.* 14, 2403; 26, 1067). Formed also, together with methylamine, by distilling tropine with soda-lime. Oil, smelling somewhat like toluene, but combining readily with bromine, forming $C_7H_8Br_2$. Gives no pp. with ammoniacal Cu_2Cl_2. Oxidised by CrO_3 to benzoic aldehyde and acid (Merling, *B.* 24, 3122).

TROPINE $C_8H_{15}NO$ *i.e.*



$\begin{matrix}CH.CH_2.CH.CH_2.CH_2.OH\\CH.CH_2.NMe\end{matrix}$ (Ladenburg) or



$\begin{matrix}CH_2.CH\\CH_2.CH\end{matrix}{>}C_2H_2OH\begin{matrix}CH_2\\NMe\end{matrix}$ (Merling). *Methyl-oxy-*

[142°]. *-l-pyridine tetrahydride.* [62°] (229°).
notas... together with tropic acid, by hydro-
ethyl). Need... ne or hyoscyamine by baryta or
Formed, ...n water). *A.* 128, 281; 133, 87; Laden-
lysis of atropi... ; 217, 115; *B.* 13, 608; 20,
HClAq (Kraut, ... 26, 1067). Hygroscopic tables
burg, *A.* 206, 2... sol. water and alcohol. Does
1653; 23, 1780; from the air. Its aqueous solu-
(from ether), v.
not absorb CO_2

tion ppts. metallic oxides from their salts. Not attacked by nitrous acid. Not volatile with steam. According to Eykman (*B.* 26, 1400) the refractive index agrees best with Merling's formula.

Reactions.—1. Decomposed by distilling with soda-lime into tropilidene, methylamine, and H_2O.—2. Loses H_2O, being converted into tropidine by heating with fuming HCl and HOAc at 180° or by heating with H_2SO_4 (1 pt.) and water (1½ pts.) at 230°.—3. Conc. HIAq and red P at 150° form tropidine and tropidine periodide, but at 140° they form '**tropine iodide**' $C_8H_{17}NI_2$ which crystallises from water in prisms [115°], whence silver chloride followed by $PtCl_4$ give $(C_8H_{17}NICl)_2PtCl_4$ crystallising in red octahedra. By treatment with Ag_2O followed by HCl and $PtCl_4$ very soluble $(C_8H_{17}NCl_2)PtCl_4$ is got.—4. Alkaline $KMnO_4$ forms tropigenin and, finally, oxalic acid and NH_3 (Merling, *A.* 216, 341).—5. CrO_3 forms tropinic acid $C_6H_{11}N(CO_2H)_2$.—6. Aqueous HOCl yields prisms [111°], whence alcohol produces $C_6H_5NCl_4.CH.OH$ [108°], which forms a hydrochloride [162°] crystallising in plates (Einhorn a. Fischer, *B.* 25, 1391).

Salts. — B'HCl. —$B'_2H_2PtCl_6$. Orange-red monoclinic crystals. [200°] (Schmidt, *A.* 208, 214).—$B'HAuCl_4$. [212°].—$B'HCl6HgCl_2$. [246°] (Ladenburg, *B.* 24, 1631).—$B'C_6H_3N_3O_7$.

Nitroxyl derivative $C_8H_{14}(ONO_2)N$. *Nitro-tropeïn.* Formed by warming tropine (2 g.) with HNO_3 (12 g. of S.G. 1·25) at 100° (Ladenburg, *B.* 15, 1025). Alkaline liquid, sol. water, alcohol, and ether. Yields KNO_2 on boiling with KOH.—$B'_2H_2PtCl_6$. Needles.—B'HI. Prisms.

Benzoyl derivative $C_8H_{14}(OBz)N$. *Benzoyl-tropeïne.* Formed by heating tropine hydrochloride with benzoic acid and dilute HCl (Ladenburg, *B.* 13, 1083; *A.* 217, 96). Crystallises as $C_{15}H_{19}NO_2$ 2aq [58°], $C_{15}H_{19}NO_2$ ⅓aq [37°], or anhydrous [42°]. Sl. sol. water, v. sol. alcohol and ether.—$B'HNO_3$.—$B'_2H_2PtCl_6$ 2aq.—$B'C_6H_3N_3O_7$.

o-Oxy-benzoyl derivative $C_8H_{14}(O.CO.C_6H_4.OH)N$. *Salicyl-tropeïne.* Formed in like manner, using salicylic acid (Gaebe a. Caro, *B.* 13, 106; L.). Silky plates. Feeble poison, ·025 g. killing a frog in a few hours. Has no apparent effect on the pupil.—B'HCl.—$B'H_2PtCl_6$.—$B'HAuCl_4$: yellow plates.

m-Oxy-benzoyl derivative $C_{15}H_{19}NO_3$. [226°]. Small plates, v. sl. sol. water. Acts slightly on the pupil of the eye.—B'HCl.—$B_{12}H_2SO_4$ 4aq.—$B'_2H_2PtCl_6$: orange plates.

p-Oxy-benzoyl derivative $C_{15}H_{19}NO_3$. [227°]. Trimetric plates (containing 2aq).—$B'HNO_3$.—$B'_2H_2PtCl_6$ 2aq. Orange plates.

Phenyl-acetyl derivative $C_{16}H_{21}NO_2$ *i.e.* $C_8H_{14}N(O.CO.CH_2Ph)$. *Phenylacettropeïne.* Aromatic oil.—B'HBr.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$. —$B'_2H_2SO_4$. Soluble tables.

Mandelyl derivative $C_{16}H_{21}NO_3$ *i.e.* $C_8H_{14}N(O.CO.CHPh.OH)$. *Homatropine.* Formed by heating tropine with mandelic acid, HCl (1 pt.), and water (40 pts.), the yield being 50 p.c. of the theoretical amount (Ladenburg, *C. R.* 90, 921; *A.* 217, 82). Deliquescent prisms (from ether), sl. sol. water. A solution of its hydrochloride is ppd. by potassio-mercuric iodide, but not by tannin. It enlarges the pupil of the eye almost as energetically as atropine, but the enlargement passes off much more rapidly (Völkers,

A. 217, 86; Bertheau, *Berl. Klin. Wochenschrift*, 1880, No. 41; Tweedy a. Ringer, *Lancet*, 1880, No. 21).—$B'HBr$. Trimetric crystals; $a:b:c$ = ·414:1:·472.—$B'C_6H_3N_3O_7$. Yellow plates.—$B'HAuCl_4$.—$B'_2H_2SO_4$. Needles.

Cinnamoyl derivative $C_{17}H_{21}NO_2$. [70°]. Small plates (from dilute alcohol). Gives pps. with tannin, picric acid, potassio-mercuric iodide, and I in KI. Strong poison, ·03 g. killing a frog in three minutes. Has little action on the pupil. —$B'HCl$.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$. Needles.

Atropyl derivative $C_{17}H_{21}NO_2$. *Atroptropeïne.* Oil.—$B'HAuCl_4$. Small needles.

Atrolactyl derivative $C_{17}H_{23}NO_3$. *Pseudo-atropine.* [120°]. Formed from atrolactic acid, tropine, and dilute HCl (1:400) by repeated evaporation (Ladenburg, *A*. 217, 87). Needles (from water). Resembles atropine in physiological action, two drops of a 1 p.c. solution expanding the pupil and paralysing accommodation for a week.—$B'HAuCl_4$. [114°].

Phthalyl derivative $C_{21}H_{22}N_2O_4$. [70°]. Formed, in very small quantity, by evaporating phthalic acid with tropine and dilute HCl. Mass of silky needles.—$B'H_2PtCl_6$.

Methylo-iodide $C_8H_{15}NOMeI$. Small crystals, nearly insol. alcohol. Yields $B'MeOH$ and $B'_2Me_2PtCl_6$ (Merling, *B*. 14, 1829; Ladenburg, *A*. 217, 131).

Ethylo-iodide $B'EtI$. Crystalline. Yields $B'_2Et_2PtCl_6$, a yellow crystalline powder.

(α)-Methyl-tropine $C_8H_{14}MeNO$. (243°). Formed by distilling tropine methylo-iodide. Liquid, v. sol. water and alcohol. Strongly alkaline. Its hydrochloride, distilled with solid KOH, yields dimethylamine.—$B'HAuCl_4$. Very unstable.

Methylo-iodide $(C_8H_{14}MeNO)MeI$. Deliquescent needles, decomposed by distilling with solid KOH into tropilidene and trimethylamine. —$(C_8H_{14}MeNO)_2Me_2PtCl_6$. Orange crystals.

(β)-Methyl-tropine $C_9H_{17}NO$. (198°-205°). Formed by shaking tropilene with an aqueous solution of dimethylamine (Ladenburg, *B*. 14, 2404). Liquid, split up by gaseous HCl into tropilene and NMe_2H.—$B'HAuCl_4$. Prisms.

(γ)-Methyl-tropine $C_9H_{17}NO$. Formed in small quantity by distilling the methylo-hydroxide of (α)-methyl-tropine (Merling, *B*. 15, 288). V. sl. sol. Aq.—$B'_2H_2PtCl_6$. V. sl. sol. Aq.

Metatropine $C_8H_{15}NO$. (238°). Formed by shaking tropine iodide with water and Ag_2O. Not solid at −30°.—$B'HCl$: tables.

Hydrotropidine $C_8H_{15}N$. (168°). S.G. ^{0} ·937; ^{15} ·926. Formed by reducing tropine iodide $C_8H_{15}NI_2$ with zinc-dust and HClAq (Ladenburg, *B*. 16, 1408). Liquid, m. sol. water.—$B'HCl$: deliquescent crystals.—$B'_2H_2PtCl_6$. Tables.

Norhydrotropidine $C_7H_{13}N$. [60°]. (161°). Formed by distilling hydrotropidine hydrochloride in a current of HCl (Ladenburg, *B*. 20, 1649). Crystalline.—$B'HCl$. [281°].—$B'_2H_2PtCl_6$.—$B'HHgCl_3$.—$B'C_6H_3N_3O_7$. Needles.

Nitrosamine $C_7H_{12}N_2O$. [117°]. Cubes.

Paratropine $C_8H_{13}NO$. (202°). Formed from hydrotropine and K_3FeCy_6 (Ladenburg, *B*. 24, 1626).—$B'_2H_2PtCl_6$. [197°].—$B'HAuCl_4$. [182°].—$B'HCl6HgCl_2$. [225°]. V. sol. water.

ψ-Tropine $C_8H_{15}NO$. [108°]. (242°). Formed, together with tropic acid, by warming hyoscine with baryta-water (Ladenburg, *B*. 13, 1551; 17, 151; Liebermann, 24, 2587). Formed also by dissolving its benzoyl derivative in hot conc. HClAq (Hesse, *A*. 271, 210). Hygroscopic prisms (from chloroform), v. e. sol. water. Yields tropinic and ecgonic acids on oxidation.—$B'_2H_2SO_4$. Hygroscopic crystals.—$B'HAuCl_4$. [198°] (Ladenburg); [202°] (H.); [225°] (Liebermann).—$B'_2H_2PtCl_6$ 4aq. [206°, anhydrous]. Trimetric prisms; $a:b:c$ = ·702:1:·879.

Methylo-iodide $B'MeI$. [270°]. Rhombohedra. Yields $B'MeCl$ and $B'_2Me_2PtCl_6$. [216°] crystallising from water.

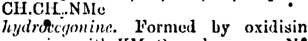
Benzoyl derivative $C_{15}H_{19}NO_2$. [48°]. Occurs in the leaves of Java coca (Liebermann, *B*. 24, 2336; Hesse, *A*. 271, 208). Colourless plates (from ether).—$B'HCl$. [270°].—$B'_2H_2PtCl_6$. Pale-yellow needles.—$B'MeI$.—$B'MeCl$.—$B'MeAuCl_4$.—$B'Me_2PtCl_6$ 2aq.

Mandelyl derivative $C_8H_{14}NO(CO.CH(OH).C_6H_5)$. *ψ-Homatropine.* Formed by heating ψ-tropine with mandelic anhydride at 200° (Liebermann a. Limpach, *B*. 25, 931).—$B'HCl$.—$B'_2H_2PtCl_6$.—$B'HAuCl_4$.

Tropyl derivative $C_8H_{14}NO(C_9H_9O_2)$. Isomeride of hyoscine. [88°]. $[\alpha]_D = -4.9°$. Nodules, insol. water, sol. alcohol.—$B'HCl$. [183°].—$B'_2H_2PtCl_6$.—$B'HAuCl_4$. [135°].

Atropyl derivative. [129°]. Formed from tropide and ψ-tropine at 200°. Crystals, sol. water. Split up by HClAq into atropic acid and ψ-tropine.

Oxy-tropine carboxylic acid



$\begin{array}{l}\underset{|}{C}H.\underset{|}{C}H_2.\underset{|}{C}H.CH(OH).CH(OH).CO_2H\\ CH.CH_2.NMe\end{array}$. *Dioxyanhydroecgonine.* Formed by oxidising hydroecgonine with $KMnO_4$ and aqueous Na_2CO_3 at 1° (Einhorn a. Rassoff, *B*. 25, 1395). Decomposes at 280°. V. e. sol. water and MeOH, insol. EtOH.—$B'HCl$. [251°].—$B'C\,H_3N_3O_7$.—KA'.

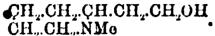
Methyl ether MeA'. [139°]. Tables, v. e. sol. $CHCl_3$. Yields $B'_2H_2PtCl_6$. [210°].

Benzoyl derivative of the methyl ether $C_5H_7MeN.CH(OH).CH(OBz).CO_2H$. [108°]. Needles.—$B'HNO_3$. [216°].—$B'HCl$. [203°].—$B'HAuCl_4$. [173°].—$B'_2H_2PtCl_6$. [208°].

Di-benzoyl derivative of the methyl ether $C_5H_7MeN.CH(OBz).CH(OBz).CO_2H$. Needles.—$B'HNO_3$. [190°].—$B'HCl$. [280°].—$B'_2H_2PtCl_6$. [205°].—$B'HAuCl_4$. [203°].

Reference.—Oxytropine.

TROPINE DIHYDRIDE $C_8H_{17}NO$ *i.e.*



$\begin{array}{l}\underset{|}{C}H_2.CH_2.\underset{|}{C}H.CH_2.CH_2OH\\ CH_2.CH_2.NMe\end{array}$. *Hydrotropine. Methyloxyethylpyridine hexahydride.* (233°). Formed from oxy-ethyl-piperidine and $KMeSO_4$ (Ladenburg, *B*. 24, 1622). V. sol. water and alcohol.—$B'HCl5HgCl_2$. [214°].—$B'HAuCl_4$. [170°]. Crystals.

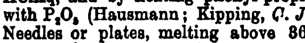
TROPINIC ACID $C_8H_{13}NO_4$. [253°] (L.); [220°] (M.). A product of oxidation of tropine and of ecgonine by chromic acid mixture (Merling, *A*. 216, 348; Liebermann, *B*. 23, 2519). Needles, v. sol. water, sl. sol. alcohol, insol. benzene. Gives off CO_2 when heated. Forms salts with acids and bases.—BaA'_2. Very hygroscopic.—CaA'_2.—AgA'. Readily reduced.—$(HA')_2PtCl_4$.—$HA'HAuCl_4$. Golden prisms.—$HA'HCl$ aq.

TROPYLENE *v.* Tropilene.

TRUXENE $(C_9H_6)_x$. Formed by heating truxone with red P and HIAq (S.G. 1·7) at 180°

(Liebermann a. Bergami, *B.* 22, 786; 23, 317). Formed also by heating hydrindone with conc. HClAq, and by heating phenyl-propionic acid with P_2O_5 (Hausmann; Kipping, *C. J.* 65, 269). Needles or plates, melting above 360°, insol. $CHCl_3$. Oxidised by boiling HOAc and CrO_3 to crystalline 'tri-benzoylene-benzene,' which is not melted at 360°. HNO_3 forms (4,2,1)-nitro-phthalic acid.

(α)-TRUXILLIC ACID $C_{18}H_{16}O_4$ *i.e.*



$$\begin{array}{r}\text{CHPh.CH.CO}_2\text{H}\\ \text{CO}_2\text{H.CH---CHPh}\end{array}\ (?)$$

(γ)-*Isatropic acid.* [274°]. Formed, together with (β)-truxillic acid, by the action of boiling HClAq on isatropylcocaïne, which is a by-product in the preparation of cocaïne (Liebermann, *B.* 21, 2342; 22, 124, 783, 2242). Small needles (from alcohol), sol. hot HOAc. Yields cinnamic acid on distillation. Nitric acid (S.G. 1·52) forms two di-nitro- derivatives, [229°] and [290°]. Yields two isomeric sulphonic acids.—Na_2A'' 10aq (Drory, *B.* 22, 2256).—BaA″ $8\frac{1}{2}$aq. Crystalline, v. sol. water.—CaA″ aq.—Ag_2A''. Flocculent pp., sol. NH_3Aq.

Methyl ether Me_2A''. [174°]. (c. 300°).

Ethyl ether Et_2A''. [146°]. H.C.p. 2,720,900 (Liebermann, *B.* 25, 92). Yields $C_{18}H_{12}(NO_2)_2Et_2O_4$ [138°] (Homans, *B.* 24, 2590).

Isoamyl ether $(C_5H_{11})_2A''$. [83°]. Prisms. Ac_2O at 150° forms (α)-truxillic anhydride, while at 170° the product is (γ)-truxillic anhydride.

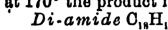
Di-amide $C_{18}H_{14}O_2(NH_2)_2$. [265°]. Needles, v. sl. sol. hot water, sl. sol. alcohol (Drory, *B.* 22, 2261).

Di-piperidide $C_{16}H_{14}(CO.NC_5H_{10})_2$. [259°]. Got from the chloride and piperidine (Herstein, *B.* 22, 2264). Crystalline powder, sol. alcohol.

Mono-piperidide $C_{16}H_{14}(CO_2H).CO.NC_5H_{10}$. [250°]. Yields MeA′ [151°] crystallising from ether in needles.

Anhydride $(C_{36}H_{30}O_7)_3$. [191°]. Mol. w. 1712 (1703 obs. by Raoult's method). Formed by heating the acid with Ac_2O and NaOAc at 100°. Needles (from benzene-ligroïn). Gives no fluorescein. When heated for an hour at 200° it changes to (γ)-truxillic anhydride.

(β)-Truxillic acid $C_{18}H_{16}O_4$ *i.e.*



$$\begin{array}{l}\text{CHPh.CH.CO}_2\text{H}\\ \text{CHPh.CH.CO}_2\text{H}\end{array}\ (?)$$

(δ)-*Isatropic acid.* [206°]. Formed at the same time as the (α)- acid (Liebermann, *B.* 21, 2342; 22, 783, 2243; 25, 90; 26, 837). More sol. water than the (α)- isomeride. Yields benzil on oxidation. Nitric acid (S.G. 1·52) forms a di-nitro- derivative [216°] (Homans, *B.* 24, 2590). Forms cinnamic acid on distillation.—Na_2A'' 2aq.—BaA″ 2aq. Sl. sol. water.—CaA″ 3 aq.—Ag_2A''.

Methyl ether Me_2A''. [76°]. Mol. w. 309 (by Raoult's method); calc. 324. H.C.p. 2,422,900. Monoclinic prisms; $a{:}b{:}c = \cdot826{:}1{:}2\cdot019$; $\beta = 89° 22'$.

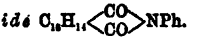
Ethyl ether Et_2A''. [47°].

Chloride $C_{16}H_{14}O_2Cl_2$. [96°]. Tabular prisms, v. sol. ether (Drory, *B.* 22, 2260).

Monopiperidide $C_{16}H_{14}(CO_2H).CONC_5H_{10}$. [224°]. Formed from (β)-truxillic anhydride and piperidine (Herstein, *B.* 22, 2264). Needles, sl. sol. cold alcohol.

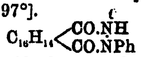
Dipiperidine $C_{16}H_{14}(CO.NC_5H_{10})_2$. [180°]. Formed from the chloride and piperidine. Prisms, v. sol. alcohol.

Phenylimide



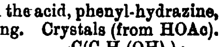
$C_{16}H_{14}\begin{matrix}<\text{CO}\\ <\text{CO}\end{matrix}>NPh$. [180°]. Mol. w. 351 (obs.). Got by heating the anhydride with aniline. Colourless needles (from alcohol). Cold alcoholic potash forms the compound $CO_2H.C_{16}H_{14}.CO.NHPh$ [197°].

Phenyl hydrazide



$C_{16}H_{14}<\begin{matrix}\text{CO.NH}\\ \text{CO.NPh}\end{matrix}$ [218°]. Formed from the acid, phenyl-hydrazine, and HOAc on warming. Crystals (from HOAc).

Fluorescein



$C_{16}H_{14}<\begin{matrix}\text{C}(C_6H_3(OH)_2)_2\\ \text{CO}\end{matrix}>O$. Formed by heating the acid or its anhydride with resorcin at 240°. Amorphous brownish-red powder, sol. alkalis forming fluorescent solutions, v. sol. alcohol, insol. benzene.

Anhydride $C_{18}H_{14}O_3$. [116°]. Mol. w. 278 calc., 289 obs. by Raoult's method. Does not change to an isomeride when heated.

(γ)-Truxillic acid $C_{18}H_{16}O_4$. ε-*Isatropic acid.* [228°]. Formed by heating the anhydride of the (α)-isomeride with HCl at 160°. Needles (from dilute alcohol), v. sl. sol. hot water, v. sol. ether. Yields cinnamic acid on distillation. Gives the same anhydride as the (α)- isomeride (Ladenburg, *B.* 22, 124). Heated with HClAq at 260° it is changed to (α)-truxillic acid. HNO_3 (S.G. 1·52) forms a di-nitro- derivative [293°].

Salts.—BaA″ 11aq.—CaA″ $3\frac{1}{2}$aq.—CaA″ $6\frac{1}{2}$aq.—Ag_2A'': crystalline pp.

Methyl ether Me_2A''. [126°]. Needles. Mol. w. 332 (calc. 324).

Mono-ethyl ether $C_{16}H_{14}(CO_2H).CO_2Et$. [172°]. Formed, together with the di-ethyl ether, by saturating an alcoholic solution of the acid with HCl (Liebermann, *B.* 22, 2240). Needles, yielding AgA′. At 320° it is converted into a mixture of (α)-truxillic acid and (α)-truxillic ether.

Di-ethyl ether Et_2A''. [98°]. Needles, v. sol. alcohol (Drory, *B.* 22, 2260).

Mono-piperidide $C_{16}H_{14}(CO.NC_5H_{10}).CO_2H$. [261°]. Plates (from water or dilute alcohol). Yields MeA′ [201°] and a piperidine salt $(C_5H_{11}N)HA'$ 3aq [218°], which crystallises (with 3aq) from alcohol (Herstein, *B.* 22, 2262).

Di-piperidide $C_{16}H_{14}(CO.NC_5H_{10})$. [248°]. Needles, insol. water, sol. alcohol.

Mono-anilide $C_{16}H_{14}(CO.NHPh).CO_2H$. [220°]. Formed by heating the acid with aniline (Liebermann, *B.* 26, 838). Needles (from dilute alcohol).

Aniline $C_{16}H_{14}(CO.NHPh)_2$. [255°].

Anhydride $C_{16}H_{14}O_3$. Mol. w. 282 (calc. 278). Gives no fluorescein.

(δ)-Truxillic acid $C_{18}H_{16}O_4$. [174°]. Formed by fusing (β)-truxillic acid with potash. Needles (from water), v. sol. alcohol (Liebermann, *B.* 22, 2250; Hesse, *A.* 271, 205). Yields a di-nitro-derivative [226°]. Yields cinnamic acid on distillation.—CaA″: rosettes of needles.—BaA″ 4aq: prisms, sl. sol. Aq.—CuA″ 2aq.—Ag_2A''.

Methyl ether Me_2A''. [77°]. Needles.

Reference.—OXY-TRUXILLIC ACID.

TRUXONE $(C_9H_6O)_x$, $x = 2$ or 3. [289°]. Formed from (α)-truxillic acid and fuming H_2SO_4 (S.G. 1·96) at 15° (Liebermann a. Bergami, *B.* 22, 784; 23, 320). Plates (by sublimation), insol. water, acids, and bases. Not attacked by HNO_3. Yields $(C_9H_6Cl_2)_3$ [178°]. Aniline and HOAc on

boiling form the anilide $(C_8H_6{:}NPh)_x$ **crystallising in needles, [270°], decomposed by fusion.**

Phenyl-hydrazide $(C_8H_6{:}N_2HPh)_x$. [c. 270°]. Needles, v. sl. sol. alcohol.

Oxim $(C_8H_6{:}NOH)_x$. Very unstable, easily changing to an anhydride. Boiling Ac_2O yields $(B_8H_6{:}NOAc)_x$ [261°], m. sol. HOAc.

TULUCUNIN $C_{20}H_{14}O_4$. Occurs in the bark of *Tarapa Tulucuna* (Caventou, *J. Ph.* [3] 35, 189). Light-yellow amorphous resin, with very bitter taste, sl. sol. water, v. sol. alcohol, insol. ether. Turned blue by cold H_2SO_4.

TUNGSTATES, *and derivatives of*; *v.* TUNGSTEN OXYACIDS, SALTS, AND DERIVATIVES OF, p. 802; also TUNGSTEN THIO-ACIDS, AND SALTS OF, p. 810.

TUNGSTEN. W. (*Wolfram.*) At. w. 183·6. Mol. w. is unknown. S.G. 18·77 (Waddell, *Am.* 8, 280); 18·77 (Moissan, *C. R.* 116, 1225); 19·13 at 4° (Roscoe, *C. J.* [2] 10, 286); for other determinations *v.* Bernoulli (*P.* 111, 576), Zettnow (*P.* 111, 16). S.H. (6° to 15°) ·035 (De la Rive a. Marcet, *A. Ch.* [2] 75, 113). S.V.S. c. 9·7.

Historical.—In 1785 a new acid was prepared by J. and F. d'Elhujar from the mineral *wolframite*, and shown to be identical with an acid obtained three years before from *tungstein* by Scheele (*Opusc.* 2, 119). The metal of the new acid was isolated by J. and F. d'E. For many years the new metal was known as *wolfram* or *tungsten* (from Swedish = heavy stone); the latter name has gradually driven out the former in England and France, but the metal is generally called wolfram in Germany; the symbol W is universally employed.

Occurrence.—Never uncombined. *Wolframite* (tungstate of Fe and Mn) is found in considerable quantities in Cornwall, Saxony, Bohemia, &c.; *tungstenite*, or *scheelite* (tungstate of Ca), *scheeletine* (tungstate of Pb), and some other tungstates occur in various localities; *wolframine* or *wolfram-ochre*, WO_3, is also found. Some tin ores contain compounds of W, and W is therefore not infrequently found in specimens of tin.

Formation.—1. By reducing WO_3 by heating to redness in H (Berzelius, *P.* 4, 147; Wöhler, *A.* 77, 262; Zettnow, *P* 111, 16; Roscoe, *C. N.* 25, 61, 78).—2. By heating WO_3 with Na and NaCl (Z., *l.c.*).—3. By reducing WO_3 by mixing with 10 p.c. charcoal and 2 p.c. resin, and heating in a closed crucible for some hours to a white heat (Filsinger, *S. C. I.* 1878. 229).—4. By passing vapour of oxychloride of W and H through a red-hot tube (von Uslar, *A.* 94, 255). 5. By heating WCl_5 in H, in a zinc bath (Roscoe, *l.c.*).—6. By strongly heating the salt $(NH_4)_2WO_4$ in a carbon crucible (Bucholz, *P.* 111, 576).—7. By strongly heating the nitride (*q. v.*, p. 800) in H (Wöhler, *A.* 73, 190).

Preparation.—1. Pure WO_3 is heated to bright redness, in a Pt tube, in a stream of pure dry H (*v. Formation*, No. 1).—2. A mixture of pure WO_3 and dry lampblack is heated in an electric furnace (Moissan, *C. R.* 116, 1225).

WO_3 is prepared from *wolframite* by heating the very finely powdered mineral with conc. HClAq, pouring off the solution from time to time and adding more HClAq, and after some time adding a little HNO_3Aq until most of the brown solid is changed to yellow $WO_3.xH_2O$, washing the residue thoroughly by decantation, adding a considerable quantity of NH_3Aq and warming, filtering from quartz, unchanged *wolframite*, &c., evaporating the solution until small lustrous crystals of an acid ammonium tungstate separate, boiling these crystals for a long time with HNO_3Aq, washing, and heating the residue (Scheibler, *J. pr.* 83, 239; *cf.* Bernoulli, *P.* 111, 590).

Properties.—A steel-grey, hard, brittle, crystalline powder (Riche, *A. Ch.* [3] 50, 5). By reducing the nitride in H, Wöhler (*A.* 73, 190) obtained W as a black powder. By reducing WO_3 by C in an electric furnace, Moissan (*C. R.* 116, 1228) obtained a lustrous, very hard, greyish white solid. As produced by passing the vapour of WO_2Cl_2 mixed with H through a red-hot tube, W forms a shining, dark steel-grey, mirror-like deposit, which can be detached from the tube in hard, brittle crusts (von Uslar, *A.* 94, 255). W can be melted in the O-H flame, part of it burning to WO_3 (Riche, *l.c.*); or by using a current from 600 Bunsen cells, in an atmosphere of N (Desprez, *C. R.* 29, 549). Considerable masses may be melted by employing the current from a dynamo (*v.* Huntington, *C. N.* 46, 163). W was regarded by Faraday as diamagnetic (*T.* 1846. 49). The emission spectrum is described by Thalén (*A. Ch.* [4] 18, 202). W is unchanged in air, but when the pulverulent metal is heated it burns to WO_3; compact W burns in air only at very high temperatures; as obtained by reducing WCl_6 by H, W is said to be pyrophoric. Water is decomposed by W at a red heat. The metal is scarcely acted on by HClAq or H_2SO_4Aq; it is oxidised by HNO_3Aq to $WO_3.xH_2O$; the pulverulent metal dissolves slowly in caustic alkali solutions. Finely divided W reduces and ppts. many metals from solutions of their salts. W combines directly with Br, Cl, I, or S. W is not acted on by heating in NH_3 nor in CO (*v.* Rideal, *C. J.* 55, 45; Smith a. Oberholtzer, *Zeit. f. anorg. Chemie*, 5, 63).

The at. w. of W has been determined (1) by reducing WO_3 in H, and again oxidising W to WO_3 (Berzelius, *P.* 4, 151 [1825]; Schneider, *J. pr.* 50, 158, 161 [1850]; Marchand, *A.* 77, 263 [1850]; von Borch, *J. pr.* 54, 254 [1851]; Riche, *A. Ch.* [3] 50, 10 [1856]; Dumas, *A. Ch.* [3] 55, 143 [1859]; Bernoulli, *P.* 111, 597 [1860]; Persoz, *A. Ch.* [4] 1, 93 [1864]; Roscoe, *C. N.* 25, 61, 73 [1872]; Waddell, *Am.* 8, 280 [1887]); (2) by determining H_2O in $BaW_4O_{13}.9H_2O$ (Scheibler, *J. pr.* 83, 324 [1861]); (3) by reducing WO_3 in H and determining H_2O produced (Bernoulli, *P.* 111, 597 [1860]); (4) by analysing Ag_2WO_4, and $FeWO_4$ (Zettnow, *P.* 130, 16, 240 [1867]); (5) by analysing WCl_6 (Roscoe, *C. N.* 25, 61, 73 [1872]); (6) by determining S.H. of W (De la Rive a. Marcet, *A. Ch.* [2] 75, 113 [1840]); (7) by determining V.D. of WCl_5, WCl_6 and $WOCl_4$ (*v.* these compounds). The older determinations gave values for at. w. varying from 186 to 189; the most recent determination (by Waddell) gave 184·04; Roscoe's determinations, made by reducing WO_3 to W and oxidising W again to WO_3, by finding the ratio of WCl_6 to AgCl and to Ag, and by reducing WCl_6 in H, gave values varying from 183·25 to 183·77. The number 183·6 is probably correct to half a unit. The atom of W is pentavalent in the gaseous molecule WCl_5, and hexavalent in the gaseous molecule WCl_6.

W is the fourth member (the third is as yet unknown) of the even series, or chromium, family of Group VI. in the periodic arrangement of the elements. W is followed in its family by U, and it succeeds Mo and Cr. W very closely resembles Mo; like that element W is both metallic and non-metallic; the balance of these properties being, however, not quite so evenly maintained in W as in Mo. It is doubtful whether any definite salt has been isolated derived from an oxyacid by replacing H by W. The oxide WO_3 acts as a fairly acidic oxide; like MoO_3 it is remarkable for the large number of compounds it forms, simultaneously, with oxides that are more basic and oxides that are less basic than itself. The chemical relations of W are discussed in the article CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168.

Reactions.—1. Heated in *air* burns to WO_3; finely divided W burns easily; compact W only at a very high temperature (*v.* Roscoe, *C. N.* 25, 61, 73).—2. Heated to redness in *steam* gives H and oxide (? WO_3).—3. Reacts with hot *nitric acid*, or *aqua regia*, to form $WO_3.xH_2O$; the same product is obtained by heating W with conc. *sulphuric* or *hydrochloric acid*, but oxides intermediate between WO_2 and WO_3 are formed at first (Riche, *A. Ch.* [3] 50, 15).—4. Pulverulent W dissolves in boiling conc. *potash solution*, giving H and a tungstate of K (Riche, *l.c.*). 5. Heated in *carbonyl chloride* to 150°-200° $WOCl_4$ is produced, mixed with C (Smith a. Oberholtzer, *Zeit. f. anorg. Chemie*, 5, 63).—6. By heating to redness with *sulphur chloride* a red, crystalline thiochloride, probably $W_2S_7Cl_8$, is formed as a sublimate, unstable in air (S. a. O., *l.c.*).—7. Finely divided W reduces solutions of several *metallic* salts; $AgNO_3$ and $AuCl_3$ solutions are reduced to Ag and Au, $HgCl_2$ to HgCl, Cu, Pd, Pt and Rh are partially ppd. from solutions; Bi, Cd, and Pb are not ppd. (Smith, *Zeit. f. anorg. Chemie*, 1, 360).

Combinations.—1. Heated in *oxygen*, WO_3 is formed.—2. Combines with *chlorine*, to form WCl_6, at c. 300°; with *bromine*, to form WBr_5, at a higher temperature; and with *iodine*, to form WI_2, when strongly heated.—3. Heated with *sulphur*, forms WS_2.—4. The compound W_3P_4 is said to be formed by strongly heating W in *phosphorus* vapour (Wöhler a. Wright, *A.* 79, 244).

Detection and Estimation.—Compounds of W form colourless beads with borax or microcosmic salt in the outer blowpipe flame. The borax bead is yellow in the inner flame if a considerable quantity of a compound of W is present. The microcosmic salt bead is blue in the inner flame in the absence of compounds that themselves form coloured beads; in presence of iron compounds the bead is blood-red, but addition of tin causes it to become blue. Soluble alkali tungstates are formed by fusion with alkali carbonate or nitrate; addition of excess of H_2SO_4Aq, HClAq, H_3PO_4Aq, $H_2C_2O_4Aq$, or $HC_2H_3O_2Aq$ to an aqueous solution of a tungstate, followed by immersion of a piece of zinc in the liquid, produces a blue colour; addition of H_2S to an acidulated solution of a tungstate gives no pp., but a blue colour. According to Mallet (*C. J.* 28, 1228), the successive addition of small pieces of zinc to the solution obtained by adding excess of conc. HClAq to an alkaline tungstate produces various colours, the most marked of which is a brilliant magenta-red. By adding KCNSAq and then small pieces of zinc to a solution of an alkaline tungstate in excess of conc. HClAq, a deep green colour is produced; and an amethyst colour is noticed when KCNSAq is added to the solution of an alkaline tungstate, the solution is then diluted, HClAq is then added, and lastly zinc is placed in the liquid. Very minute quantities of W can be detected by adding SO_2Aq and Zn to solution of an alkaline tungstate, whereby a light-blue colour is obtained (M., *l.c.*, p. 1233). W is estimated as WO_3, obtained by evaporation and strongly heating; for separation from other elements a *Manual of Analysis* must be consulted.

Tungsten, alloys of. By reducing mixtures of WO_3 with oxides of Sb, Bi, Co, Cu, Pb, Ni, or Zn, Bernoulli (*P.* 111, 573) obtained alloys of W with these metals, provided there was not more than 10 p.c. of the foreign metal present. An alloy with *aluminium*, approximately WAl_4, was obtained by Wöhler a. Michel (*A.* 115, 102) by heating a mixture of WO_3, Al, cryolite, and NaCl and KCl. W alloys with *iron*; *v.* Poleck a. Grützer (*B.* 26, 35) for an alloy approximately W_2Fe. An alloy of 9 or 10 p.c. W with steel is extremely hard (*v.* Bernoulli, *l.c.*; Philipp, *Hofmann's Ber. über chem. Industrien*, 745; Le Guen, *C. R.* 56, 593; 59, 786; 63, 967; 64, 619; 68, 592; Caron, *A. Ch.* [3] 68, 143; Osmond, *C. R.* 104, 985; Gruner, *C. R.* 96, 197).

Tungsten, amidonitrides of, *v.* TUNGSTEN NITRIDES, AND ALLIED COMPOUNDS, p. 799.

Tungsten, bromides of. The elements combine when heated together to form WBr_5, and by partial reduction in H this gives WBr_2.

TUNGSTEN PENTABROMIDE WBr_5. The formula is probably molecular, from the analogy of WCl_5. Prepared by heating W in excess of Br vapour, taking care that every trace of water and O are excluded. Dark, violet-brown needles, resembling I; melts at 276° and boils at 333°, giving off a dark-brown vapour; decomposed on distillation, with separation of Br; moist air or water forms HBrAq and blue oxide of W; heated to 350° in a stream of H, WBr_2 is formed (Roscoe, *C. N.* 25, 73; *cf.* Borck, *J. pr.* 54, 254; Blomstrand, *J. pr.* 82, 408).

TUNGSTEN DIBROMIDE WBr_2. Obtained, as a bluish-black, velvety solid, when WBr_5 is heated at c. 350° (in a bath of $ZnCl_2$) in a stream of dry H; WBr_5, $WOBr_4$, and Br distil over, and WBr_2 remains. Heated above c. 400° in H gives W and HBr; with HNO_3Aq gives WO_3, HBrAq, and NH_4NO_3Aq (Roscoe, *l.c.*).

Tungsten, chlorides of. When W is heated in Cl the compound WCl_6 is formed, and by reduction in H or CO_2 this gives WCl_5, WCl_4, and WCl_2. Great confusion existed about the compositions of the chlorides of W until Roscoe's researches in 1872 established the formulæ.

TUNGSTEN HEXACHLORIDE WCl_6. Mol. w. 395·82. Prepared by heating W in Cl (Roscoe, *C. N.* 25, 61). The materials must be perfectly dry, and every trace of air must be excluded, else $WOCl_4$ is formed; the WCl_6 sublimes on the cooler part of the tube, and is then distilled several times in a stream of *dry* Cl, and then in a current of *dry* H (a small quantity of WCl_5 is formed, and distils off with the H). Teclu (*A.* 187, 255) obtained WCl_6 by heating WO_3 and PCl_5 in a sealed tube at 170°. WCl_6 forms dark-violet crystals; crystallises from CS_2 in brown, six-sided tablets, from $POCl_3$ in steel-blue, metal-like, regular crystals (T., *l.c.*). Melts, out of contact with air, at 275°, and boils at 346·7° at 760 mm. pressure (R., *l.c.*). V.D. 190 at 350° (Debray, *C. R.* 60, 820; Roscoe, *l.c.*); V.D. 168·8 at 440° (D., *l.c.*; R., *l.c.*; Rieht, *B.* 3, 666). Dissolves readily in CS_2, or $POCl_3$ (T., *l.c.*). Distilled in CO_2 gives WCl_5 and Cl; this fact taken in connection with V.D. at 440° shows that at somewhat above b.p. WCl_6 probably dissociates to WCl_5 and Cl. WCl_6 is unchanged in air; but if a trace of $WOCl_4$ is present, HClAq and WO_3 are formed. Hot water produces WO_3 and HClAq. Heated in air, or in O, forms $WOCl_4$ (Roscoe, *l.c.*; Blomstrand, *J. pr.* 82, 417). $WOCl_4$ is also formed by heating WO_3 with WCl_6. WCl_6 interacts with NH_3, at the ordinary temperature, to form NH_4Cl and W_2N_3 (Rideal, *C. J.* 55, 44).

TUNGSTEN PENTACHLORIDE WCl_5. Mol. w. 360·45. Prepared by repeatedly heating WCl_6 somewhat above its b.p. (346·7°) in a stream of dry H, and when a solid residue has been formed removing the WCl_5 from less volatile lower chlorides by heating in CO_2 (Roscoe, *C. N.* 25, 61). Black, lustrous, needle-shaped crystals; very deliquescent; melts at 248°, and boils at 275·6° (R., *l.c.*). V.D. 175·6 to 179·9 at 350°; 185·7 to 186·4 at 440° (R., *l.c.*). Slightly soluble in CS_2 forming a blue liquid; forms an olive-green solution in water, but is mostly decomposed to HClAq and blue oxide of W. Heated in O forms $WOCl_4$ and Cl (R., *l.c.*; *cf.* Blomstrand, *J. pr.* 82, 425; 89, 230).

TUNGSTEN TETRACHLORIDE WCl_4. This compound is present in the solid residue obtained by heating WCl_6 in H in the preparation of WCl_5 (*v. supra*); it is prepared by distilling this residue, in a bath of H_2SO_4, in a stream of dry CO_2, returning the distillate to the distilling vessel and heating again, and repeating these processes several times (Roscoe, *l.c.*). A soft, crystalline, greyish-brown powder; very hygroscopic; has not been fused or volatilised; heated strongly, it gives WCl_5 and WCl_2. Heated in H to c. 440° pyrophoric W is produced. Decomposed by water to WO_2 and a greenish-brown solution (R., *l.c.*).

TUNGSTEN DICHLORIDE WCl_2. Prepared by heating WCl_4, in a bath of zinc, in a stream of dry CO_2; WCl_5 distils off and WCl_2 remains. A loose, grey, amorphous powder; water forms WO_2 and HClAq, with evolution of H; interacts with H which has been passed through HNO_3Aq to form WO_3, HCl, and NH_4NO_3 (R., *l.c.*).

Tungsten, cyanides of. No cyanides of W have been isolated; according to Wyrouboff (*A. Ch.* [5] 8, 444; *cf.* Atterberg, *Bl.* [2] 24, 355), compounds containing W, K, and $FeCy_6$ are obtained by adding HClAq to a mixture of K tungstates and K ferrocyanide.

Tungsten, fluorides of. No fluoride of W has been isolated. According to Berzelius (*P.* 4, 147), when a solution of $WO_3.H_2O$ in HFAq is evaporated and the residue is treated with water, a solid remains which is free from F after being heated in NH_3. According to Riche (*A. Ch.* [3] 50, 41), a solution of tungstic hydroxide in HFAq gives crystals of $WO_3.H_2O$ on evaporation.

Tungstoxyfluorides. (*Fluotungstates.*) By dissolving tungstates of the form M_2WO_4 in HFAq, Marignac obtained a series of compounds of the forms $2M^IF.WO_2F_2.xH_2O$ and $M^{II}F_2.WO_2F_2.xH_2O$, and also a few compounds of the form $M^IF.WO_2F_2.H_2O$ (*A. Ch.* [3] 69, 67). These compounds may be regarded as salts of the hypothetical acids $H_2WO_2F_4$ and HWO_2F_3; they are similar to some classes of the compounds described as *fluomolybdates* (this vol. p. 425).

The *tungstoxyfluorides* etch glass even when dry; they react slowly with acids, giving $WO_3.H_2O$. The salts of the forms $M^I_2WO_2F_4$ and $M^{II}WO_2F_4$ were prepared by dissolving $M^I_2WO_4$ and $M^{II}WO_4$ in HFAq and evaporating; in some cases also by dissolving $WO_3.H_2O$ in HFAq, adding MOH, and evaporating. The salts of the form $M^IWO_2F_3$ were formed by dissolving acid tungstates in HFAq and evaporating. The following compounds were isolated: (1) $M^I_2WO_2F_4.xH_2O$; $M = NH_4$, $x = 0$; $M = K$, $x = 1$; $M = Na$, $x = 0$; (2) $M^{II}WO_2F_4.xH_2O$; $M = Zn$, $x = 10$; (3) $MWO_2F_3.xH_2O$; $M = NH_4$, $x = 1$; $M = K$, $x = 1$. The salts $(NH_4)_4WO_2F_6.(NH_4)_2WO_4$ and $CuWO_2F_4.NH_3$ were also obtained.

By dissolving $K_2WO_2F_4.H_2O$ in 4 p.c. H_2O_2Aq, and crystallising from dilute H_2O_2Aq containing a little HF, Piccini (*Zeit. f. anorg. Chemie*, 2, 21) obtained $K_2WO_3F_4.H_2O$. P. calls this compound *fluoroxypertungstate*; it might also be named *pertungstoxyfluoride*.

Tungsten, haloid compounds of. When W is heated in a stream of Cl the compound WCl_6 is formed, and this by reduction in H gives WCl_5, WCl_4, and WCl_2. The compound WBr_5 is formed by heating W in Br vapour, and WBr_2 is obtained by partially reducing WCl_5 in H. Small quantities of WI_2 are obtained by heating W in vapour of I. No fluoride of W has been isolated. Oxychlorides and oxybromides of the forms WOX_4 and WO_2X_2 are obtained by heating W oxides in Cl or Br, and in other ways. The following compounds have been vaporised, and the simplest formulæ are molecular: WCl_6, WCl_5, $WOCl_4$. The formulæ WBr_5, $WOBr_4$, WO_2Cl_2, and WO_2Br_2 are probably molecular; but if the analogy of the chlorides and bromides of Mo of the form Mo_xX_{2x} is to be followed (*v.* vol. iii. pp. 427, 428) it is probable that the molecular formulæ of the dichloride and dibromide of W are not less than W_3X_6.

Tungsten, hydroxides of, *v.* TUNGSTEN OXIDES AND HYDRATED OXIDES (p. 800), also TUNGSTEN OXYACIDS (p. 802).

Tungsten, iodide of, WI_2. This, the only iodide of W that has been isolated, is obtained, in very small quantities, by passing I vapour, mixed with CO_2, over red-hot W. It forms a metal-like, greenish crust; heated in air it gives off I and leaves WO_3; it is not decomposed by water (Roscoe, *C. N.* 25, 73).

Tungsten, nitrides of; *and allied compounds.* Compounds of W with N, and probably also with N and H, are formed by heating WCl_6 or $WOCl_4$ in NH_3; the interaction of NH_3 and

WO_3 probably produces a compound, or compounds, of W, N, H, and O; and a compound of W, N, and O is perhaps formed by heating WO_3 with NH_4Cl.

TUNGSTEN NITRIDES. By passing dry NH_3 over WCl_6, and washing away the NH_4Cl produced, by water, Rideal (*C. J.* 55, 44) obtained a black lustrous powder, agreeing fairly with the composition W_2N_3. This substance is insoluble in HNO_3Aq, dilute H_2SO_4Aq, or NaOHAq; hot conc. H_2SO_4 produces NH_3 and WO_3; fusion with NaOH forms Na tungstate; heating in air, or with *aqua regia*, oxidises it to WO_3 (*R.*, *l.c.*).

By continued heating WCl_6 in NH_3, to a temperature difficult to regulate, as slightly too high a temperature produces W, Uhrlaub obtained a black substance to which he gave the formula W_3N_2 (*Die Verbindungen einiger Metalle mit Stickstoff*, Göttingen, 1859).

TUNGSTEN AMIDONITRIDES. By the action of NH_3 on WCl_6, Wöhler (*A.* 73, 198) obtained a black substance containing from 86·76 to 90·8 p.c. W, and 8·24 p.c. N; W. supposed this substance to be a mixture of two amidonitrides, $2WN_2.W(NH_2)_2$ and $2WN.W(NH_2)_2$. W. obtained similar black substances, which he did not analyse, by heating chlorides of W with NH_4Cl (*A.* 105, 258).

Compounds of tungsten with N, H, and O. Wöhler (*A.* 73, 198) obtained a black substance by heating WO_3 to dull redness in dry NH_3; the percentage of W in this substance varied from 87·65 to 88·47, and it contained 7·15 p.c. N, and c. ·2 p.c. H. To this substance W. gave the formula $W_8N_{10}H_4O_4$ ($=4WN_2.W_2(NH_2)_2.2WO_2$). Rideal (*C. J.* 55, 44) passed dry NH_3 over WO_3 heated to a dull redness until the yellow WO_3 was changed to a black, amorphous powder; he allowed to cool, and removed excess of NH_3 by passing a current of dry air through the tube. The black substance thus obtained contained 85·26 p.c. W, and 7·4 p.c. N; assuming c. ·3 p.c. H, the numbers agreed fairly with the formula $W_5N_6H_3O_5$.

Compound of tungsten with N and O. Rideal (*l.c.*) obtained a black powder, agreeing in composition approximately with the formula $WN_2.WO_3$, by heating WO_3 with NH_4Cl until the weight became constant. According to Rideal (*l.c.*) finely divided W does not change when heated in a stream of dry NH_3, after having been heated to redness in dry H; nor does NH_3 react with the blue oxide of W when heated therewith.

Tungsten, oxides and hydrated oxides of. When powdered W is heated in O it combines to form WO_3; by heating this oxide in H a blue oxide is formed, to which various formulæ intermediate between WO_3 and WO_2 have been assigned; by further heating in H, or with C, the dioxide WO_2 is produced. There are indications of an oxide with more O than WO_3. WO_2 dissolves in acids, but corresponding salts have not been isolated; the blue oxide separates from these solutions; WO_2 is also soluble in alkali solutions. WO_3 is insoluble in acids; it dissolves in alkali and alkaline carbonate solutions, forming tungstates (*v.* under TUNGSTEN OXYACIDS, p. 802). WO_3 combines with many acidic oxides to form compounds which react as acids (*v.* p. 801). WO_3 is the anhydride of more than one tungstic acid (*v.* p. 801). None of the oxides has been vaporised; the mol. w. of none is known.

TUNGSTEN DIOXIDE WO_2. (*Brown oxide of tungsten.*)

Formation.—1. By heating a mixture of WO_3 and C to redness (Buchholz, *S.* 3, 1).—2. By heating WO_3 to incipient redness in H (Wöhler, *A.* 73, 198; 77, 262).—3. By decomposing WCl_4, or WCl_2, by H_2O (Roscoe, *C. N.* 25, 61, 73).—4. By the reaction of Zn and HClAq on WO_3 (Wöhler, *P.* 2, 345), or on solution of a metatungstate (Riche, *l.c.*).

Preparation.—WO_3 is placed in a porcelain tube closed at one end and provided with a long opening in the middle; this tube is placed inside another porcelain tube which is kept at red heat, while H is passed through as long as water continues to be formed (Wöhler, *A.* 77, 262 *note*); the product is allowed to cool in H, and is kept in H for 24 hours (Riche, *A. Ch.* [3] 50, 29).

Properties.—A brown powder with a slight violet sheen; prepared by reducing WO_3 by Zn and HClAq, the oxide is obtained in metal-like lustrous crystals, pseudomorphs of WO_3. S.G. 12·11 (Karsten, *S.* 65, 394).

Reactions.—1. Moist WO_2 oxidises rapidly in *air* to WO_3; as prepared by reducing WO_3 in H it is pyrophoric, but if allowed to cool slowly in H the product is not pyrophoric (Berzelius, *P.* 4, 147; 8, 267; Wöhler, *l.c.*; Riche, *l.c.*).—2. Heated strongly in *hydrogen* gives W.—3. *Chlorine* forms WO_2Cl_2 when heated with WO_2 (Roscoe, *l.c.*, p. 63).—4. Heated to dull redness in a stream of *ammonia*, a compound, or compounds, of W with N, H, and O is formed (*v.* Compounds of W with N, H, and O, under TUNGSTEN NITRIDES, *supra*).—5. By heating with *sal ammoniac*, Rideal (*C. J.* 55, 44) obtained a black powder approximately $WN_2.WO_3$ (*v. Compound of W with N and O, supra*).—6. Moist WO_2 dissolves easily in warm *hydrochloric* or *sulphuric acid*, forming reddish-brown solutions from which blue oxide of W separates. WO_2 prepared in the dry way is scarcely acted on by acids, except *aqua regia*, which oxidises it to WO_3.—7. WO_2 dissolves in conc. *potash solution*, giving off H, and forming K tungstate. 8. Reduces *mercuric chloride* to HgCl, and ppts. Cu_2O from solutions of *copper salts* (Riche, *A. Ch.* [3] 50, 5).—9. Heated in *nitric oxide* to below 500° gives the blue oxide; oxidised to WO_3 by heating in *nitrogen dioxide* to c. 300° (Sabatier a. Senderens, *C. R.* 114, 1429; 115, 236).

BLUE OXIDE OF TUNGSTEN. Blue compounds of W and O are obtained by heating WO_3 with reducing agents; analyses lead to formulæ such as W_2O_5, W_3O_8, or W_4O_{11}, intermediate between WO_2 and WO_3. Malaguti (*A. Ch.* [2] 60, 273) gave the formula W_2O_5 to the blue product of heating WO_3 in H to c. 250°; von Uslar (*Beiträge zur Kenntniss des W und Mo* [Göttingen, 1855]) gave the formula W_3O_8. Gmelin said that a blue oxide of the composition W_4O_{11} is formed by strongly heating WO_3 in CO.

Blue compounds are also obtained by strongly heating NH_4 tungstates out of contact with air (Malaguti, *l.c.*; von Uslar, *l.c.*). Aqueous solutions of WO_3 or tungstates are coloured blue by the action of very weak reducers, *e.g.* by exposing moist WO_3 on paper to sunlight (Liesegang, *C. C.* 1865. 943), or by the action of $SnCl_2$Aq on tungstates (Bunsen, *A.* 138, 289; *v.* also Scheibler, *J. pr.* 83, 313). Conc. H_2SO_4 or HClAq gives a blue colour when heated with W (Riche, *A. Ch.* [3] 50, 15). Tungstates boiled with acetic acid and then electrolysed give blue coloured substances (Smith, *B.* 13, 753).

Peroxides of tungsten. Fairley (*C. J.* 31, 141) obtained indications of an oxide with more O than WO_3, by dissolving $WO_3.2H_2O$ in H_2O_2Aq, and evaporating over H_2SO_4 *in vacuo*; the green, transparent, yellow scales thus obtained dissolved in water, forming a solution which could be titrated with $KMnO_4$Aq, with separation of $WO_3.xH_2O$. Cammerer (*Chem. Zeitung*, 15, 957) found that WO_3 dissolved in boiling H_2O_2Aq, with evolution of O; on spontaneous evaporation he obtained a yellow powder, to which he gave the formula $WO_3.H_2O_2.H_2O$ (*cf.* reaction of H_2O_2Aq with CrO_3Aq, vol. ii. p. 166). According to Péchard (*C. R.* 112, 1060), a salt $Na_2O.W_2O_7.2H_2O$ is formed by boiling Na paratungstate solution with H_2O_2Aq and evaporating *in vacuo*.

Tungsten trioxide WO_3. (*Tungstic anhydride.* Sometimes erroneously called *tungstic acid.*)

Occurrence.—As *tungstic ochre* or *wolframine* in Cumberland, Connecticut, North Carolina, &c.

Formation.—1. By strongly heating in air tungstate of NH_4 or of Hg^I.—2. By strongly heating $WO_3.xH_2O$.—3. By burning W in air or O.

Preparation.—An aqueous solution of commercial Na_2WO_4 is poured into boiling HClAq (1:1); the ppd. WO_3 is washed with HClAq until NaCl is completely removed; it is then washed with water to remove all HCl, and dissolved in NH_3Aq; the solution is evaporated to dryness, and the NH_4 salt thus obtained is heated in an open crucible until every trace of NH_3 is driven off (Roscoe, *C.N.* 25, 73). Bernoulli (*P.* 111, 590) recommends to boil the NH_4 salt for a long time with successive quantities of HNO_3Aq (to remove traces of Na salts), and to wash the residual WO_3 quite free from acids (*cf.* Zettnow, *P.* 130, 16, 240). WO_3 is obtained in crystals by very strongly heating the amorphous oxide (Bernoulli, *P.* 111, 595; Schafarik, *W. A. B.* 47, 246); by dissolving WO_3 in molten borax (Nordenskjold, *P.* 114, 612); by strongly heating the oxide in a current of HCl (Debray, *C. R.* 55, 287); or by heating to whiteness a mixture of Na_2WO_4 and Na_2CO_3 imbedded in NaCl, when crystals of WO_3 sublime (D., *l.c.*).

Na_2WO_4 may be prepared from *wolframite* by heating a mixture of 150 pts. of the finely powdered mineral with 100 pts. calcined Na_2CO_3 and 15 pts. $NaNO_3$, for four or five hours, in an iron vessel, lixiviating with water and crystallising (*v.* Franze, *J. pr.* [2] 4, 238; *cf.* Huntington, *B.* 17, 203; Scheibler, *J. pr.* 83, 239).

Waddell (*Am.* 8, 380) prepares pure WO_3 from *tungstenite*, by treating the powdered mineral with *aqua regia*, washing the residue, fusing it with $KHSO_4$, dissolving in water, and fractionally ppg. by $HgNO_3$Aq; the first pps. are then decomposed by *aqua regia*, the WO_3 thus obtained is dried and fused with Na_2CO_3, the fused mass is dissolved in water, tartaric acid is added, and H_2S is passed into the solution; the filtrate from ppd. MnS, &c., is boiled till H_2S is expelled, and is then fractionally ppd. by $HgNO_3$Aq; the later pps. are collected, washed, and decomposed by heating in an open vessel. For a method of preparing WO_3 from *wolframite* *v. Preparation* of Tungsten, p. 797.

Properties.—A heavy, canary-yellow powder; becoming orange-coloured when heated (Roscoe, *C. N.* 25, 73). Crystalline WO_3 is described as wine-yellow, very lustrous, rhombic tablets (Nordenskjold, *P.* 114, 612). A trace of Na tungstate gives a green colour to WO_3 (R., *l.c.*). S.G.: amorphous, 7·13 to 7·16 (Zettnow, *P.* 130, 16, 240; Karsten, *S.* 65, 394); crystalline, 7·23 at 17° (Z., *l.c.*); 6·38 (N., *l.c.*). S.H. (8° to 98°) ·07983 (Regnault, *A. Ch.* [3] 1, 129); (22° to 52°) ·0894 (Kopp, *T.* 1865. 71). Melts readily in the blowpipe (Riche, *A. Ch.* [3] 50, 29); can be sublimed by mixing with Na_2CO_3 and heating to whiteness (Debray, *C. R.* 55, 287); also by strongly heating in HCl (Schafarik, *W. A. B.* 47, 246). Not decomposed at m.p. of Pt (c. 1750°) (Read, *C. J.* 65, 313 [1894]). On exposure to light WO_3 turns greenish, owing to partial reduction (Roscoe, *l.c.*; *cf.* Liesegang, *C. C.* 1865. 943) WO_3 is insoluble in water or acids, even in boiling conc. H_2SO_4; it dissolves in hot KOHAq, NH_3Aq, or K_2CO_3Aq, also in molten K_2CO_3, $KHSO_4$, or K_2WO_4; also in molten alkali chlorides, in air, with evolution of Cl (Schultze, *J. pr.* [2] 21, 437, 441). WO_3 acts as an acidic oxide, forming tungstates (*v.* Tungsten oxyacids, p. 802).

Reactions.—1. Heated in *hydrogen*, WO_3 is reduced to the blue oxide, then to WO_2, and finally to W (*v.* Blue oxide of tungsten, p. 800; Tungsten dioxide, p. 800; and Tungsten, p. 797).—2. Reduction to WO_2 or W is effected by heating with *carbon*.—3. Heated with *potassium* or *sodium*, WO_3 gives W.—4. Reduction to the blue oxide, and then to WO_2, is brought about by *zinc and hydrochloric acid*, by *stannous chloride*, and also by heating with water and different *organic compounds*.—5. Heating with *carbon* in *chlorine* produces WO_2Cl_2 and $WOCl_4$.—6. $WOCl_4$ is formed by passing vapour of *tungsten hexachloride* over heated WO_3 (Roscoe, *C. N.* 25, 63).—7. A mixture of WO_3 and *calcium chloride* heated to redness in *carbon dioxide* gives WO_2Cl_2 (Schultze, *J. pr.* [2] 21, 441).—8. Mixed with *carbon* and heated in *bromine*, WO_3 gives $WOBr_4$; and WO_2Br_2 is formed by passing vapour of *tungsten pentabromide* over hot WO_3 (Roscoe, *l.c.* p. 73).—9. WO_3 is said to dissolve in *molten alkali chlorides*, in air, giving off Cl; heated in absence of air (in a stream of CO_2) with *chlorides of calcium, cobalt, iron, magnesium*, or *nickel*, it is said to give WO_2Cl_2 and MWO_4 (Schultze, *l.c.*).—10. Heating with *phosphorus pentachoride* produces WCl_6 and $POCl_3$ (Teclu, *A.* 187, 255): but WO_2Cl_2 and $WOCl_4$ are also formed, according to the relative masses of WO_3 and PCl_5, and the temperature (Schiff, *A.* 197, 185).—11. WO_2Cl_2, $WOCl_4$, and CO_2 are formed by heating WO_3 in vapour of *carbon tetrachloride* (Watts a. Bell, *C. J.* 33, 442).—12. Compounds of W with N, H, and O (*v.* p. 800) are formed by heating WO_3 in *ammonia*; and a compound of W with N and O is probably produced by heating WO_3 with *sal ammoniac* (*v.* p. 800).—13. WS_3

*is formed by passing **sulphur vapour**, or **hydrogen sulphide**, over WO_2 heated to whiteness (Berzelius); also by heating to redness a mixture of WO_2 with 6 pts. of mercuric sulphide (B.; Brock, J. pr. 54, 254).*

HYDRATES OF TUNGSTEN TRIOXIDE. Various compounds of the form $WO_3.xH_2O$ have been isolated; as these compounds act as acids, they are described under TUNGSTEN OXYACIDS.

Tungsten oxyacids, salts, and derivatives of. Several hydrates of WO_3 that react as acids are known. WO_3 also combines with many acidic oxides—such as P_2O_5, B_2O_3, SiO_2, &c.—and the compounds so formed combine with basic oxides to form salt-like bodies.

TUNGSTIC ACIDS. The hydrates of WO_3 fall into two classes: *tungstic acids*, which are insoluble, or nearly insoluble, in water; and *metatungstic acids*, which dissolve in water.

TUNGSTIC ACIDS. The *monohydrate* $WO_3.H_2O$, or *orthotungstic acid* $WO_2(OH)_2$, is obtained by dissolving WO_3 in hot alkali or alkaline carbonate solutions, and boiling these solutions with excess of a mineral acid. It is also said to be obtained by decomposing an ammoniacal solution of WO_3 by Cl (Dumas, *A. Ch.* [3] 55, 144); and also by boiling powdered *wolframite* with *aqua regia*. This acid is a yellow solid; it reddens litmus; is insoluble, or almost insoluble, in water. According to Braun (*J. pr.* 91, 39), it is changed to $2WO_3.H_2O$ at 100°; according to Zettnow (*P.* 130, 16, 240), this change is effected at 50°. The acid is slowly reduced by Zn and HClAq, the final product being WO_2 (O. v. d. Pfordten, *B*, 16, 508).

The *dihydrate* $WO_3.2H_2O$ is said to be formed by adding a mineral acid to a dilute solution of an alkali tungstate M_2WO_4, and drying in the air; also by decomposing WCl_6, $WOCl_4$, or WO_2Cl_2 by water (Forcher, *W. A. B.* 44 [2], 173; *cf.* Riche, *A. Ch.* [3] 50, 36; Anthon, *J. pr.* 9, 6). Forms $WO_3.H_2O$ by drying over H_2SO_4 (Braun, *J. pr.* 91, 39). This hydrate is described as an amorphous, white solid; reddens litmus; somewhat soluble in water, but insoluble if a little acid is present. By boiling with dilute acids is said to give $WO_3.H_2O$.

The *hemihydrate* $2WO_3.H_2O$, or *ditungstic acid* $H_2W_2O_7$, is said by Braun (*l.c.*) to be formed by heating the monohydrate to 100°; the change is complete at 50° according to Zettnow (*P.* 130, 16, 240).

METATUNGSTIC ACIDS. Acids of the composition $4WO_3.xH_2O$ are obtained by decomposing hot conc. $BaW_4O_{13}Aq$ by the equivalent quantity of H_2SO_4, filtering from $BaSO_4$, and evaporating (Scheibler, *J. pr.* 83, 310); also by decomposing $PbW_4O_{13}Aq$ by H_2S, filtering, and evaporating (Forcher, *W. A. B.* 44 [2], 173). The composition of the acid formed by evaporating *in vacuo* over H_2SO_4 is probably $H_2W_4O_{13}.?H_2O$ (Scheibler, *l.c.*; *cf.* Persoz, *C. R.* 34, 135; Lotz, *A.* 91, 52). BaW_4O_{13} is obtained by ppg. a hot conc. solution of $(NH_4)_2W_4O_{13}$ by $BaCl_2Aq$; PbW_4O_{13} by ppg. $(NH_4)_2W_4O_{13}Aq$ by $Pb(C_2H_3O_2)_2Aq$; $(NH_4)_2W_4O_{13}$ is formed by boiling $(NH_4)_2WO_4$ with WO_3Aq and evaporating.

According to Zettnow (*P.* 130, 16, 240), the pp. obtained by decomposing Na_2WO_4Aq by a mineral acid has the composition
$4WO_3.H_2O(=H_2W_4O_{13})$ after drying at 200°.

Metatungstic acid crystallises in sulphur-yellow octahedra; the acid is readily soluble in water, forming a very sour, intensely bitter liquid. A conc. solution gives a pp. of $WO_3.2H_2O$ on standing; when a dilute solution is boiled it coagulates and gives a pp. of white $WO_3.2H_2O$, and then of yellow $WO_3.H_2O$. The heats of neutralisation of $H_2W_4O_{13}Aq$ by Na_2OAq, K_2OAq, BaOAq, and SrOAq are given by Péchard (*C. R.* 108, 1167); the values are nearly the same as those for HNO_3Aq and H_2SO_4Aq. When four equivalents of base are added to $H_2W_4O_{13}Aq$, orthotungstates M_2WO_4 are formed (P., *l.c.*).

By long-continued boiling 2 pts. Na_2WO_4 with 1 pt. As_2O_5, evaporating, treating with alkali solution, and repeatedly crystallising, Lefort (*A. Ch.* [5] 25, 205) obtained fine, very lustrous crystals, which were very soluble in water and in alcohol; to this acid L. gave the composition $H_2W_4O_{13}.6H_2O$, and the name *luteo-metatungstic acid.*

Colloidal (*meta?*) *tungstic acid.* By adding to 5 p.c. Na_2WO_4Aq rather more HClAq than sufficed to neutralise the Na, and dialysing, with addition from time to time of a little HClAq, Graham (*C. J.* 17, 318) obtained a solution in water of tungstic acid. The solution was not gelatinised by acids, salts, or alcohol at the ordinary temperature; it remained clear at 200°. According to Sabanéeff (*J. R.* 21, 515; Abstract in *C. J.* 58, 1215), determinations of the freezing-point of an aqueous solution of Graham's soluble acid point to the formula $3WO_3.H_2O(=H_2W_3O_{10})$. As the values for mol. w. obtained by S. varied from 679 to 995, there seems little reason for adopting the formula $H_2W_3O_{10}$ (713) rather than $H_2W_4O_{13}$ (944).

TUNGSTATES. A great many tungstates have been prepared. The proportion of basic to acidic radicle varies much in these compounds. The better studied tungstates have been divided into three classes—*orthotungstates* $MO.WO_3$, *paratungstates* $3MO.7WO_3$, or perhaps $5MO.12WO_3$, and *metatungstates* $MO.4WO_3$—but as many tungstates are known which do not fit into any of these classes it seems better to adopt a nomenclature and arrangement similar to those employed for the molybdates (*cf.* vol. iii. p. 423), based on the number of WO_3 radicles in the salts. Arranging the tungstates on this plan we get the following table. R = divalent metal, or two atoms of a monovalent metal.

(Ortho) *Monotungstates* $RO.WO_3$ or RWO_4; derived from the acid H_2WO_4.

Ditungstates $RO.2WO_3$ or RW_2O_7; derived from the acid $H_2W_2O_7$.

$$\textbf{(Para)}\begin{cases}3{:}7\ \textit{tungstates}\ 3RO.7WO_3\ \text{or}\ R_3W_7O_{24}.\\ 5{:}12\ \textit{tungstates}\ 5RO.12WO_3\ \text{or}\\ \quad R_5W_{12}O_{41}.\end{cases}$$

2:5 *tungstates* $2RO.5WO_3$ or $R_2W_5O_{17}$.
3:8 *tungstates* $3RO.8WO_3$ or $R_3W_8O_{27}$.

Tritungstates $RO.3WO_3$ or RW_3O_{10}; ?derived from Graham's colloidal acid.

(Meta) *Tetratungstates* $RO.4WO_3$ or RW_4O_{13}; derived from the acid $H_2W_4O_{13}$.

Pentatungstates $RO.5WO_3$ or RW_5O_{16}.
Hexatungstates $RO.6WO_3$ or RW_6O_{19}.
Octotungstates $RO.8WO_3$ or RW_8O_{25}.

The tungstates which have been most thoroughly examined are the monotungstates or orthotungstates; the paratungstates, which

are either 3:7 or 5:12 salts; and the tetra- or metatungstates.

For *thiotungstates* v. TUNGSTEN, THIO-ACIDS AND SALTS OF, p. 810.

ORTHOTUNGSTATES OR MONOTUNGSTATES, **$RO.WO_3$ or RWO_4.** Salts of H_2WO_4, which is the monohydrate of WO_3. The alkali orthotungstates are obtained by dissolving WO_3 or $WO_3.H_2O$ in alkali or alkali-carbonate solutions; or by fusing WO_3 with alkalis, alkaline carbonates, or alkali acid sulphates, and dissolving in water. The other orthotungstates are generally obtained from solutions of the alkali salts by ppn.; also by strongly heating WO_3 with metallic oxides or carbonates; also by fusing the alkali salts with metallic chlorides, and washing with water (Manross, *A.* 81, 243; 82, 356; Geuther a. Forsberg, *A.* 120, 268; Schultze, *A.* 126, 56). The orthotungstates are insoluble in water, except the alkali salts and the Mg salt. Solutions of the alkali salts give pps. of $WO_3.H_2O$ (yellow) or $WO_3.2H_2O$ (white), with dilute H_2SO_4Aq, HClAq, HNO_3Aq, or H_3PO_4Aq; the pp. by HClAq dissolves in a considerable excess of conc. HClAq (Mallet, *C. J.* 28, 1228); cold solutions of metatungstates are not ppd. by acids. According to Marignac (*A. Ch.* [3] 69, 5) the pp. obtained by adding an acid to a solution of an alkali tungstate sometimes contains alkali, and sometimes the ppg. acid, according to the relative quantity of acid used, the dilution, and probably also the temperature. Orthotungstates which are insoluble in water, and the metals of which form carbonates that are insoluble in alkali carbonate solutions, can be brought into solution by fusion with alkali carbonates and treatment with water.

Solutions of orthotungstates give a white pp. with $HgNO_3Aq$; a bluish-white pp. with $Cu(NO_3)_2Aq$; a brown flocculent pp. on adding K_4FeCy_6Aq, after adding HClAq; no pp. with tincture of galls until an acid is added, when a copious chocolate-coloured pp. is formed; and a yellow pp. with $SnCl_2Aq$, which pp. turns blue when it is warmed with a little HClAq or H_2SO_4Aq. For the reactions with Zn and acid, and with KCNSAq, Zn and acid, v. TUNGSTEN, DETECTION OF, p. 798.

Barium orthotungstate $BaWO_4$. Prepared by fusing 7 parts $BaCl_2$ with 4 parts NaCl and 2 parts Na_2WO_4, and washing with water; white octahedra (Geuther a. Forsberg, *A.* 120, 270); fusible with difficulty (Zettnow, *P.* 130, 256); S.G. 5·0035 at 13·5° (Clarke, *Am. S.* [3] 14, 281). *Hydrates*: (1) $2BaWO_4.H_2O$, by ppg. a hot solution of $3Na_2O.7WO_3$ by BaOAq (Scheibler, *B. B.* 1860. 208); (2) $BaWO_4.H_2O$ and $BaWO_4.2H_2O$, by adding four equivalents BaO in solution to $H_2W_4O_{13}Aq$ (Péchard, *C. R.* 108, 1167).

Cadmium orthotungstate $CdWO_4$. Obtained as a yellow crystalline powder by fusing together 11 parts $CdCl_2$, 16 parts NaCl, and 4 parts Na_2WO_4 (G. a. F., *l.c.*, p. 268; Z., *l.c.*, p. 240). The *dihydrate* $CdWO_4.2H_2O$ is obtained by ppg. a solution of a salt of Cd by Na_2WO_4Aq (Anthon, *J. pr.* 8, 399; 9, 337; Smith a. Bradbury, *B.* 24, 2935).

Calcium orthotungstate $CaWO_4$. Occurs native as *scheelite*, S.G. 6·02 (Bernoulli, *J.* 13, 783). Obtained by adding K_2WO_4Aq to $CaCl_2Aq$. Quadratic octahedra are formed by fusing Na_2WO_4 with excess of $CaCl_2$ (Manross, *A.* 81, 243; 82, 348); also by heating the ppd. salt with CaO in a stream of HCl (Debray, *C. R.* 55, 287).

Chromium orthotungstate $Cr_2(WO_4)_3.20H_2O$. Obtained as a green pp. by adding Na_2WO_4Aq to $CrCl_3Aq$; loses $13H_2O$ at 100° (Lotz, *A.* 91, 66).

Cobalt orthotungstate $CoWO_4.2H_2O$. A violet powder; obtained by ppg. Co salt solutions by K_2WO_4Aq (Anthon, *J. pr.* 9, 344).

Copper orthotungstate $CuWO_4.2H_2O$. A green powder, melting at a red heat and cooling to chocolate-coloured crystals; formed by ppg. Cu salts by Na_2WO_4Aq (A., *l.c.*).

Ferrous orthotungstate $FeWO_4$. Obtained as opaque crystals by heating WO_3 and Fe_2O_3 in a stream of HCl (Debray, *C. R.* 55, 288); also by fusing 2 parts $FeCl_2$, 2 parts NaCl, and 1 part Na_2WO_4 (Geuther a. Forsberg, *A.* 120, 278; Zettnow, *P.* 130, 30). The *trihydrate* $FeWO_4.3H_2O$ was obtained by Anthon (*J. pr.* 9, 343) as a brown powder by ppg. a ferrous salt by K_2WO_4Aq. *Double compounds* of the form $mFeWO_4.nMnWO_3$ with the ratios $m:n = 7:1$, 4:1, 3:1, 3:2, 1:2, and 1:7 were obtained by fusing $FeCl_2$, $MnCl_2$, NaCl, and Na_2WO_4 in varying proportions (G. a. F., *l.c.* p. 270; *cf.* Z., *l.c.* p. 250). *Wolframite* has approximately the composition $FeO.MnO.WO_3$.

Lead orthotungstate $PbWO_4$. Occurs native as *scheelctine*; obtained, as a white pp., by adding K_2WO_4Aq to solution of a salt of Pb (A., *l.c.*, p. 342); quadratic octahedra are formed by fusing 10 parts Na_2WO_4 with 47 parts $PbCl_2$, S.G. 8·235 (Manross, *A.* 82, 357).

Magnesium orthotungstate $MgWO_4$. Formed, in white octahedra, by fusing 2 parts $MgCl_2$ with 2 parts NaCl and 1 part Na_2WO_4 (G. a. F., *l.c.* p. 272).

Manganese orthotungstate $MnWO_4$. Garnet-brown, lustrous, rhombic crystals; S.G. 6·7; obtained by fusing 2 parts $MnCl_2$, 2 parts NaCl, and 1 part Na_2WO_4 (G. a. F., *l.c.*; Z., *l.c.*).

Mercurous orthotungstate Hg_2WO_4. A yellow pp., formed by adding solution of a mercurous salt to solution of an alkali tungstate (A., *l.c.*).

Nickel orthotungstate $NiWO_4$. Formed by fusing 2 parts $NiCl_2$ with 2 parts NaCl and 1 part Na_2WO_4; brown, lustrous crystals (Schultze, *A.* 126, 56); S.G. 6·8845 at 20·5°, 6·8522 at 22° (Clarke, *Am. S.* [3] 14, 281). The *hexahydrate*, $NiWO_4.6H_2O$, is obtained by ppn. (A., *l.c.*).

Potassium orthotungstate K_2WO_4. White, triclinic needles; obtained by boiling WO_3 with an equivalent weight of KOHAq or K_2CO_3Aq, and evaporating (Marignac, *A. Ch.* [3] 69, 18; Anthon, *J. pr.* 8, 399; 9, 337). Decrepitates when heated; melts at red heat (M., *l.c.*), taking up CO_2 (Ullik, *W. A. B.* 56 [2], 148; *cf.* Knorre, *J. pr.* 27, 89). Various *hydrates* are obtained by crystallising a solution of WO_3 in K_2CO_3Aq under different conditions (M., *l.c.*; A., *l.c.*; Riche, *A. Ch.* [3] 50, 45).

Silver orthotungstate Ag_2WO_4. A pale-yellow, amorphous pp. by adding Na_2WO_4Aq to solution of a salt of Ag; melts below redness, and becomes crystalline on cooling; easily soluble in HNO_3Aq; soluble in NH_3Aq (Zettnow, *P.* 130, 30; *cf.* Muthmann, *B.* 20, 984; Wöhler a.

Rautenberg, A. 114, 120). By evaporating a solution in NH_3Aq over CaO and NH_4Cl, Widmann obtained the compound $Ag_2WO_4.4NH_3$ (*Bl.* [2] 20, 64).

Sodium orthotungstate $Na_2WO_4.2H_2O$. Obtained by crystallising a solution of WO_3 in the equivalent quantity of NaOHAq or Na_2CO_3Aq. Transparent, colourless, rhombic tablets (Marignac, *A. Ch.* [3] 69, 22). Effloresces *in vacuo*, or in dry air. Loses all H_2O at 100°. S.G. 3·2588 at 17·5°, 3·2314 at 19°; S.G. of Na_2WO_4 = 4·1743 at 20·5°, 4·1833 at 18·5° (Clarke, *Am. S.* [3] 14, 281). Solubility = 41 at 0°, 55 at 15°, 123·4 at 100° (Riche, *J. pr.* 69, 10). For S.G. of Na_2WO_4Aq of different concentrations, *v.* Franz (*J. pr.* [2] 4, 238). For E.C. of Na_2WO_4Aq *v.* Walden (*Z. P. C.* 1, 529).

Strontium orthotungstate $SrWO_4$. Obtained by ppn. (Anthon, *l.c.*); also by fusing 2 parts $SrCl_2$, 2 parts NaCl, and 1 part Na_2WO_4 (Zettnow, *l.c.*; Schultze, *A.* 126, 56).

Zinc orthotungstate $ZnWO_4$. Colourless tablets; formed by fusing 2 parts $ZnCl_2$ with 2 parts NaCl and 1 part Na_2WO_4 (Geuther a. Forsberg, *A.* 120, 270; *cf.* Zettnow, *P.* 130, 240).

PARATUNGSTATES. A number of acid tungstates have been isolated, the composition of which is expressed by one of the formulæ $3RO.7WO_3$ or $5RO.12WO_3$. The former formula was given by Lotz (*A.* 91, 49) and Scheibler (*J. pr.* 83, 273); the latter formula by Laurent (*A. Ch.* [3] 21, 54) and Marignac (*A. Ch.* [3] 69, 5). The two formulæ represent salts of almost identical composition, and no way has been found of deciding which formula is the better (*cf.* Knorre, *J. pr.* [2] 27, 83). The acid tungstates of this series are more easily formed and crystallise better than the other acid salts; they are generally called *paratungstates*, following the suggestion made by Marignac.

The alkali paratungstates are obtained by saturating hot alkali solutions with WO_3 and crystallising; most of the other paratungstates are prepared by ppn. from solutions of the alkali salts. The alkali salts are soluble in water, the other salts are insoluble. Solutions of alkali paratungstates give, with dilute HClAq, white pps. which become yellow on boiling ($WO_3.xH_2O$). Metatungstates, $RO.4WO_3$, are formed by gradually adding HClAq to boiling solutions of paratungstates; meta- salts are also formed by boiling para- salts with $WO_3.H_2O$. Solutions of paratungstates are not ppd. by SO_2Aq, HIAq, citric, tartaric, or oxalic acid; but the presence of one of these acids does not hinder ppn. by HClAq. Solutions of alkali paratungstates give pps. with salts of almost all the heavy metals. H_2S reacts with alkali paratungstates in solution to form solutions of thiotungstates which give brown pps. with acids, soluble in $(NH_4)_2SAq$. Paratungstates readily react with H_3PO_4, H_3AsO_4, &c., to form complex acids (*v.* p. 807), solutions of which are not ppd. by acids, except these are added in considerable excess; solutions of paratungstates are, therefore, not ppd. by HClAq in presence of H_3PO_4, H_3AsO_4, $H_2B_2O_4$, &c. For the reactions of paratungstates with PtO_4H_4 *v.* Rosenheim (*B.* 24, 2397; the reaction is rather indefinite).

If the simpler (3:7) formula is adopted, the ***paratungstates are represented as*** $3R^I_2O.7WO_3$, $3R^{II}O.7WO_3$, *and* $R^{III}_2O_3.7WO_3$, *i.e.* as salts of the hypothetical acid $H_6W_7O_{24}$, wherein 6H are replaced by $6R^I$, $3R^{II}$, or $2R^{III}$; if the less simple formula (5:12) is adopted, the paratungstates of monovalent and divalent metals are regarded as salts of the hypothetical acid $H_{10}W_{12}O_{41}$ ($=12WO_3.5H_2O$), wherein 10H are replaced by $10R^I$ or $5R^{II}$; paratungstates of R^{III} must be represented in this scheme by the complicated formula $R^{III}_{10}(W_{12}O_{41})_3$. In the paratungstates which have been best examined $R^I = NH_4$, Li, Hg, K, Ag, and Na; R^{II} = Ba, Cd, Ca, Co, Cu, Pb, Mg, Mn, Ni, Sr, and Zn; and R^{III} = Al and Cr. The simpler formulæ are employed in the descriptions of the individual salts.

Aluminium paratungstate $Al_2W_7O_{24}.9H_2O$. A flocculent pp., drying to gum-like lumps; obtained by adding $(NH_4)_6W_7O_{24}Aq$ to a solution of a salt of Al (Lotz, *A.* 83, 65; Anthon, *J. pr.* 8, 399; 9, 337).

Ammonium paratungstate $(NH_4)_6W_7O_{24}.6H_2O$. Obtained by dissolving $WO_3.H_2O$ in NH_3Aq and crystallising at the ordinary, or a little above the ordinary, temperature (Lotz, *A.* 91, 55). Crystallises in white, rhombic needles (Marignac, *A. Ch.* [3] 69, 25; Kerndt, *J. pr.* 41, 190); also in rhombic tablets (M., *l.c.*); and is, therefore, dimorphous. Solubility = 2·8 to 4·5 at 15°–22°; when the solution is boiled the very soluble meta- salt $(NH_4)_2W_4O_{13}$ is formed. Loses 3·9 p.c. H_2O at 100°; when heated to redness the blue oxide of W remains mixed with compounds containing N (M., *l.c.*). Marignac (*l.c.*) gave the formula $(NH_4)_{10}W_{12}O_{41}.11H_2O$ to this salt; Berzelius, and Anthon (*l.c.*) gave the formula $(NH_4)_2W_2O_7.H_2O$; and Riche (*v.* Marignac, *l.c.*) the formula $(NH_4)_2W_4O_{13}.5$ or $6H_2O$.

Various *double salts* have been isolated; with $Na_6W_7O_{24}$ (*v.* Knorre, *B.* 19, 821; Gibbs, *Am.* 7, 236); with $K_6W_7O_{24}$ (*v.* Laurent, *A. Ch.* [3] 21, 59; Marignac, *A. Ch.* [3] 69, 55); with $Mg_3W_7O_{24}$ *v.* M. (*l.c.*), Lotz (*A.* 91, 61); with $Zn_3W_7O_{24}$ *v.* Lotz (*l.c.*); with $Cd_3W_7O_{24}$ *v.* L. (*l.c.*); with $Hg_3W_7O_{24}$ *v.* Anthon (*J. pr.* 8, 399; 9, 337).

Barium paratungstate $Ba_3W_7O_{24}.8H_2O$. A white pp. formed by adding $(NH_4)_6W_7O_{24}Aq$ to excess of $BaCl_2Aq$, washing and drying over H_2SO_4 (Lotz, *A.* 93, 60; *cf.* Knorre, *B.* 18, 327; 19, 820). Forms a *double salt* with $Na_6W_7O_{24}$ (Scheibler, *J. pr.* 83, 314).

Cadmium paratungstate $Cd_3W_7O_{24}.16H_2O$; white needles, obtained by adding $Na_6W_7O_{24}Aq$ to excess of solution of a salt of Cd (Gonzalez, *J. pr.* [2] 36, 44).

Calcium paratungstate $Ca_3W_7O_{24}.18H_2O$; a crystalline pp. formed by ppg. excess of $CaCl_2Aq$ by $Na_6W_7O_{24}Aq$, and drying in the air (Knorre, *B.* 18, 328). Forms a *double salt* with $Na_6W_7O_{24}$ (Gonzalez, *l.c.*).

Chromium paratungstate $Cr_2W_7O_{24}.9H_2O$; a grey powder, obtained by heating $CrCl_3$ with $(NH_4)_6W_7O_{24}$; insoluble in water, but dissolves in $CrCl_3Aq$ (Lotz, *A.* 91, 66).

Cobalt paratungstate $Co_3W_7O_{24}.25H_2O$ (Gonzalez, *l.c.*); forms a *double salt* with $Na_6W_7O_{24}$ (G., *l.c.*).

Copper paratungstate $Cu_3W_7O_{24}.19H_2O$; a pale-green pp. formed by adding $Na_6W_7O_{24}Aq$ to excess of $CuSO_4Aq$ (Knorre, *B.* 19, 826; *v.* also Gonzalez, *J. pr.* [2] 36, 44). Forms a *double salt* with $Na_6W_7O_{24}$ (K., *l.c.*).

Lead paratungstate $Pb_3W_7O_{24}$; a white pp. formed by adding $(NH_4)_6W_7O_{24}Aq$ to $Pb(NO_3)_2Aq$ (Lotz, *A.* 91, 49). Forms a *double salt* with $Na_6W_7O_{24}$ (Gonzalez, *l.c.*).

Lithium paratungstate $Li_6W_7O_{24}.19H_2O$. Large prisms, unchanged in air; obtained by boiling the proper quantities of WO_3 and Li_2CO_3 in water, and allowing to crystallise (Scheibler, *J. pr.* 83, 321).

Magnesium paratungstate $Mg_3W_7O_{24}.24H_2O$; obtained by ppn. (Knorre, *B.* 19, 824). Forms a *double salt* with $Na_6W_7O_{24}$ (K., *l.c.*).

Manganese paratungstate $Mn_3W_7O_{24}.34H_2O$ (Gonzalez, *J. pr.* [2] 36, 44). Forms a *double salt* with $Na_6W_7O_{24}$ (K., *l.c.*).

Nickel paratungstate $Ni_3W_7O_{24}.14H_2O$ (Anthon, *J. pr.* 9, 344).

Potassium paratungstate $K_6W_7O_{24}.6H_2O$ (Marignac, *A. Ch.* [3] 69, 33, gave the formula $K_{10}W_{12}O_{41}.11H_2O$). Prepared by saturating hot KOHAq with $WO_3.xH_2O$, and allowing to cool; by boiling K_2WO_4 with H_2O; or by fusing *wolframite* with $\frac{2}{3}$ of its weight of K_2CO_3, boiling the product with water, saturating the aqueous solution with CO_2, and crystallising (M., *l.c.*). White rhombic crystals, isomorphous with the NH_4 salt (M., *l.c.*). Decomposed, by melting, to K_2WO_4 and $5K_2O.14WO_3$, without forming any meta- salt (Knorre, *J. pr.* [2] 27, 91). Solubility = 2·15 cold water, 6·6 boiling water.

Various *hydrates* have been obtained (*v.* Zettnow, *P.* 130, 241; *cf.* Lefort, *A. Ch.* [5] 9, 93; 15, 321; 17, 470; 25, 200). Forms *double salts* with $Na_6W_7O_{24}$ (*v.* Marignac, *A. Ch.* [3] 69, 55; Laurent, *A. Ch.* [3] 21, 54).

Silver paratungstate $Ag_6W_7O_{24}$; a yellow, crystalline pp. formed by adding $Na_6W_7O_{24}Aq$ to excess of $AgNO_3Aq$ (Gonzalez, *J. pr.* [2] 36, 44).

Sodium paratungstate $Na_6W_7O_{24}.16H_2O$. This formula is given by Scheibler (*J. pr.* 83, 285); the formula $Na_{10}W_{12}O_{41}$ is given by Laurent (*l.c.*), Marignac (*l.c.*), and by Friedheim a. Meyer, (*Zeit. f. anorg. Chemie*, 1, 81). Prepared by saturating hot NaOHAq, or Na_2CO_3Aq, with $WO_3.xH_2O$ and evaporating to the crystallising point; also by passing CO_2 into Na_2WO_4Aq until the reaction is only faintly alkaline. Large, well-formed, white, triclinic crystals (Scheibler, *l.c.*; Marignac, *A. Ch.* [3] 69, 39). Effloresces in air; loses c. $\frac{3}{4}$ of its H_2O over H_2SO_4; is dehydrated without decomposition at 300° (S., *l.c.*); heated to dull redness leaves a residue, insoluble in water, containing more than $5WO_3$ to Na_2O (M., *l.c.*; also Knorre, *J. pr.* [2] 27, 71). Melts above dull redness, giving Na_2WO_4 and $Na_2W_4O_{13}$ (meta- salt). Heated with water to 150° gives much meta- salt (K., *l.c.*). Solubility 8 to 9 at 35° to 40°; for the salts obtainable from an aqueous solution *v.* M. (*l.c.*), and also K. (*B.* 18, 2362). By boiling a solution with Na_2CO_3 transformation to Na_2WO_4 is complete (*v.* Schmidt, *Am.* 8, 16). A *hydrate* with $21H_2O$ has been obtained (M., *l.c.*). Forms *double salts* with $Sr_3W_7O_{24}$ (Gonzalez, *J. pr.* [2] 36, 44), and with $Zn_3W_7O_{24}$ (Knorre, *B.* 19, 823).

Strontium paratungstate $Sr_3W_7O_{24}.8H_2O$ (Knorre, *B.* 18, 327).

Zinc paratungstate $Zn_3W_7O_{24}.xH_2O$ (Gonzalez, *J. pr.* [2] 36, 44).

METATUNGSTATES OR TETRATUNGSTATES, $R^{II}O.4WO_3$ or $R^{II}W_4O_{13}$. Salts of the acid $H_2W_4O_{13}$ (*v.* METATUNGSTIC ACIDS, p. 802). The metatungstates may be obtained by causing metatungstic acid $H_2W_4O_{13}.xH_2O$ (*v.* p. 802) to interact with carbonates, chlorides, or nitrates; also by the reaction of a weak acid (H_3PO_4Aq is the best) with orthotungstates, the acid being added as long as the pp. of $WO_3.xH_2O$ which is at first formed re-dissolves; also from the alkali salts by double decomposition, or better from the Ba salt by interacting with sulphates; the alkali metatungstates are prepared by boiling solutions of the ortho-tungstates for some time with $WO_3.xH_2O$.

Most of the metatungstates are very soluble in water and are crystallisable from aqueous solutions; aqueous solutions are not ppd. by acids in the cold, but pps. are obtained after long standing or boiling. Metatungstates are changed to ortho- salts by excess of alkali; when strongly heated, orthotungstates are formed. Solutions of metatungstates are not ppd. by H_2S; $(NH_4)_2SAq$ gives a blue pp.; pps. are not obtained with salts of the heavy metals except Pb and Hg^I; K_4FeCy_6Aq does not form a pp.

Ammonium metatungstate $(NH_4)_2W_4O_{13}.8H_2O$. This formula is given by Scheibler (*J. pr.* 83, 303); more complicated formulæ are given by Marguerittе (*A. Ch.* [3] 17, 477), Laurent (*A. Ch.* [3] 21, 62), and Lotz (*A.* 91, 55). Obtained by boiling the para- salt $(NH_4)_6W_7O_{24}.xH_2O$ with $WO_3.H_2O$ (Margueritte, *A. Ch.* [3] 17, 477); also by boiling the para- salt with a little HNO_3Aq (Laurent, *A. Ch.* [3] 21, 62); also by heating the dry para- salt to 250°–300° (Scheibler, *J. pr.* 83, 304; *cf.* Persoz, *A. Ch.* [4] 1, 101; and Marignac, *A. Ch.* [4] 3, 71). White octahedra; effloresces in air; loses $7H_2O$ at 100°. Solubility in cold water = 120 (Lotz, *l.c.*), = 286 (Riche, *A. Ch.* [3] 50, 45). The solution is optically refractive. Insoluble in alcohol or ether. Forms a *double salt* with NH_4NO_3 (Marignac, *A. Ch.* [3] 69, 61).

Barium metatungstate $BaW_4O_{13}.9H_2O$. Obtained by adding $BaCl_2Aq$ to a hot conc. solution of $Na_2W_4O_{13}$ acidified by HClAq (Scheibler, *J. pr.* 83, 304). Crystallises in large, white, tetragonal octahedra; S.G. 4·298 at 14°; loses $6H_2O$ at 100°; easily soluble in hot water, decomposed by much cold water to WO_3 and $BaW_2O_{10}.6H_2O$, which dissolve again on heating.

Cadmium paratungstate $CdW_4O_{13}.10H_2O$. Lustrous, white octahedra; unchanged in air; obtained by decomposing $BaW_4O_{13}Aq$ by $CdSO_4Aq$ (S., *l.c.*, p. 273).

Calcium metatungstate $CaW_4O_{13}.10H_2O$. Quadratic octahedra; obtained by dissolving $CaCO_3$ in $H_2W_4O_{13}Aq$ and crystallising (S., *l.c.*, p. 314).

Cobalt metatungstate $CoW_4O_{13}.9H_2O$ (S., *l.c.* p. 317).

Copper metatungstate $CuW_4O_{13}.11H_2O$ (S., *l.c* p. 317).

Magnesium metatungstate $MgW_4O_{13}.8H_2O$ (S., *l.c.*).

Manganese metatungstate $MnW_4O_{13}.10H_2O$ (S., *l.c.* p. 273).

Mercurous metatungstate *$Hg_2W_4O_{13}.25H_2O$. Obtained, as a white pp., by adding $HgNO_3Aq$ to* solution of $H_2W_4O_{13}$ or a meta- salt (S., *l.c.*, p. 319).

Nickel metatungstate $NiW_4O_{13}.8H_2O$ (S., *l.c.*, p. 273).

Potassium metatungstate $K_2W_4O_{13}.8H_2O$. Lustrous octahedra; obtained by boiling $K_6W_7O_{24}Aq$ with $WO_3.xH_2O$; very soluble in hot water, considerably less soluble in cold water (S., *l.c.*, p. 303). A *pentahydrate* was obtained by Marignac (*A. Ch.* [4] 3, 71).

Silver metatungstate $Ag_2W_4O_{13}$. Obtained, as a crystalline crust, by adding $AgNO_3Aq$ to $Na_2W_4O_{13}Aq$, evaporating, separating from Ag_2WO_4, and evaporating again (S., *l.c.* p. 318).

Sodium metatungstate $Na_2W_4O_{13}.10H_2O$. Obtained by boiling $Na_6W_7O_{24}Aq$ with $WO_3.xH_2O$ and allowing to evaporate; white, lustrous octahedra; S.G. 3·8647 at 13°; very soluble in hot, but less in cold, water (S., *l.c*, p. 303).

Strontium metatungstate $SrW_4O_{13}.8H_2O$ (S., *l.c.* p. 314).

Zinc metatungstate $ZnW_4O_{13}.10H_2O$ (S., *l.c.* p. 273).

TUNGSTATES OTHER THAN ORTHO-, PARA-, AND META- SALTS.

Ditungstates. Salts of the form $R^I_2O.2WO_3 = R^I_2W_2O_7$. Salts of K and Na of this composition were said by Lefort (*A. Ch.* [5] 17, 470) to be formed by neutralising cold solutions of K_2WO_4 and Na_2WO_4 by acetic acid; Knorre (*J. pr.* [2] 27, 83) obtained only metatungstates, $R_2W_4O_{13}$, by this method.

Two to five tungstates. The existence of salts of the class $2R^I_2O.5WO_3 = R^I_4W_5O_{17}$ is doubtful. Marignac obtained a salt to which he gave the formula $Na_4W_5O_{17}.11H_2O$ along with the para- salt $Na_6W_7O_{24}.16H_2O$ (*A. Ch.* [3] 69, 50). The same salt seems to have been obtained by Lefort (*l.c.*; *cf.* Forcher a. Gibbs, *J.* 1880. 341) by adding acetic acid and alkali to Na_2WO_4Aq and allowing to stand for some time (*cf.* also Schmidt, *Am.* 8, 16).

Three to eight tungstates. A salt $(NH_4)_6W_8O_{27}.8H_2O = 3(NH_4)_2O.8WO_3.8H_2O$ seems to have been prepared by Marignac (*A. Ch.* [3] 69, 61).

Tritungstates $R^{II}O.3WO_3 = R^{II}W_3O_{10}$. Lefort (*A. Ch.* [5] 17, 470) prepared a salt to which he gave the formula $Na_2W_3O_{10}.6H_2O$, by pouring a boiling solution of $Na_2W_2O_7.6H_2O$ (obtained by adding acetic acid to Na_2WO_4Aq until the liquid shows an acid reaction) into boiling acetic acid, allowing to cool, separating the lower syrupy layer, and crystallising it. A corresponding salt $K_2W_3O_{10}.2H_2O$ was obtained by a similar method; and a series of tritungstates was prepared by mixing equivalent quantities of the Na salt and metallic acetates, in solution, and adding alcohol. L. describes the tritungstates as easily decomposing in aqueous solutions to di- and tetra- salts. The following salts were formed by L.:— $BaW_3O_{10}.4H_2O$; $CdW_3O_{10}.4H_2O$; $CaW_3O_{10}.6H_2O$; $CoW_3O_{10}.4H_2O$; $FeW_3O_{10}.4H_2O$; $PbW_3O_{10}.2H_2O$; $MgW_3O_{10}.4H_2O$; $MnW_3O_{10}.5H_2O$; $NiW_3O_{10}.4H_2O$; $K_2W_3O_{10}.2H_2O$; $Na_2W_3O_{10}.4H_2O$; $SrW_3O_{10}.5H_2O$. Knorre's experiments led him to regard Lefort's tritungstates as mixtures (*J. pr.* [2] 27, 83).

Penta- and octo- tungstates. Salts *of K and Na of the composition $R_2W_5O_{16}$ and $R_2W_8O_{25}$ are said to have been isolated*, the former by fusing mixtures of R_2WO_4 and WO_3, the latter by fusing $R_2W_4O_{13}$ with R_2WO_4 (Knorre, *J. pr.* [2] 27, 81, 91).

A few tungstates that do not find places in any of the foregoing classes have been described by different observers (*v.* especially Lefort, *A. Ch.* [5] 9, 93; 15, 324; 17, 470; 25, 200; also Schreibler, *J. pr.* 83, 237; Gonzalez, *J. pr.* [2] 36, 44; Knorre, *J. pr.* [2] 27, 93; Lotz, *A.* 91, 49; Feit, *B.* 21, 133; Cleve, *Bl.* [2] 43, 170; Högborn, *Bl.* [2] 42, 2).

PERTUNGSTATES. By boiling a solution of the paratungstate $Na_6W_7O_{24}.16H_2O$ with H_2O_2Aq, and then evaporating *in vacuo*, Péchard (*C. R.* 112, 1060) obtained small white crystals of a salt to which he gave the formula $Na_2O.W_2O_7.2H_2O = NaWO_4.H_2O$; and by treating $(NH_4)_6W_7O_{24}.6H_2O$ in a similar way he isolated the corresponding NH_4 pertungstate. According to P. these salts are decomposed by alkalis with evolution of O; solutions of them set free I from KIAq, and react with HClAq, giving off Cl.

TUNGSTEN BRONZES. Bright-coloured, lustrous, metal-like, crystalline solids, obtained by the action of reducers—such as H, coal-gas, Sn, or Fe—on tungstates of Li, K, or Na; also by the electrolysis of these tungstates when molten. The composition of these compounds, which are known as bronzes and are used as pigments, is represented by the formula $M_x(WO_3)_y$, where M = Li, K, or Na. The constitutions of the compounds are not known; they may be represented as compounds of tungstates with WO_2, by the general formula $xM_2O.yWO_3.zWO_2$; they may also be represented as compounds of M_2O with a radicle composed of W and O in a ratio greater than W:2O and less than W:3O—that is, as compounds of M_2O with oxides intermediate between WO_2 and WO_3. The tungsten bronzes are insoluble in most acids, also in alkali solutions.

Sodium tungsten bronzes. These compounds are formed by the interaction of Na tungstates and H (Wöhler, *P.* 2, 350), Sn (Wright, *A.* 79, 221), coal-gas (Schnitzler, *D. P. J.* 211, 484), Zn or Fe (Zettnow, *P.* 130, 261), or by electrolysing Na tungstates (Scheibler, *J. pr.* 83, 321). According to Philipp (*B.* 15, 499), the different processes yield the same bronze if the same tungstate is used, and the more WO_3 there is in the tungstate employed the richer in WO_3 is the bronze produced. All the compounds are insoluble in acids or alkalis; they dissolve in NaClOAq; heated with NH_3Aq and $AgNO_3Aq$ they give Ag and WO_3 (*cf.* P. a. Schwebel, *B.* 12, 2234; 15, 500; Knorre, *J. pr.* [2] 27, 51). These compounds are slowly oxidised to tungstates by heating to redness in air (K., *l.c.*). Philipp (*l.c.*) gave S.G. of all the sodium bronzes as 7·2 to 7·3 at 16° to 18°.

Purple-red bronze $Na_2W_3O_9 = Na_2O.2WO_3.WO_2 = Na_2O.W_3O_8 = Na_2WO_4.W_2O_5$. Prepared by fusing for c. half an hour a mixture of 10·9 g. Na_2CO_3, 71·7 g. WO_3 and 20 g. tinfoil, and boiling successively with H_2O, NaOHAq, and HClAq. Red cubes; the powder transmits green light when suspended in water (*P.*, *l.c.*).

Red-yellow bronze $Na_4W_5O_{15} = 2Na_2O.3WO_3.2WO_2 = 2Na_2O.W_5O_{13}$. Prepared by melting 60 to 80 g. of a mixture of Na_2WO_4 and WO_3 in the ratio $2Na_2WO_4:WO_3$, adding 30 g. tinfoil, and keeping molten for 1 to 2 hours. Red-yellow cubes; the powder is brownish yellow, and transmits blue light when suspended in water (P., *l.c.*).

Gold-yellow bronze $Na_5W_6O_{18} = 5Na_2O.7WO_3.5WO_2 = 5Na_2O.W_{12}O_{31}$. Prepared by heating $Na_2W_2O_7$ to dull redness in H, powdering and again heating in H, and then boiling with H_2O, HClAq, and Na_2CO_3Aq successively. Golden yellow, crystalline powder (P., *l.c.*; *cf.* Wöhler, *P.* 2, 350; Wright, *A.* 79, 221).

Blue bronze $Na_2W_5O_{15} = Na_2O.4WO_3.WO_2 = Na_2O.W_5O_{14}$. Prepared by fusing Na_2WO_4 with more than $2WO_3$, and adding tinfoil; also by melting $Na_6W_7O_{24}$ (paratungstate) and electrolysing with 6 Zn-Pt elements (P., *l.c.*; Scheibler, *J. pr.* 83, 321; *cf.* Knorre, *J. pr.* [2] 27, 49; and Zettnow, *P.* 130, 261). Dark-blue cubes, with a red sheen; S.G. 7·28 at 17°.

Potassium tungsten bronzes. The compound $K_2W_4O_{12} = K_2O.3WO_3.WO_2 = K_2O.W_4O_{11}$ seems to be the only one of this class that has been isolated. Prepared by fusing K_2WO_4 with WO_3 and adding tinfoil; also by fusing K_2CO_3 with from $3WO_3$ to $4WO_3$, and reducing by H or coal gas; also by electrolysing a molten mixture of K_2WO_4 and WO_3. Reddish-violet prisms, giving a blue powder which transmits greenish light when suspended in water; S.G. c. 7·1 (Laurent, *A. Ch.* [2] 67, 219; Zettnow, *P.* 130, 262; Knorre, *J. pr.* [2] 27, 63).

Lithium tungsten bronzes. A compound of this class, probably $Li_2W_5O_{15}$, is obtained by fusing $Li_6W_7O_{24}$ (paratungstate) with tin. Dark-blue crystals (Scheibler, *J. pr.* 83, 321; Knorre, *l.c.*, p. 69; Feit, *B.* 21, 133).

A *potassium sodium bronze* and a *potassium lithium bronze* have been obtained (Knorre, *l.c.* p. 66; Feit, *l.c.*).

COMPLEX TUNGSTIC ACIDS AND SALTS. Tungstic oxide WO_3 combines with several anhydrides, *e.g.* B_2O_3, P_2O_5, As_2O_5, SiO_2, &c., and water, to form acidic compounds, and also with these anhydrides and basic oxides to form salt-like compounds; the whole of these compounds are usually grouped together as *complex tungstic acids* and *complex tungstates*, and they are divided into such classes as *arsenotungstates*, *phosphotungstates*, &c.

ANTIMONOSOTUNGSTIC ACIDS AND SALTS. According to Lefort (*A. Ch.* [5] 17, 487), the compounds $Sb_2O_3.5WO_3.4H_2O$ and $Sb_2O_3.6WO_3.8H_2O$ are formed by dissolving tartar emetic in $Na_2O.3WO_3Aq$ and $Na_2O.2WO_3Aq$ respectively. Gibbs (*Am.* 7, 392) obtained
$4BaO.6Sb_2O_3 22WO_3.36H_2O$ and
$6K_2O.4Sb_2O_3.12WO_3.25H_2O$.

ARSENOTUNGSTIC ACIDS AND SALTS. Compounds of the form $As_2O_5 16WO_3.xH_2O$ have been obtained by Kehrmann (*A.* 245, 45; *cf.* Fremery, *B.* 17, 296); and series of compounds of As_2O_5 with WO_3 and basic oxides (Na_2O, K_2O, BaO, &c.), in which the ratio of $As_2O_5:WO_3$ is 1:6 and 1:3, have been described by Gibbs (*Am.* 7, 313). Compounds of WO_3 with As_2O_3 and bases, and also with As_2O_3 and As_2O_5 and bases, and finally with As_2O_3 and P_2O_5 and bases, are described by Gibbs (*l.c.*).

BOROTUNGSTIC ACIDS AND SALTS. Two compounds of B_2O_3 and WO_3 have probably been isolated, in which the ratios of the oxides are 1:14 and 1:9 respectively; compounds of each of these with bases are known (Klein, *A. Ch.* [5] 28, 350).

Borotungstic acid and salts $B_2O_3.14WO_3.xH_2O$. A solution containing B_2O_3 and WO_3 in the ratio 1:14 is obtained by boiling Na_2WO_4Aq with B_2O_3Aq, ppg. by $HgNO_3Aq$, decomposing the pp. by H_2S, and expelling H_2S from the filtrate by warming (for details *v.* K., *l.c.*). Compounds of the form $xMO.B_2O_3.14WO_3.yH_2O$ have been formed, where $x = 2$, 3, and 4, and M is Ba, K_2, Ag_2, Na_2 and Sr.

Tungstoboric acid and salts. The compound $B_2O_3.9WO_3.xH_2O$, usually known as tungstoboric acid, is obtained in yellowish octahedra by evaporating the solution of borotungstic acid. A considerable number of compounds of bases with B_2O_3 and WO_3, in the ratio $B_2O_3:9WO_3$, has been obtained; most of them are of the form $2MO.B_2O_3.9WO_3.xH_2O$, $M = (NH_4)_2$, Ba, Cd, Ca, Co, Cu, Li_2, Mg, Mn, Hg_2, Ni, K_2, Na_2, Tl_2; a few salts $2M_2O_3.B_2O_3.9WO_3.xH_2O$ ($M = Al$ or Cr) are also described by Klein (*l.c.*).

FLUOTUNGSTATES *and allied compounds*; *v.* TUNGSTOXYFLUORIDES (p. 799).

IODOTUNGSTATES. Blomstrand (*J. pr.* 40, 327) described a compound $2K_2O.I_2O_5.2WO_3.3H_2O$, obtained by adding the calculated quantity of HIO_3 to K_2WO_4Aq.

PHOSPHOTUNGSTIC ACIDS AND SALTS. The oxides WO_3 and P_2O_5 combine in several proportions, in presence of H_2O, to form complex acids which contain large quantities of WO_3 relatively to the P_2O_5. A great many compounds are known containing WO_3 and P_2O_5 combined with basic oxides.

Phosphotungstic acids. Compounds of the form $P_2O_5.xWO_3.yH_2O$; compounds wherein $x = 24$, 21, 20, 16, and 12 seem to have been isolated. The existence of these compounds was made known by Scheibler (*B.* 5, 802); they have been investigated chiefly by Gibbs (*Am.* 2, 217, 281; 4, 377; 5, 361, 391; 7, 313, 392; Péchard, *C. R.* 109, 301; 110, 754; and Kehrmann, *B.* 20, 1805, 1811; 24, 2326; 25, 1966; *A.* 245, 45; *Zeit. f. anorg. Chemie*, 1, 428; also Drechsel, *B.* 20, 1452; and Brandhorst a. Kraut, *A.* 249, 373). The phosphotungstic acids are obtained by boiling H_3PO_4Aq with $H_2W_4O_{13}.xH_2O$ (meta- acid); by decomposing the mercurous salts by HClAq; and by boiling $Na_6W_7O_{24}.xH_2O$ (para- salt) with Na_2HPO_4Aq, decomposing by HClAq, and dissolving the acids thus formed in ether. The phosphotungstic acids are unchanged in solutions in dilute acids; these solutions are scarcely acted on by H_2S, and very slightly by zinc; they give phosphates and tungstates when boiled with alkalis; characteristic pps. are produced with alkaloids, urea, albumen, &c.

Phosphoduodecitungstic acid and salts $P_2O_5.24WO_3.xH_2O$ and $yMO.P_2O_5.24WO_3.xH_2O$. The acid is obtained by evaporating a solution of H_3PO_4 and $H_2W_4O_{13}.xH_2O$ in the proper proportion (Péchard, *l.c.*); by boiling a solution of tungstate and phosphate of Na, in the ratio $24Na_2WO_4:2Na_2HPO_4$, acidulating with HNO_3Aq, ppg. by $HgNO_3Aq$, decomposing the Hg salt by HClAq, filtering, and evaporating *in vacuo*

(Gibbs, *Am.* 2, 217); by boiling H_3PO_4Aq with $BaWO_4$ in the proper proportion, decomposing by a small excess of H_2SO_4Aq, removing H_2SO_4 by BaOAq, filtering, and evaporating (Sprenger, *J. pr.* [2] 22, 418). The acid crystallises in *white, regular octahedra, or cubes. The value for x in the formula* $P_2O_5.24WO_3.xH_2O$ *varies according to different observers, from 40 to 53,* 59, and 61. The salts $yMO.P_2O_5.24WO_3.xH_2O$ are obtained by mixing tungstates (normal or para- salts) with H_3PO_4Aq or a phosphate, and decomposing by slight excess of HClAq, HNO_3Aq, or H_2SO_4Aq; in most cases the salts ppt. as fine, white powders; in some cases it is advisable to evaporate to dryness, extract with alcohol and ether, and evaporate. The salts have been described by Gibbs (*l.c.*); Kehrmann (*Zeit. f. anorg. Chemie*, 1, 430); K. a. Freinkel (*B.* 24, 2327); Sprenger (*J. pr.* [2] 122, 418); and Brandhorst a. Kraut (*A.* 249, 373). Salts have been obtained wherein $MO = (NH_4)_2O$, BaO, CuO, K_2O, Ag_2O, and Na_2O, and $y = 1$, 2, and 3.

Phospholuteotungstic acid and salts. $P_2O_5.16WO_3.xH_2O$ and $yMO.P_2O_5.16WO_3.xH_2O$. The acid is obtained by boiling Na_2WO_4Aq with H_3PO_4Aq, acidulating with HNO_3Aq, adding NH_4Cl and boiling, crystallising the pp. from NH_4ClAq, evaporating the NH_4 salt thus produced with *aqua regia*, and crystallising the acid so formed from water (for details *v.* K., *l.c.*). To an acid obtained by decomposing the K salt by H_2SiF_6Aq, or the Ag salt by HClAq, K. gives the formula $P_2O_5.18WO_3.xH_2O$; and he says that the salts are $yMO.P_2O_5.18WO_3.xH_2O$. The acid forms citron-yellow, six-sided tablets; it melts by the heat of the hand, and is very soluble in water. According to K. (*B.* 20, 1805; *A.* 245, 45), salts of this series are obtained by boiling any phosphotungstates with excess of H_3PO_4Aq in presence of an alkali salt. It is probable that two series of salts exist—one with $16WO_3$ and another with $18WO_3$ (*cf.* Gibbs, *l.c.*; and Péchard, *l.c.*). Salts have been obtained wherein $MO = (NH_4)_2O$, BaO, CaO, CuO, PbO, and K_2O, and $y = 1$, 3, 4, and 6.

Other phosphotungstic acids and salts.

I. Salts of the form $yMO.P_2O_5.22WO_3.xH_2O$ have been obtained, wherein $MO = (NH_4)_2O$, BaO, and K_2O, and $y = 2, 3, 4$, and 7 (*v.* K. a. F., *B.* 24, 2327; 25, 1966; K., *Zeit. f. anorg. Chemie*, 1, 435; Sprenger, *l.c.*; Gibbs, *l.c.*).

II. An acid of the form $P_2O_5.21WO_3.xH_2O$, and salts $yMO.P_2O_5.21WO_3.xH_2O$, where $MO = (NH_4)_2O$, K_2O, and Ag_2O and $y = 3$, have been isolated (K. a. F., *l.c.*; K., *l.c.*).

III. The acid $P_2O_5.20WO_3.xH_2O$ and a salt $6BaO.P_2O_5.20WO_3.xH_2O$ were obtained by Péchard (*l.c.*) and Gibbs (*l.c.*).

IV. For the acid $P_2O_5.12WO_3.xH_2O$ and the salts $yMO.P_2O_5.12WO_3.xH_2O$, where $MO = (NH_4)_2O$, BaO, CaO, CuO, PbO, Li_2O, MgO, Hg_2O, K_2O, Ag_2O, Na_2O, Tl_2O, and ZnO, *v.* Péchard (*C. R.* 110, 754).

V. A few salts of the form $yMO.P_2O_5.7WO_3.xH_2O$ have been obtained ($MO = (NH_4)_2O$, BaO, CaO, Hg_2O, Na_2O; y doubtful) (Gibbs, *l.c.*; K., *l.c.*).

VI. Compounds of alkali phosphates with WO_3, and with phosphoric acids and WO_3, have been isolated; also compounds of alkalis with H_3PO_3 and WO_3, and with H_3PO_2 and WO_3, are described by Gibbs (*Am.* 5, 361; 7, 313, 392).

PLATINITUNGSTATES, *v.* this vol., p. 283.

SILICOTUNGSTIC ACIDS AND SALTS. Three compounds *of* SiO_2 *with* WO_3 *and* H_2O*, which react as acids, have been isolated, and many compounds* of bases with SiO_2 and WO_3 have been obtained (Marignac, *A. Ch.* [4] 3, 5).

Silicoduodecitungstic acid, and salts $SiO_2.12WO_3.xH_2O$; as most of the salts contain $4M_2O$ (or 2MO) the acid is usually written $4H_2O.SiO_2.12WO_3.xH_2O$ ($= H_8SiW_{12}O_{42}.xH_2O$). According to Drechsel (*B.* 20, 1452), the acid is most easily obtained by dissolving Na_2WO_4 in boiling water, nearly neutralising with HNO_3Aq, dissolving the crystals that separate in cold water, boiling this solution with gelatinous $SiO_2.xH_2O$ until HClAq ceases to give a pp., filtering, evaporating, adding a large excess of H_2SO_4Aq, extracting with ether, separating the lowest layer and evaporating (for details *v.* D., *l.c.*). Large, colourless, dimetric octahedra (with $x = 29$); loses $25H_2O$ at 100°, and all H_2O at 350°. Very soluble in water and alkali solutions. Most of the salts of this acid have the composition $4M_2O.SiO_2 12WO_3.xH_2O$, or $2MO.SiO_2.12WO_3.xH_2O$; $M_2O = (NH_4)_2O$, Hg_2O, K_2O, Ag_2O, Na_2O; $MO = BaO$, CaO, MgO; x varies from 7 to 28 (Marignac, *l.c.*).

Tungstosilicic acid, and salts. This name is generally given to an acid containing SiO_2 and WO_3 in the same ratio (1:12) as silicoduodecitungstic acid. The formula of the acid is generally written $4H_2O.SiO_2.12WO_3.20H_2O$. The acid is obtained by evaporating a solution of silicodecitungstic acid to dryness, taking up with water, filtering from separated SiO_2, evaporating to a syrup, and allowing to crystallise. Forms short, white, triclinic prisms; melts under 100°, giving off $16H_2O$ and again solidifying. The salts of this acid are obtained by dissolving carbonates in a solution of the acid, and evaporating; they are more soluble and less easily crystallised than the salts of the duodeci- acid; the salts are of the forms

(1) $2MO(4M_2O).SiO_2.12WO_3.xH_2O$, where $M = Ca$, or $M_2 = K_2$;

(2) $2M_2O.2H_2O.SiO_2.12WO_3.xH_2O$, where $M_2 = K_2$ or Na_2; some more complex salts have also been isolated (Marignac, *l.c.*).

Silico-decitungstic acid, and salts. The acid $4H_2O.SiO_2.10WO_3.xH_2O$ (x probably $= 3$) is obtained by decomposing the Ag salt by HClAq, filtering, and evaporating *in vacuo*; the Ag salt is prepared by adding $AgNO_3Aq$ to the NH_4 salt which is obtained by boiling an acid tungstate of NH_4 with $SiO_2.xH_2O$, filtering, and evaporating. The acid forms a clear, yellowish, glassy solid, which does not wholly dissolve in water; loses $3H_2O$ at 100°; on boiling with water most of the SiO_2 separates, and the filtrate contains tungstosilicic acid. A few salts have been obtained; they are difficult to purify from silicotungstates and tungstosilicates (Marignac, *l.c.*).

STANNIPHOSPHOTUNGSTATES. Gibbs (*Am.* 7, 392) obtained the salt $2(NH_4)_2O.P_2O_5.2SnO_2.22WO_3.15H_2O$ by the reaction of $SnCl_4.2NH_4Cl$ and $2Na_2O.P_2O_5.24WO_3.xH_2O$.

TITANOTUNGSTIC ACIDS. Two acids, $H_2O.TiO_2.12WO_3.xH_2O$ and $H_2O.TiO_2.10WO_3.xH_2O$, are described by Lecarme (*v.* Klein, *Bl.* [2] 36, 17).

VANADOTUNGSTIC ACIDS AND SALTS. Several compounds of WO_3 with V_2O_5 and H_2O have been described by Gibbs (*Am.* 4, 377; 5, 361, 391) and Rosenheim (*A.* 251, 197); they belong to the forms $V_2O_5.10WO_3.xH_2O$, $V_2O_5.18WO_3.xH_2O$, and $V_2O_5.4WO_3.xH_2O$. Compounds of these with yM_2O and yMO are also described; and a great variety of compounds coming under the general formula $mMO.nV_2O_5.pWO_3.xH_2O$ have been obtained (*cf.* Friedheim, *B.* 23, 1505; and Rothenbach, *B.* 23, 3050).

Tungsten, oxybromides of. Two oxybromides, WO_2Br_2 and $WOBr_4$, are formed by the reaction of Br on WO_2, and in other ways. The formula $WOBr_4$ is very probably molecular, from the analogy of $WOCl_4$.

TUNGSTEN DIOXYDIBROMIDE WO_2Br_2. Obtained by heating WO_2 in a stream of Br vapour, also by passing vapour of WBr_5 over heated WO_2 (Roscoe, *C. N.* 25, 73); also by heating WS_2 or a mixture of WO_3 and C in Br (Borck, *J. pr.* 54, 254). Red, transparent, prismatic crystals; appearing black when hot, and giving a yellow powder. Volatilised at red heat with partial decomposition to WO_3 and $WOBr_4$.

TUNGSTEN OXYTETRABROMIDE $WOBr_4$. Obtained by passing Br vapour over a heated mixture of equal parts of WO_3 and W, and cautiously distilling from less volatile WO_2Br_2 (Roscoe, *C. N.* 25, 73). Also formed by passing Br mixed with some O over heated W, or by heating a mixture of WO_3 and C in Br vapour (Blomstrand, *J. pr.* 82, 430). Brownish black, lustrous, crystalline needles; melts at 277° and boils at 27°. Heated in moist air gives WO_3 and HBr, and is decomposed to the same products by water.

Tungsten, oxychlorides of. Two oxychlorides, WO_2Cl_2 and $WOCl_4$, are formed by heating W in Cl mixed with some O, and in other reactions.

TUNGSTEN DIOXYDICHLORIDE WO_2Cl_2. Obtained by heating WO_2 in a stream of Cl, and subliming (Roscoe, *C. N.* 25, 63); also by passing CO_2 over a mixture of WO_3 and $CaCl_2$ heated to redness (Schultze, *J. pr.* [2] 21, 430). Also formed, along with $WOCl_4$, by heating W in Cl mixed with O; by heating WO_3 and C in Cl; by heating WO_3 in CCl_4 (Watts a. Bell, *C. J.* 33, 442); and by heating WO_3 with PCl_5 (Schiff, *A.* 197, 185; *cf.* TUNGSTEN TRIOXIDE, *Reactions*, No. 10, p. 801). Yellow, four-sided tablets; sublimes without melting at c. 266°, with partial decomposition to WO_3 and $WOCl_4$. Not decomposed in moist air, nor by cold water (R., *l.c.*). Heated in dry NH_3 gives off NH_4Cl and leaves WO_2 (Rideal, *C. J.* 55, 43); in this reaction WO_2Cl_2 behaves like CrO_2Cl_2 (R., *C. J.* 49, 367). According to Smith a. Shinn (*Zeit. f. anorg. Chemie*, 4, 381), a black compound $W_4O_4N_4H_2$ is formed by heating WO_2Cl_2 in dry NH_3.

TUNGSTEN OXYTETRACHLORIDE $WOCl_4$. Mol. w. 341·04. Formed by heating W in Cl containing a little O; also by passing Cl over a hot mixture of WO_3 and C; by heating WO_3 in CCl_4 (Watts a. Bell, *C. J.* 33, 442); by heating WCl_5 or WCl_6 in O and Cl; by heating WCl_6 with $H_2C_2O_4$; and by heating WO_2Cl_2. Prepared by passing vapour of WCl_6 over heated WO_3 in a current of Cl (Roscoe, *C. N.* 25, 63). Also by heating WO_3 and PCl_5, in the ratio WO_3:PCl_5 or WO_3:$2PCl_5$, distilling off $POCl_3$ and the small quantities of WCl_5 and WCl_6 that are formed, washing the reddish residue with a little cold CS_2 (to remove WCl_6), then dissolving in a larger quantity of warm CS_2, evaporating, and carefully heating the residue in a stream of CO_2, whereby the more volatile $WOCl_4$ is separated from WO_2Cl_2 (Schiff, *A.* 197, 185).

$WOCl_4$ forms ruby-red, transparent needles; melts at 210·4°, and volatilises at 227·5°, forming a yellow vapour (R., *l.c.*). V.D. 170·2 to 175·8 at 350°, 171·5 at 440° (R., *l.c.*; *cf.* Debray, *C. R.* 60, 820). Exposure to air produces a crust of yellow WO_2Cl_2. Heated in NH_3 probably gives W_2N_3 (Rideal, *C. J.* 55, 43). Decomposed by water, with a hissing sound, to WO_3 and HClAq (Roscoe, *l.c.*).

Tungsten, oxyfluorides of. No compound of W with O and F has been isolated, but compounds are known which may be regarded as containing WO_2F_2. These compounds, $WO_2F_2.2MF$ and $WO_2F_2.MF$, and also a compound $WO_3F_2.2KF$, are described under TUNGSTOXYFLUORIDES (p. 799).

Tungsten, phosphides of. By heating W in vapour of P, a dark-grey powder was obtained by Wöhler a. Wright (*A.* 79, 244), to which they gave the composition W_3P_4. By heating a mixture of WO_3 and P_2O_5 in a graphite crucible, W. a. W. (*l.c.*) obtained large, dark-grey, lustrous, six-sided prisms; S.G. 5·207; insoluble in acids, including *aqua regia*, soluble in a molten mixture of Na_2CO_3 and $NaNO_3$; unchanged by heating in air, but burns brilliantly in O. From an estimation of the P, W. a. W. gave the formula W_2P.

Tungsten, salts of. No salts have been isolated by replacing the H of oxyacids by W. Except the halides, the only salts of W that are known are those wherein W forms part of the negative radicle.

Tungsten, selenides of. By saturating a solution of $Na_2W_4O_{13}$ with H_2Se, and then adding dilute H_2SO_4Aq, Uelsmann (*A.* 116, 125) obtained a black pp., to which he gave the formula WSe_3 (one estimation of W is given); by heating this in a tube a grey solid was obtained, said by U. to be WSe_2 (no analyses). WSe_3 is said to be easily soluble in solutions of alkalis, alkali sulphides, or alkali selenides.

Tungsten, sulphides of. Two compounds of W and S are known, WS_2 and WS_3; the latter is acidic, forming salts M_2WS_4. The V.D. of neither has been determined.

TUNGSTEN DISULPHIDE WS_2. Obtained by heating WO_3 to whiteness in vapour of S or in H_2S (Berzelius); also by heating W and S; also by heating WO_3 with 6 pts. HgS out of contact with air (Borck, *J. pr.* 54, 254). According to Carnot (*Bl.* [2] 32, 164), WS_2 is usually formed when a compound of W is heated in a stream of dry H_2S (*v.* also von Uslar, *A.* 94, 256; Corleis, *A.* 232, 262). A dark-grey, graphite-like, lustrous, crystalline powder (*v.* Riche, *A. Ch.* [3] 50, 26). Is said to decompose steam at a full red heat; reduced to W by very long continued heating in H.

Tungsten trisulphide WS_3. *Obtained by fusing powdered wolframite with ·2 pts. C, 3 pts. S, and 3 pts.* Na_2CO_3, dissolving in water, decomposing the Na_2WS_4Aq thus produced by HClAq, washing the pp. completely out of contact with O, and drying at 100° (von Uslar, *A.* 94, 256; Corleis, *A.* 232, 264). A black powder; slightly soluble in water, more soluble on boiling, probably with partial decomposition. Soluble in alkali sulphide solutions, forming thio- salts (*v.* Tungsten, thio- acids and salts of, *infra*). By adding to Na_2WS_4Aq a little more HClAq than was needed to combine with the Na, Winssinger (*Bl.* [2] 49, 452) obtained a colloidal form of WS_3.

Tungsten, sulpho- acids and salts of, *v.* next article.

Tungsten, thio- acids and salts of. By saturating $(NH_4)_2WO_4Aq$ and K_2WO_4Aq with H_2S, Berzelius obtained $(NH_4)_2WS_4$ and K_2WS_4 (*P.* 8, 267); these salts were more fully examined by Corleis (*A.* 232, 258), who also obtained Na_2WS_4, and also some thio-oxy-tungstates. All the thio-tungstates that have been isolated are ortho- salts, *i.e.* salts of H_2WS_4. Very dilute solutions of thiotungstates can be titrated with IAq in presence of $KHCO_3$ (C., *l.c.*).

Ammonium thiotungstate $(NH_4)_2WS_4$. Obtained by passing H_2S for four or five hours into a solution of 10 g. $WO_3.H_2O$ in 100 c.c. NH_3Aq S.G. ·94, + 20 c.c. water, allowing to stand for some hours in a closed vessel, and washing the crystals that separate with alcohol and ether. Forms orange-yellow prisms, isomorphous with $(NH_4)_2MoS_4$; very easily decomposed in moist air; easily soluble in water, slightly soluble in alcohol. Heated in CO_2 gives WS_2 (B., *l.c.*; C., *l.c.*).

Ammonium dithio-oxy-tungstate $(NH_4)_2WS_2O_2$. Obtained by passing H_2S into a solution of 10 g. $WO_3.H_2O$ in 40 c.c. NH_3Aq S.G. ·90, + 10 c.c. water, until the liquid becomes turbid, and washing the crystals that form with alcohol and ether. Forms yellow, prismatic crystals. When dry, the salt is unchanged in air. Decomposed by re-crystallising from water, giving paratungstate $(NH_4)_6W_7O_{24}.6H_2O$ (C., *l.c.*).

Potassium thiotungstate K_2WS_4. Obtained by warming $(NH_4)_2WS_4$ with KHSAq, adding alcohol, and crystallising from conc. KHSAq. Forms yellow, prismatic needles; easily soluble in water. By continued boiling with KHSAq paratungstate is formed, $K_6W_7O_{24}.6H_2O$ (C., *l.c.*). Forms a *double salt* with KNO_3, with the composition $K_2WS_4.KNO_3$ (B., *l.c.*).

Potassium trithio-oxy-tungstate $K_2WS_3O.H_2O$. Obtained in citron-yellow, quadratic tablets, by passing H_2S for three or four hours into a solution of 10 g. K_2WO_4 in 10 c.c. water, and evaporating *in vacuo*, or precipitating by alcohol (C., *l.c.*).

Potassium monothio-oxy-tungstate $K_2WSO_3.H_2O$. Obtained, in almost colourless, very hygroscopic, crystalline masses, by passing H_2S into a solution of 10 g. K_2WO_4 in 5 c.c. water until the liquid is turbid, filtering, adding 4 to 5 vols. alcohol, separating the under layer of liquid, allowing to crystallise, and washing with alcohol and ether (C., *l.c.*).

Sodium thiotungstate Na_2WS_4. Obtained, *but not pure, by Corleis (l.c.), by decomposing* $(NH_4)_2WS_4$ *by NaHSAq.*

Tungsten, thiochloride of. By heating W to redness with S_2Cl_2, Smith a. Oberholtzer (*Zeit. f. anorg. Chemie*, 5, 63) obtained a red, crystalline sublimate, unstable in air, probably $W_2S_7Cl_4$.

M. M. P. M.

TUNGSTEN BRONZES *v.* under Tungsten oxyacids, p. 806.

TUNGSTIC ACIDS *v.* Tungsten oxyacids, p. 802; also Tungsten thio-acids, *supra*.

TUNGSTOXYFLUORIDES *v.* under Tungsten fluorides, p. 799.

TUNGSTEN, ORGANIC COMPOUNDS OF. Tungsten, heated with MeI at 240°, forms WMe_4I_2 [110°], which crystallises in tables, and is converted by Ag_2O into WMe_4O, which dissolves in acids (Riche, *C. R.* 42, 203; Cahours, *A.* 122, 70).

TUNICIN *v.* Animal cellulose, vol. i. p. 718.

TURMERIC. The root of *Amomum Curcuma*. It contains curcumin (*q. v.*) and turmerol.

TURMERIC ACID $C_{11}H_{14}O_2$. [35°]. A product of oxidation of turmerol by cold $KMnO_4$ (Jackson a. Menke, *Am.* 6, 77). Needles, sl. sol. water, v. sol. alcohol.—CaA'_2 3aq. S. (of CaA'_2) 1·28 at 16°. White needles.—AgA'.

TURMEROL $C_{19}H_{28}O$ (?). (193°–198° at 60 mm.). S.G. ^{17} ·902. $[\alpha]_D = 33·5°$. An oil occurring in turmeric. Distils with decomposition at 285°–290° (Jackson a. Menke, *Am.* 4, 368; 6, 77). Dextrorotatory. Does not combine with $NaHSO_3$. $KMnO_4$ oxidises it to acetic, terephthalic, turmeric, and apoturmeric acids. PCl_5 forms $C_{19}H_{27}Cl$, which is also got by heating turmerol with conc. HClAq at 150°. Sodium forms $C_{19}H_{27}ONa$, whence isobutyl iodide forms oily $C_{19}H_{27}OC_4H_9$.

Apoturmeric acid $C_8H_8(CO_2H)_2$ (?). [221°]. Woolly mass, sol. boiling water.

TURPENTINE. Semi-fluid resins exuding from coniferous trees. They consist of resin dissolved in oil of turpentine. On distillation oil of turpentine passes over and colophony remains behind. The various oils of turpentine are described under Terpenes. The chief constituent of colophony is abietic anhydride (*v.* Abietic acid and Sylvic acid). On oxidation by dilute HNO_3 colophony yields isophthalic, trimellitic, and terebic acids (Schreder, *A.* 172, 93). On the products of distillation of colophony *v.* Resins.

TURPETHIN $C_{34}H_{56}O_{16}$. [c. 183°]. Occurs in the root of *Convolvulus Turpethum* (*Ipomœa Turpethum*) (Boutron-Charlard, *J. Ph.* 8, 131; Spirgatis, *J. pr.* 92, 97; *A.* 139, 41). Purgative yellowish-brown resin, v. sol. alcohol, insol. ether (difference from jalapin). Conc. H_2SO_4 forms a red solution. Boiling alkalis convert it into turpethic acid. Boiling dilute mineral acids yield glucose (3 mols.) and turpetholic acid (1 mol.).

Turpethic acid $C_{34}H_{60}O_{18}$. Amorphous yellowish mass, v. sol. water. Split up by boiling HClAq into glucose and turpetholic acid.—BaA''.—$BaH_2A''_2$ (dried at 100°).

Turpetholic acid $C_{16}H_{32}O_4$. [c. 88°]. Minute needles (from dilute alcohol), sl. sol. ether.—NaA' (dried at 100°).—BaA'_2. Amorphous.—AgA'. Amorphous pp.

Ethyl ether EtA'. [72°]. Plates.

TYLOPHORINE. An alkaloid in *Tylophora asthmatica* (Hooper, *Ph.* [3] 21, 617). Crystalline, sl. sol. water, sol. alcohol and ether.

TYPE METAL. An alloy of 15–20 parts Sb with c. 70 parts Pb, and 10 to 15 parts Sn; *v.* Lead alloys, vol. iii. p. 124.

TYPES. The object of classification is to put together like things, and to put apart things that are unlike. A perfect system of chemical classification would place side by side those elements and compounds that are chemically similar, and it would also indicate the relations that exist between all the elements and all the compounds. Inasmuch as the object of chemistry is the study of the connections between composition and properties, and between changes of composition and changes of properties, a complete scheme of chemical classification must indicate the relations of the substances classified, both as regards composition and also as regards properties. To connect composition with properties necessitates a thorough knowledge of both, and this knowledge can be gained only by comparing one substance with other substances. But, because of the large amount of detailed investigation that is required before the chemical properties of an element or a compound are known, chemists have often forgotten the larger issues of their labours, and have busied themselves rather with the examination of individual bodies than with the comparative study of many bodies. And, because of the imperfection of chemical knowledge at any time, those who have attempted the classification of chemical substances have generally paid chief attention either to the composition or to the properties of the substances to be classified. Hence systems of classification have sometimes prevailed that were founded chiefly on similarities of composition, and at other times classificatory schemes have been in vogue that rested mainly on similarities of properties. But there has always been a desire, and generally an effort, to classify on the bases of composition and properties. To classify satisfactorily demands the recognition of a simple class-mark, which shall also be clear, definable, and invariably applicable. It is probably correct to say that none of the larger classes of chemical compounds has a class-mark of this description. Hence the main difficulty in chemical classification. Take, for instance, the great class of acids. What is the class-mark? What must be known about the composition of a compound before it is put into the class of acids? There is no single and sufficient class-mark to be gained by studying the compositions of acids. What, then, about the properties of acids? Here, too, no simple, definable, and applicable property has been found which serves to distinguish acids from all other compounds. Acids, it is usually said, are compounds containing *replaceable hydrogen.* But the expression replaceable hydrogen has not been, and cannot be, exactly defined. Hence, all that can be done is to set up an ideal or typical acid, and to place in the class *acids* those compounds which fairly closely approach this type as regards both properties and composition. And as with acids so with other classes of compounds. A classification by means of types becomes inevitable in such a science as chemistry, but a typical classification cannot be final in any exact science.

Lavoisier's system of classification rested on oxygen; compounds were regarded as formed by the union of oxygen with other elements or groups of elements; the non-oxygenated part of a compound was called by Lavoisier the *rest* or *radicle*; compounds of oxygen with certain radicles were bases, compounds with other radicles were acids, and salts were formed by the union of bases with acids. Lavoisier used the term *radicle* to include elements and groups of elements.

'J'ai déjà fait observer, que dans le règne minéral presque tous les radicaux oxidables et acidifiables etaient simples; que dans le règne végétal au contraire, et surtout dans le règne animal, il n'en existait presque pas qui ne fussent composés au moins de deux substances, d'hydrogène et de carbone; que souvent l'azote et le phosphore s'y réunissaient, et qu'il en résultait des radicaux à quatre bases.'—*Traité élémentaire de Chimie*, [1793], p. 251.

About twenty-four years after Lavoisier made this statement Berzelius repeated it.

'Nachdem wir den Unterschied zwischen den Producten der organischen und der unorganischen Natur, und die verschiedene Art und Weise wie ihre entfernteren Bestandtheile untereinander verbunden sind, näher kennen gelernt, haben wir gefunden, dass dieser Unterschied eigentlich darin besteht, dass in der unorganischen Natur alle oxydirten Körper *ein einfaches Radical haben*, während dagegen alle organischen Substanzen aus *Oxyden mit zusammengesetztem Radical* bestehen.'—*Lehrbuch der Chemie*, 2 Aufl. [Stockholm, 1817], vol. i. p. 544.

Why do acids and bases unite to form salts? What is the cause of the formation of compounds by the union of radicles, either simple or compound? These questions were answered by Berzelius by appealing to the fact that the electric current very often resolves compounds into two parts, and in many cases also effects the combination of elements or groups of elements. Radicles combine, said Berzelius, because the negative electricity on one is thereby neutralised by the positive electricity on the other. Thus arose the electro-chemical conception of dualism (*v.* Dualism, vol. ii. p. 415; *cf.* Radicle, vol. iv. p. 393).

In 1832 Liebig and Wöhler made an exhaustive study of compounds obtained from bitter-almond oil; they showed that the relations of composition and properties of these compounds were brought together, and expressed in a consistent conception by supposing that all the compounds contained a radicle having the composition C_7H_5O($C = 12$, $O = 16$); this group of elements, common to all the derivatives of bitter-almond oil, they called *benzoyl*. The work of Liebig and Wöhler marked a great advance in chemical classification; it was the actual working out of the connections between composition and properties of a number of compounds, and the expression of these connections in clear and definite language. The term *radicle* became henceforth the expression of a vivifying conception. The compounds derived from bitter-almond oil had certain common properties, and they had also a common composition; they belonged to the same type. The compounds of benzoyl examined by Liebig and Wöhler included such compounds as these: $C_7H_5O.OH$, $C_7H_5O.H$, $C_7H_5O.Cl$, $C_7H_5O.CN$, $C_7H_5O.NO_2$. The radicle C_7H_5O is common to all; this radicle is united with H, Cl, NO_2, CN, or some other radicle, in the different compounds; nevertheless, the properties of the compounds are so similar that all are said to belong to one type. To what extent, then, it was asked, may the properties of one radicle differ from those of another before the replacement of one of these by the other carries with it a change of type? The answer generally given to this question was: If the replacing radicle is chemically similar to the radicle replaced the type will not be destroyed. In 1834 Dumas, from the study of the action of chlorine on various organic compounds, announced the *empirical laws of substitution* as follows: (1) When a compound containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, &c., one atom of chlorine, bromine, iodine, or oxygen, is taken up for each atom of hydrogen lost by the compound. (2) The same rule applies, without modifications, when the compound contains oxygen. (3) If a hydrogenised compound contains water the hydrogen of the water is given up without replacement, and then another quantity of hydrogen is absorbed, so that the final result is a replacement of hydrogen. A year or so later Laurent propounded a *theory of substitution*, which asserted that when equivalent substitution of hydrogen by chlorine or bromine occurs the chlorine or bromine takes the place of the hydrogen, and to a certain extent plays the same part as the hydrogen, and hence the chlorinated or brominated product must be similar to the compound from which it has been prepared. Laurent's views were much opposed, for a time by Dumas himself; but they gradually prevailed, and chemists became familiarised with the notion of the replacement of such a decidedly electro-positive element as hydrogen by an element so decidedly electro-negative as chlorine, resulting in the production of a compound of the same chemical type as the original substance.

About 1839 Dumas sought to distinguish mechanical types from chemical types. Compounds formed one from the other by the replacement of a certain number of equivalents of one radicle by the same number of equivalents of another radicle, and having their radicles similarly combined, and exhibiting similar properties, were said to belong to the same *chemical type*. Compounds were said to belong to the same *mechanical type* when they were composed of equal numbers of equivalents of radicles, but differed essentially in their properties. Dumas at this time regarded the properties of compounds as conditioned more by the arrangement than by the nature of their parts. He compared compounds to planetary systems, the planets being represented by the atoms of the compounds. One atom, he said, might be replaced by another atom, or an atom by a group of atoms, without destroying the system; if the number of replacing atoms, or radicles, were the same as the number of atoms, or radicles, replaced, and the relative arrangement of all the atoms or radicles were not altered, the compounds belonged to the same type. By some such development as this the theory of types came to include the older theory of radicles.

It is evident that the terms used by Dumas and others to express the conceptions of the theory of types are vague and incapable of exact definition. The expression 'equivalent radicles' cannot be defined, nor can an exact and invariable connotation be given to the expressions 'radicles similarly combined' and 'compounds having similar properties.' But if it had been possible to classify chemical substances in an ideally perfect way the theory of types would not have arisen. If there is to be a typical classification the language whereby that classification is expressed must be more or less vague. Whether a compound formed from another by replacing equivalents of one kind by an equal number of equivalents of another kind does or does not belong to the same type as the parent compound can be determined only by a careful study of the properties of both compounds and by a comparison of the compounds one with another. The application of the theory of types was possible only when the properties and the compositions of compounds were exhaustively compared. The theory of types produced much fruit, because it suggested and demanded much inquiry into the fundamental problem of chemistry.

In 1849 Wurtz prepared two compounds which resembled ammonia in their prominent characters. These compounds were found to have the compositions C_2H_5N and C_4H_7N respectively (C = 6). The similarities between the properties of these compounds and ammonia led Wurtz to regard them as *substituted ammonias*, and to express this conception by the formulæ $C_2H_3.NH_2$ and $C_4H_5.NH_2$. One method by which these compounds were prepared consisted in treating methyl and ethyl bromides (C_2H_3Br and C_4H_5Br; C = 6) with ammonia, and then decomposing the products by potash. These reactions suggested the view that the new compounds were derived from methylic and ethylic ethers (C_2H_3O and C_4H_5O, according to the notation then used) by substituting NH_2 for O. Both views agreed in representing the new compounds as $C_2H_3.NH_2$ and $C_4H_5.NH_2$ respectively. But the properties of the compounds resembled those of ammonia; hence the view that Wurtz's compounds were derived from ammonia prevailed. This view was expressed by saying that these compounds belonged to the ammonia type, and by comparing the formula of the typical compound with the formulæ of the compounds formed after that exemplar; thus:

Type:	*Derivatives:*
Ammonia $NH_2.H$.	Methylamine $NH_2.C_2H_3$.
	Ethylamine $NH_2.C_4H_5$.

Very soon after Wurtz's preparation of methylamine and ethylamine Hofmann argued that it should be possible to substitute each of the three atoms of hydrogen in NH_3 by the radicles C_2H_3 and C_4H_5, and so to obtain the compounds $NH(C_2H_3)_2$, $N(C_2H_3)_3$, $NH(C_4H_5)_2$, and $N(C_4H_5)_3$ (C = 6), all which compounds ought to resemble ammonia in their properties. Hofmann fulfilled his own prophecy by preparing di- and tri-methylamine and di- and tri-ethylamine; and, basing his methods on the conception of the ammonia type, he prepared a large series of ammonia-like compounds derived from NH_3, $2NH_3$, &c., by substituting for H various radicles composed of carbon and hydrogen. The *ammonia type* was thus established.

About the year 1850 Williamson studied the relations of ether to alcohol. The formula of ether was then written C_4H_5O (C = 6, O = 8), and that of alcohol $C_4H_6O_2$. Williamson heated potassium alcoholate ($C_4H_5KO_2$) with ethylic iodide (C_4H_5I), expecting to obtain ethylated alcohol ($C_4H_5(C_4H_5)O_2$); but he obtained common ether. Williamson suggested that the formula then accepted for ether should be doubled, and written $(C_4H_5)_2O_2$. He also found that by heating common alcohol with sulphuric acid, and adding methylic alcohol to the hot mixture, an ether-like compound was obtained, the simplest formula of which was C_3H_4O (C = 6, O = 8). Williamson argued that if common ether is C_4H_5O, then the ether of methylic alcohol must be C_2H_3O, and that, in the reaction of sulphuric acid with ethylic and methylic alcohols simultaneously, a mixture of these two ethers might be expected to be produced. To account for the facts he had observed Williamson proposed to double the formulæ of the two ethers and to write them $(C_4H_5)_2O_2$ and $(C_2H_3)_2O_2$; and for the formula of the ether formed by the action of sulphuric acid on the two alcohols simultaneously he proposed the formula $C_4H_5(C_2H_3)O_2$ [$= 2C_3H_4O$]. Williamson compared the relations between the alcohols and ethers with the relations between water, potash, and potassium oxide. These relations are made clearer if the formulæ are expressed in terms of the atomic weights C = 12 and O = 16; thus:

Type:	*Derivatives:*
Water $H.H.O$	Alcohol $C_2H_5.H.O$
	Ether $C_2H_5.C_2H_5.O$
	Potash $K.H.O$
	Potassium oxide $K.K.O$.

Thus arose the *water type*. To this were referred such compounds as acetic acid $C_2H_3O.H.O$, anhydrous acetic acid $C_2H_3O.C_2H_3O.O$, and many others.

Gradually the greater number of compounds, both organic and inorganic, came to be referred to four fundamental types—the *hydrochloric acid type* HCl, the *water type* HHO, the *ammonia type* NHHH, and the *marsh gas type* CHHHH. To these were added so-called *condensed types* and *mixed types*; sulphuric acid, for instance, $SO_2.OH.OH$, was said to belong to the *double water type*.

$$\text{Thus:}\quad \begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}\ \text{gives}\ SO_2\begin{matrix}\left.\begin{matrix}H\\ \end{matrix}\right\}O\\ \left.\begin{matrix} \\H\end{matrix}\right\}O\end{matrix}$$

Oxamic acid $CO.NH_2.CO.OH$ was regarded by Wurtz as derived from the *water-ammonia type*.

$$\text{Thus:}\quad \begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\ \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\end{matrix}\ \text{gives}\ \begin{matrix}\left.\begin{matrix}H\end{matrix}\right\}O\\ \left.\begin{matrix}C_2O_2\\H\\H\end{matrix}\right\}N\end{matrix}$$

The great danger attending the development of the theory of types was, that careful investigations into the reactions of compounds might easily be abandoned in favour of a superficial examination of a compound, followed by a relegation of it to this or that type. The theory began by being very vague and elastic; the adoption of a few definite types rendered it more exact; but the temptation to manipulate formulæ on paper, and to invent condensed types and mixed types, gradually led chemists to see that the theory had done its work, and that it must give place to wider views, which should also be more accurate, regarding the connections between composition and properties.

The conception of types carried with it, from the first, more or less vague notions regarding the arrangements of the atoms in those collocations of atoms that form the reacting units of compounds; at any rate, this conception was bound up with the general conception of atomic arrangement. The reacting units of compounds that showed similar properties were thought of as composed of atoms similarly arranged. Moreover, the type was said to be maintained when an atom, or a group of atoms, in the parent compound was replaced by an equivalent number of atoms, or groups of atoms. These two conceptions, that of equivalency, and that of atomic arrangement, led gradually to the representation of the reacting unit, or molecule, of a compound as a definitely arranged group of atoms held together by actions and reactions between individual atoms; these conceptions led to the wider conception of valency, and to a system of classification based on the notion that each kind of atom is capable of directly combining with a limited, and determinable, number of other atoms. The formula given to chlorosulphonic acid, with the object of connecting the composition with the properties of this compound, and of suggesting relations between this and other compounds, may be taken as an example of the merging of the notion of types into that of valency. This acid was regarded as derived both from water and hydrochloric acid; it was supposed to belong to the mixed *water-hydrochloric acid type*. Hence the formula, $ClSO_3H$, was written thus:—

$$\textit{Type}\ \begin{matrix}HCl\\H\\HO\end{matrix}\qquad \textit{Chlorosulphonic acid}\ \left.\begin{matrix}Cl\\ \\HO\end{matrix}\right\}SO_2$$

The radicle SO_2 was regarded as equivalent to 2H; and it was said that the residues of the two parts of the mixed type, *i.e.* Cl and OH, were bound together by the radicle SO_2. Again, monochlorhydrin, $C_3H_7ClO_2$, was regarded as a derivative of the triple type HHO.HCl.HHO, and was said to be formed by the binding together of the three residues OH, Cl, OH by the radicle C_3H_5 regarded as equivalent to 3H. Thus:—

$$\textit{Type}\ \begin{matrix}HO\\H\\HCl\\H\\HO\end{matrix}\qquad \textit{Monochlorhydrin}\ \left.\begin{matrix}HO\\Cl\\HO\end{matrix}\right\}C_3H_5$$

The moment the conceptions underlying these formulæ, and formulæ like these, were expressed in the language of atoms and molecules, the notion of atomic valencies was gained. The group of atoms SO_2 replaces two atoms of hydrogen, one atom in the molecule HCl and one atom in the molecule HHO; and as the atomic group SO_2 is capable of directly combining with two atoms of hydrogen, or such a number of atoms as is equivalent to two atoms of hydrogen, this group binds together the atom Cl and the atomic group OH, and so the new molecule

$SO_2.OH.Cl$ is produced. This statement contains the fundamental conception of atomic valency; it also contains the conception of types, and that of radicles.

The radicles were compared as regards their equivalency, generally in terms of hydrogen; then the elementary atoms were compared, and arranged in classes, such that all in one class were exchangeable, any number of one kind for the same number of another kind.

When the atoms had been classified in accordance with the number of atoms of hydrogen, or atoms equivalent thereto, with which each was capable of combining, the foundations had been laid of a system of classification which was more accurate than that based on the notion of types, and which at the same time included the essential characters of the typical system. The article CLASSIFICATION in the first edition of this *Dictionary* represents the stage which had then (1863) been reached in the process of fusion of the theories of radicles, types, and valency. The system of classification developed in that article is based (1) on the compositions of compounds interpreted by help of the theory of valency, and (2) on the properties of the compounds interpreted by the help of the theory of types; the study of the properties of a compound is used to determine the radicles that the compound contains, and a knowledge of the valencies of these radicles determines the form of the compound, and, taken along with the reactions of the compound, the type to which it is to be referred.

Although the introduction of the principle of atomic equivalency widened the conception of chemical types, it also tended towards a method of classification which was based on too slight a study of the bodies to be classified. A superficial examination of a compound generally sufficed to bring out some similarities between it and a well-known typical substance; the new compound was at once referred to its type; the form of the type determined the form of the compound under examination; it was then only necessary to manipulate the empirical formula by arranging the elements in groups, or radicles, and to assign to each radicle such a valency as satisfied the general rules that had been deduced from the study of a few typical compounds. The conception of types became very mechanical in its applications, so mechanical indeed that it was in danger of becoming metaphysical. New radicles were easily invented, and their valencies were deduced by *a priori* arguments. Kekulé recalled chemists to the study of properties by insisting that the properties of a compound are conditioned by the properties of the atoms which compose the molecule of the compound; and at a later date Mendeléeff made the same demand by asserting that the properties and the compositions of all compounds are periodic functions of the atomic weights of the elements.

The notion of types plays an important part in the classification of elements and compounds that has arisen from the practical examination of the meaning of Mendeléeff's periodic law. The periodic classification of the elements lays considerable stress on the study of the typical oxides, hydrides, hydroxides, &c., of each group of elements; for instance, the highest salt-forming oxide of Group I. belongs to the type R_2O, that of Group II. to the type R_2O_2, and so on. But the word *type* is not used here with quite the same connotation as was given to it by the theory of types. All that is implied in statements such as those just made is, that the elements of Group I. combine with oxygen in the ratio of two atoms of element to a single atom of oxygen, that these oxides are salt-forming, and that they are characteristic of the elements of this group. The typical oxide-form of each group expresses the composition of that oxide which contains the greatest number of atoms of oxygen relatively to one atom of the group-element, and which oxide reacts either with acids or with alkalis to form corresponding salts. The oxides that belong to the typical oxide-form of a group may be acidic or basic, or some of them may be acidic and some basic; all that is asserted of their properties is that they are salt-forming. The properties of the typical oxide of any individual element are conditioned by the general character of the group, and the general character of the series, wherein the element is placed; by the special character of the element itself; and by the position of the element in the whole periodic system of classification. The term *type* is used in the nomenclature arising from the comparative study of the elements and compounds based on the periodic law with a wider, and at the same time a more exact, meaning than that which was given to it when the notion of types was made the basis of chemical classification. In the older classification the conception of types was the basis of the system; the conception was of necessity vague, and hence it was necessary sometimes to widen, and sometimes to narrow, the application of the conception. The modern system of classification is based on the relative weights of the atoms of the elements, and the conception of types plays a subsidiary part; the form of the typical oxide, or hydroxide, or other compound, is determined, as the compositions of all the compounds are determined, by the relative masses of the atoms of the elements; and the general character of the typical oxide, hydroxide, &c., of each group is determined, as the special character of each compound of each element is determined, also by the relative masses of the atoms of the elements.

The periodic classification of the elements and compounds makes use of the notion of types in another way, by applying the conception to certain elements. The elements placed in series 1 and 2, viz. H, Li, Be, B, C, N, O, and F, exhibit almost the whole range of properties of all the elements. The properties of the succeeding elements may almost be said to be but variations on the theme announced in the change from hydrogen to fluorine. These eight elements are types of all the others. In a somewhat narrower sense the element lithium summarises the range of properties shown in Group I.; beryllium summarises the range of properties shown in Group II.; boron, the properties of Group III.; carbon, the properties of Group IV.; nitrogen, the properties of Group V.; oxygen, the properties of Group VI.; and fluorine, the properties of Group VII. Each of the seven elements is the typical element of its group. Objections have been raised to this use of the term *typical*, on the ground that each of the elements in question differs more from any member of its group than any other two members of the group differ from one another. But if an element is to summarise the properties of some ten or eleven other elements, it must differ considerably from each of these, while at the same time it resembles them all. The question of typical elements, and also that of typical oxide-forms, &c., are discussed in the article Periodic law (vol. iii. p. 808); that article should be consulted.

The older classification by types prepared the way for the wider conception of valency, which took up and utilised the permanent features of the typical arrangements of elements and compounds. The study of valency led chemists to see the importance of examining the properties of the atoms of the elements, and thus made them ready to accept the more elastic, and more exact, generalisation of the periodic law. The theory of types developed into the theory of valency, and the theory of valency has been included in the theory of the periodicity of the connection between the atomic weights of the elements and the compositions and properties of the compounds of the elements. The general conception of types remains; we are still obliged to picture to ourselves a typical acid, a typical base, a typical salt, a typical alcohol, a typical amide, and so on. But this conception is no longer the basis of chemical classification. We have gone deeper down, and laid the foundations of our system on the firmer basis of the atomic weights of the elements. M. M. P. M.

TYPHOTOXINE $C_7H_{17}NO_2$. An alkaloid obtained from pure cultures of the typhogen bacillus (Gautier, *Bl.* [2] 48, 13).

TYROSINE $C_9H_{11}NO_3$ *i.e.* $C_6H_4(OH).CH_2.CH(NH_2).CO_2H$. *p-Oxy-α-amido-phenyl-propionic acid.* Mol. w. 181. [235°]. S.G. 1·456 (Siber, *B.* 17, 2837). S. ·04 at 20°; ·65 at 100°. S. (90 p.c. alcohol) ·0074 in the cold. H.F. 156,400. H.C.v. 1,070,800. H.C.p. 1,071,200 (Berthelot a. André, *Bl.* [3] 4, 227). $[\alpha]_D = -8°$ in HClAq at 16°; $-9°$ in KOHAq at 20° (Mauthner, *M.* 3, 343).

Occurrence.—Occurs abnormally in the liver and urine (*e.g.* in cases of poisoning by phosphorus (Frerichs a. Städeler, *J.* 1855, 729; 1856, 702; Blendermann, *H.* 6, 242), in the cutaneous scales in pellagra (Schmetzer, *Dissert.*, Erlangen, 1862), in cochineal (De la Rue, *A.* 64, 35), in sprouting pumpkin seeds (Schulze a. Barbieri, *J. pr.* [2] 20, 401; 32, 457), in the roots of *Stachys tuberifera* (Planta, *B.* 23, 1699), in dahlia bulbs (Leitgeb, *C. C.* 1888, 1397), in alcoholic extract of woad leaves (Schunck, *C. N.* 37, 223), and in beetroot molasses (Lippmann, *B.* 17, 2835).

Formation.—1. By potash fusion from caseïn (Liebig, *A.* 57, 127; 62, 269), globulin, feathers, hairs (Leyer a. Köller, *A.* 83, 332), and albumen (Nencki, *J. pr.* [2] 17, 97).—2. By the action of boiling dilute H_2SO_4 on ox-horn (Hinterberger, *A.* 71, 72), on fibrin (Städeler, *A.* 111, 12; 116, 57), and on silk (Weyl, *B.* 21, 1529).—3. By putrefaction of yeast (A. Müller, *J. pr.* 57, 162; Béchamp, *C. R.* 74, 115, 184), albumen and gelatin (Jeanneret, *J. pr.* [2] 15, 353).—4. In small quantity by heating conglutin with HClAq (Siegfried, *B.* 24, 419).—5. From *p*-amido-phenyl-alanine and HNO_2 (Friedländer a. Mähly, *B.* 16, 854; Erlenmeyer a. Lipp, *A.* 219, 161).

Properties.—Stellate groups of slender silky needles (from water), insol. alcohol and ether, m. sol. NH_3Aq and KOHAq. Lævorotatory. Its solution is not ppd. by lead acetate or subacetate until NH_3Aq is added. Boiling $Hg(NO_3)_2$ containing HNO_3 turns its solution red, forming a brownish-red pp. (R. Hoffmann, *A.* 87, 123; L. Meyer, *A.* 132, 156). After warming with conc. H_2SO_4, diluting with water, and neutralising with $BaCO_3$, the solution is turned violet by $FeCl_3$. Tyrosine gives off less N_2 when its solutions are decomposed by NaOH and Br in presence of NH_3 than when the NH_3 is absent.

Reactions.—1. At 270° it splits up into CO_2 and $C_6H_4(OH).CH_2.CH_2.NH_2$ (Schmitt a. Nasse, *A.* 133, 211).—2. *Potash-fusion* forms *p*-oxy-benzoic and acetic acids (Barth, *A.* 136, 110; Ost, *J. pr.* [2] 12, 159; Baumann, *H.* 4, 304). 3. $KClO_3$ and HClAq form tetra-chloro-quinone.—4. By *putrefactive fermentation* it is converted into hydro-*p*-coumaric acid, and finally into *p*-cresol and phenol (Weyl, *B.* 12, 1450).—5. HIAq and P at 150° from NH_3 and *p*-oxy-phenyl-propionic acid (Hüfner, *Z.* [2] 4, 391; 6, 113). Conc. HClAq and HBrAq at 240° have no action.—6. Conc. H_2SO_4 (4 pts.) at 100° forms crystalline $C_9H_{10}(SO_3H)NO_3$, v. sl. sol. cold water, which also occurs in a hydrated amorphous form (containing 2aq). H_2A'' yields $(NH_4)HA''$aq, $Ba(HA'')_2$ 4aq, and $Ca(HA'')_2$ 5aq (Städeler, *A.* 116, 57). $BaC_9H_9NO_3$ 3aq is obtained from the product of the action of H_2SO_4 (10 pts.) on tyrosine (1 pt.).—7. MeOH, potash, and MeI yield crystalline $C_{12}H_{18}NIO_3K$, sol. water, decomposed by warm KOHAq into NMe_3 and the methyl derivative of *p*-coumaric acid (Körner a. Menozzi, *G.* 11, 550).—8. *Potassium cyanate* added to boiling water containing tyrosine forms tyrosine-hydantoic acid $C_6H_4(OH).CH_2.CH(NH.CO.NH_2).CO_2H$ crystallising from water in needles, insol. ether (Jaffé, *H.* 7, 310). This body begins to melt at 155°, being decomposed above 170°. It gives a red colour and pp. on warming with Millon's reagent. It forms KA'aq, crystallising from alcohol-benzene.—9. *Tyrosine* administered to a dog appears in the urine as tyrosine-hydantoïn $C_6H_4(OH).CH_2.CH{<}\begin{smallmatrix}NH.CO\\ CO.NH\end{smallmatrix}$ [275°–280°], which crystallises from water in needles, and is decomposed by heating in sealed tubes with baryta-water into CO_2, ammonia and tyrosine. Other products found in the urine of a rabbit after a dose of tyrosine are hydro-*p*-coumaric and *p*-oxy-phenyl-acetic acids and phenols (Blendermann, *H.* 6, 251).

Salts. — $Na_2C_9H_9NO_3$. — $CaC_9H_9NO_3$. — $BaC_9H_9NO_3$ 2aq. Prisms, more sol. cold than hot water.—$Cu(C_9H_{10}NO_3)_2$. S. ·98 in the cold; ·4 at 100°. Got by adding $Cu(OH)_2$ to a boiling solution of tyrosine (Hofmeister, *A.* 189, 6). Insol. alcohol. Deposits black cupric oxide on boiling with water.—$C_9H_{11}NO_3(HgO)_2$ 2aq.—$C_9H_{11}NO_3(HgO)_2$ aq. — $C_9H_{11}NO_3(HgO)_3$ aq (Vintschgau, *J.* 1869, 985).—$Ag_2C_9H_9NO_3$ aq: amorphous pp. — $AgC_9H_{10}NO_3\frac{1}{2}$aq: crystalline powder. — B'HCl 2aq: needles, decomposed by water.—$B'_2H_2PtCl_6$ (Gintl, *Z.* [2] 5, 704).—$B'H_2SO_4$. Slender needles, not coloured by $FeCl_3$.

Di-bromo-tyrosine $C_9H_9Br_2NO_3$ 2aq. S. ·46 at 16°; 4 at 100°. Formed from dry tyrosine and Br vapour (Gorup-Besanez, *A.* 125, 281). Needles or tables (from water), sl. sol. alcohol. $Ag_2C_9H_7Br_2NO_3$ 2aq. — B'HCl 1½aq. — B'HBr. — $B'_2H_2SO_4$. Prisms, sol. water and alcohol.

Nitro-tyrosine $C_9H_{10}N_2O_5$ *i.e.* $C_9H_{10}(NO_2)NO_3$. Formed from tyrosine (1 pt.), water (4 pts.), and nitric acid (4 pts. of S.G. 1·3) in the cold (Strecker, *A.* 73, 70; Städeler, *A.* 116, 77). Pale-yellow needles, sl. sol. cold water. — Salts: $Ba(C_9H_9N_2O_5)_2$ (dried at 100°). Blood-red amorphous mass.—$Ag_2C_9H_8N_2O_5$ aq: orange pp. changing to a red powder.—B'HCl ½aq. Tufts of lemon-yellow needles.—$B'HNO_3$. S. 20. Lemon-yellow needles.—$B'_2H_2SO_4$. Yellow needles or granules.

Di-nitro-tyrosine $C_9H_9(NO_2)_2NO_3$. [115°]. Formed by warming nitro-tyrosine with dilute HNO_3. Golden plates (from water).—Salts: $CaC_9H_7N_3O_7$ 3aq. Golden six-sided tables.—$BaC_9H_7N_3O_7$ 2aq. Ruby-red prisms with yellow reflex, exploding when heated.

Reference.—AMIDO-TYROSINE.

TYROTOXICON. A poisonous substance formed in milk, containing the butyric acid ferment, which has stood for some days. Occurs also sometimes in cheese (Vaughan, *Ph.* [3] 18, 470; *H.* 10, 146). When its alcoholic solution is mixed with $PtCl_4$ and evaporated violent explosion takes place.

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ULEXINE $C_{11}H_{14}N_2O$. [151°]. An alkaloid in the seeds of common furze (*Ulex europeus*) (Gerrard a. Symons, *Ph.* [3] 17, 101, 229; 19, 1029; 20, 978, 1017). Deliquescent crystals, v. sol. chloroform, insol. ether. Poison, paralysing respiration (Bradford, *J. Physiol.* 8, 79). Possibly identical with cytisine.—B'HCl. Deliquescent.—$B'H_2PtCl_6$.—$B'2HAuCl_4$.

ULTRAMARINE. The blue-coloured material contained in *lapis-lazuli*. Until 1828 ultramarine was obtained by powdering and washing *lapis-lazuli*; but since that year it has been manufactured by heating to bright redness mixtures of Al silicate (*china clay*), Na_2CO_3 (*carbonated soda ash*), S, and charcoal, and washing, powdering, drying, and sifting the product. (For details of the manufacture v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 891.) The constituent elements of ultramarine are Al, Na, Si, S, and O. Treated with HClAq, ultramarine gives off H_2S; the solution contains NaCl, $AlCl_3$, and SiO_2, and the residue consists of SiO_2, S, and some Al_2O_3; these reactions point to ultramarine being a compound of silicates and polysulphides. Much work has been done on the constitution of ultramarine, but the results obtained have not finally settled the question. From analyses and investigations made in 1891, Brögger a. Bäckström (*W. J.* 1891. 454) conclude that the composition of the essential colouring compound in natural ultramarine is represented by the formula $Na_4[Al(S_3Na)]Al_2(SiO_4)_3$. They also conclude that artificial ultramarines may be expressed by the following formulæ:—

$$Na_3Al_3Si_3O_{12} = N$$
$$Na_2Al_2Si_4O_{12} = A$$
$$Na_4[Al(SNa)]Al_2Si_3O_{12} = U(S_1)$$
$$Na_4[Al(S_2Na)]Al_2Si_3O_{12} = U(S_2)$$
$$Na_4[Al(S_3Na)]Al_2Si_3O_{12} = U(S_3).$$

The main constituents of the different varieties of blue ultramarine are N, A, and $U(S_3)$; of green ultramarine $U(S_2)$ and N; and $U(S_1)$ is the main constituent of white ultramarine, according to B. a. B. Formulæ more or less approaching those given above have been assigned to ultramarine by other observers; thus Silber in 1880 represented blue ultramarine as $Si_6Al_4Na_6S_4O_{20}$ (*B.* 13, 1854). On the other hand, some chemists have regarded the essential constituent of ultramarine as a sodium thiosilicate; for instance, Rickmann (*B.* 11, 2013 [1878]) gives $S.Si(ONa)_2$ as the composition of 'ideal ultramarine blue'; and he regards artificial ultramarine as a mixture, the only essential part of which is sodium thiosilicate. Clarke (*Am.* 10, 126) suggested a formula for ultramarine which should indicate the relations of this body to various natural silicates; in this respect Clarke's formula is important (*v.* this vol. p. 451).

White ultramarine is obtained by completely cutting off air during the roasting of the materials; it is changed to blue by heating in O, SO_2, or Cl (*v.* Ritter, *W. J.* 1160. 226; *cf.* Philipp, *B.* 9, 1109; 10, 1227; Böttinger, *A.* 182, 311; R. Hoffmann, *A.* 194, 1).

Red ultramarine was observed by Scheffer, in 1873, to be formed in preparing the ordinary substance in a muffle furnace very strongly heated and freely exposed to the air; it contains less Na and more Al than the blue variety (*B.* 6, 1450; *v.* also Büchner, *D. P. J.* 231, 446; Zettner, *B.* 8, 259, 353).

Yellow ultramarine is formed by heating the red variety in the air a little above 360°, for a short time (R. Hoffmann, *A.* 194, 1). According to Büchner (*B.* 7, 990), both the yellow and red forms are produced by heating blue ultramarine to 300°-400° in O or SO_2; the colour changes to red and then to yellow. If Cl is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green, and then reddish-yellow (Zettner, *B.* 8, 259, 353); by heating the product with alkali, all Cl is removed and a *violet ultramarine* is produced. This variety goes to the red form when heated in vapour of HNO_3 or HCl at 130°-150° (Zettner, *l.c.*).

Green ultramarine is formed when a little Sn is used in the roasting process; it is converted into the blue substance by roasting with S. This form seems to be intermediate between white and blue ultramarine. According to Philipp (*B.* 9, 1109), S is not taken up in the change from green to blue; by heating the green form in sealed tubes with water, at 100°, he obtained the blue, the water removing a very small quantity of sodium compounds.

Substituted ultramarines. Blue to green, and reddish-grey, substances have been formed by heating ultramarine with $AgNO_3Aq$, and by treating the product of this reaction with KI, LiI, BaI_2, ZnI_2, &c. These substances, known as *silver ultramarine*, *potassium ultramarine*, &c., probably contain Ag, K, Li, Ba, &c., in place of Na (*v.* Unger, *D. P. J.* 212, 224, 301; Philipp, *B.* 10, 1227; Heumann, *A.* 199, 253; 201, 262; Forcrand a. Ballin, *Bl.* [2] 30, 112). By heating silver ultramarine with various alcoholic iodides, Forcrand (*C. R.* 88, 30) obtained ultramarines containing alcoholic radicles, such as *ethyl ultramarine*, *amyl ultramarine*, &c. *Selenion* and *tellurium ultramarines* have also been produced, wherein S is substituted by Se or Te (*v.* Leykauf, *W. J.* 1876. 555; Guimet, *A. Ch.* [5] 13, 102; Plicque, *Bl.* [2] 28, 518; Morel, *Bl.* [2] 28, 522). Various substituted ultramarines have been examined by Wunder (*Chem. Zeit.* 1890. 1119). M. M. P. M.

ULMIC ACID. C. 66·4–63·9; H. 4·6–4·5; O. 29–31·5. $C_{18}H_{14}O_8$ or $C_{18}H_{16}O_7$. H.C. 1983, 200. H.F. 266,200. Formed by action of HCl on cane sugar. Is an anhydride or mixture of anhydrides $C_{18}H_{14}O_8$ (humic anhydride) (Berthelot a. André, *Bl.* [3] 7, 441, 451). Turns yellow in air and sunlight, giving off CO_2. The same thing happens with the humic acid extracted from vegetable mould by KOHAq and ppd. by HCl. Dilute alkalis cause it to swell up, forming insoluble *salts* and a small quantity of a soluble basic salt. When conc. KOHAq is used a salt is formed, from which two-thirds of the alkali can be removed by washing, leaving $KC_{18}H_{15}O_7aq$, and is reconverted into the acid $C_{18}H_{16}O_7$ by HClAq. Ammonia converts humic anhydride (ulmic acid) into an amido- acid $C_{54}H_{47}NO_{18}NH_3$, whence HCl sets free $C_{54}H_{47}NO_{19}$.

Salts.—$KC_{18}H_{15}O_7$ aq. Hard, black, insoluble mass, yielding a brown powder. The 'ulmin' of Malaguti. Formed by shaking the anhydride with KOH (1 pt.) and water (120 pts.). —$NaC_{18}H_{15}O_7$ aq.—$Na_3C_{18}H_{13}O_7$ *x*aq.

References.—Humic, Saccharumic, and Sacculmic acids.

UMBELLIC ACID $C_9H_8O_4$ *i.e.* [4:2:1] $C_6H_3(OH)_2.CH{:}CH.CO_2H$. Mol. w. 132. Di-oxy-cinnamic acid. Formed by warming its lactone, umbelliferone with KOHAq (Tiemann a. Reimer, *B.* 12, 994; Posen, *B.* 14, 2745). Yellowish powder. Turns brown at 240°, and decomposes below 260°. Sol. alcohol and warm water, insol. ether. Resinified by boiling its aqueous solution. Reduces warm ammoniacal $AgNO_3$, forming a mirror. $FeCl_3$ gives a brown pp.

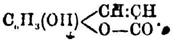
Methyl derivative $C_{10}H_{10}O_4$. [180°–185°]. Got by heating herniarin with alcoholic potash at 160° (Barth a. Herzig, *M.* 10, 165). Needles (from water).

(α)-*Di-methyl derivative* $C_6H_3(OMe)_2.CH{:}CH.CO_2H$. [138°]. Formed by the action of MeI and KOH in MeOH on the methyl derivative of umbelliferone in the cold (W. Will, *B.* 16, 2115; 19, 1777). Needles, v. sol. alcohol and ether. Converted into the (β)-isomeride by boiling alone or with HClAq. Both isomerides are reduced by sodium-amalgam to the same $C_6H_3(OMe)_2.CH_2.CH_2.CO_2H$, and are oxidised by $KMnO_4$ to the same $C_6H_3(OMe)_2.CO_2H$. —CaA'_2 2aq: crystals.—BaA'_2 2aq: needles.

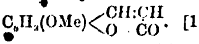
(β)-*Di-methyl derivative.* [184°]. Formed as above, and also by saponification of its methyl ether $C_6H_3(OMe)_2.CH{:}CH.CO_2Me$ [87°], which is got by evaporating methyl-umbelliferone (1 mol.) with NaOH (2 mols.) nearly to dryness, and digesting the residue with MeI and MeOH (Tiemann a. Will, *B.* 15, 2079). Needles, sol. alcohol and ether. Sl. sol. cold water.

(α)-*Di-ethyl derivative* [4:2:1] $C_6H_3(OEt)_2.C_2H_2.CO_2H$. *Di-ethyl-umbellic acid.* [107°]. Formed by mixing ethyl-umbelliferone (5 g.) with EtI (10 g.) and a solution of KOH (4 g.) in alcohol (Will a. Beck, *B.* 19, 1780). Small plates, v. sol. alcohol, ether, and benzene.

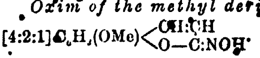
(β)-*Di-ethyl derivative.* [200°]. Formed by boiling the (α)-isomeride for some time, and also by heating ethyl-umbelliferone (10 g.) with EtI (9 g.) and a solution of Na (2⅓ g.) in alcohol for six hours at 150°. Crystals, m. sol. alcohol, sl. sol. water.

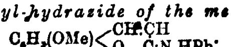
UMBELLIFERONE $C_9H_6O_3$ *i.e.*  $C_6H_3(OH)<\begin{matrix}CH{:}CH\\ O{-}CO\end{matrix}$. Mol. w. 162. [224°]. S. 1 at 100°. Formed by the dry distillation of various resins, chiefly those derived from umbelliferous plants, *e.g.* galbanum, sagapenum, and asafœtida (Sommer a. Zwenger, *A.* 115, 15; Mössmer, *A.* 119, 260; Hlasiwetz a. Grabowski, *A.* 139, 100; Hirschsohn, *C. C.* 1877, 182). Formed by heating malic acid (1 mol.) with resorcin (1 mol.) and H_2SO_4 (Pechmann, *B.* 17, 932). Prepared by distilling the alcoholic extract of gum galbanum (Tiemann a. Reimer, *B.* 12, 993). Needles, sl. sol. cold water and ether, v. sol. alcohol. Dissolves in acids, without change. Alkalis above 50° form umbellic acid. Its solution in dilute alkalis shows blue fluorescence. H_2SO_4 forms a solution with green fluorescence. Reduces $AgNO_3$ on boiling. Yields (4,2,1)-di-oxy-benzoic acid on oxidation (Tiemann a. Parrisius, *B.* 13, 2354). Fuming HNO_3 and H_2SO_4 form $C_9H_4(NO_2)_2O_3$ [216°] (Posen, *B.* 14, 2744).

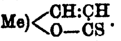
Acetyl derivative $C_{11}H_8O_4$. [140°]. Formed by acetylation, and also by boiling di-oxy-benzoic aldehyde with Ac_2O and NaOAc (Tiemann, *B.* 10, 2216; 12, 995). Needles, sl. sol. water.

Methyl derivative $C_{10}H_8O_3$ *i.e.*  $C_6H_3(OMe)<\begin{matrix}CH{:}CH\\ O{-}CO\end{matrix}$. [114°]. Formed by heating umbelliferone with KOMe and MeI (T. a. R.). Leaflets, nearly insol. water. Appears to be identical with herniarin [118°], which is extracted by alcohol from *Herniaria hirsuta* (Barth a. Herzig, *M.* 10, 161).

Ethyl derivative $C_{11}H_{10}O_3$. [88°]. Plates, v. sol. alcohol (Will a. Beck, *B.* 19, 1779).

Oxim of the methyl derivative  $[4{:}2{:}1]\,C_6H_3(OMe)<\begin{matrix}CH{:}CH\\ O{-}C{:}NOH\end{matrix}$. [138°]. Formed from the methyl derivative of thio-umbelliferone and hydroxylamine (Aldringen, *B.* 24, 3465). Needles, v. sol. hot water and alcohol. $FeCl_3$ colours its solution brownish-red.

Phenyl-hydrazide of the methyl derivative  $C_6H_3(OMe)<\begin{matrix}CH{:}CH\\ O{-}C{:}N_2HPh\end{matrix}$ [115°]. Yellow needles, giving a blue colour with H_2SO_4.

Thio-umbelliferone. *Methyl derivative* $C_6H_3(OMe)$$<\begin{matrix}CH:CH\\O-CS\end{matrix}$. [114°]. Formed by heating the methyl derivative of umbelliferone with P_2S_5 (Aldringen, *B.* 24, 3465). Needles, sol. alcohol, v. sl. sol. water.

References.—BROMO- and METHYL- UMBELLIFERONE.

UMBELLOL $C_8H_{12}O$. (216°). V.D. 4·29. Occurs in the volatile oil of the Californian laurel (Stillmann, *B.* 13, 679). Oil, sol. H_2SO_4 with red colour, becoming black. Attacked by Na.

UMBELLULIC ACID *v.* HENDECOÏC ACID.

UNDECANE *v.* HENDECANE.

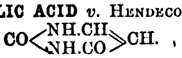
UNDECOÏC ACID *v.* HENDECOÏC ACID.

UNDECOLIC ACID *v.* HENDECINOIC ACID.

UNDECYLENE *v.* HENDECYLENE.

UNDECYLENIC ACID *v.* HENDECENOIC ACID.

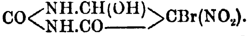
UNDECYLIC ACID *v.* HENDECOÏC ACID.

URACIL $CO<\begin{matrix}NH.CH\\NH.CO\end{matrix}>CH$. *Di-oxy-pyrimidine.* Derivatives of this compound are formed by the action of acetoacetic ether on urea, thio-urea, and guanidine (Behrend, *A.* 229, 1; 240, 6; List, *A.* 236, 1; Jäger, *A.* 262, 365; Warmington, *J. pr.* [2] 47, 201).

Amido-uracil $C_4H_5N_3O_2$. Formed, together with oxyuracil $C_4H_4N_2O_3$, by reducing nitro-uracil (Behrend), and by boiling di-bromo-pyruvuramide with baryta-water (Fischer, *A.* 239, 193). Yellow needles, sol. water. Converted by cyanic acid into oxyxanthine $C_5H_6N_4O_3$, which crystallises in needles, sl. sol. water, sol. alkalis, gives with Cl the murexide reaction, may be oxidised to alloxantin, and gives some alloxan with bromine-water.

Acetyl derivative $C_7H_9N_3O_3\frac{1}{2}aq$. Prisms.

Nitro-uracil *v.* NITRO-DI-OXY-PYRIMIDINE.

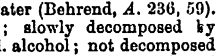
Bromo-nitro-oxy-uracil. *Dihydride* $C_4H_4N_3O_5Br$ *i.e.* $CO<\begin{matrix}NH.CH(OH)\\NH.CO\text{———}\end{matrix}>CBr(NO_2)$. Formed by adding Br to nitro-uracil suspended in water (Behrend, *A.* 240, 11). Crystalline mass, sl. sol. cold water and alcohol. Boiling with water produces brominated nitro-methanes and a crystalline compound $C_5H_7N_5O_5$, formed by the action of urea upon nitro-uracil. Tin and HCl reduce it to amido-uracil.

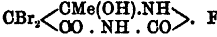
Methyl-uracil *v.* DI-OXY-METHYL-PYRIMIDINE.

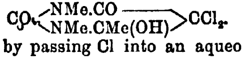
Nitro-methyl-uracil $C_5H_5N_3O_4$. Prepared by nitrating methyl-uracil with HNO_3 (S.G. 1·5) mixed with an equal volume of H_2SO_4 (S.G. 1·84) (Behrend, *A.* 240, 3). Prisms or tables (from water), sl. sol. hot alcohol.

Isomeride *v.* NITRO-DI-OXY-METHYL-PYRIMIDINE.

Nitro-di-methyl-uracil *v.* NITRO-DI-OXY-DI-METHYL-PYRIMIDINE.

Di-chloro-oxy-methyl-uracil. *Dihydride* $C_5H_6Cl_2N_2O_3$ *i.e.* $CCl_2<\begin{matrix}CMe(OH).NH\\CO\text{———}NH\end{matrix}>CO$. Formed by the action of chlorine on methyl-uracil suspended in water (Behrend, *A.* 236, 59). Tables (from water); slowly decomposed by boiling water. M. sol. alcohol; not decomposed by boiling alcohol. M. sol. ether. A solution of $SnCl_2$ in HClAq at 100° reduces it to chloro-methyl-uracil $C_5H_5ClN_2O$, which crystallises from water in needles. Fuming HNO_3 gives di-chloro-barbituric acid.

Di-bromo-oxy-methyl-uracil $C_5H_6N_2Br_2O_3$ *i.e.* $CBr_2<\begin{matrix}CMe(OH).NH\\CO\,.\,NH\,.\,CO\end{matrix}>$. From methyl-uracil (or bromo-methyl-uracil), and bromine-water (Behrend, *A.* 229, 18; 236, 57). Cubes (from hot water). Boiling alcohol converts it into bromo-methyl-uracil $C_5H_5N_2BrO_2$. Fuming HNO_3 forms di-bromo-barbituric acid.

Di-chloro-oxy-tri-methyl-uracil. *Dihydride* $CO<\begin{matrix}NMe.CO\text{———}\\NMe.CMe(OH)\end{matrix}>CCl_2$. [144°]. Formed by passing Cl into an aqueous solution of tri-methyl-uracil (Hagen, *A.* 244, 14). Crystals, sl. sol. hot water. Reduced by boiling with $SnCl_2$ to chloro-tri-methyl-uracil, which crystallises in prisms, m. sol. hot water.

Nitro-ethyl-uracil *v.* NITRO-DI-OXY-ETHYL-PYRIMIDINE.

Methyl-ethyl-uracil *v.* DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Nitro-methyl-ethyl-uracil *v.* NITRO-DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Amido-uracil carboxylic acid *v.* DI-OXY-AMIDO-PYRIMIDINE CARBOXYLIC ACID.

References.—THIO-METHYL-URACIL and UR-AMIDO-CROTONIC ACID.

URAMIDO - ACETIC ACID *v.* HYDANTOÏC ACID.

***p*-URAMIDO-BENZENE SULPHONIC ACID** $NH_2.CO.NH.C_6H_4.SO_3H$. Formed by evaporating a solution of *p*-amido-benzene sulphonic acid and potassium cyanate (Pellizzari, *A.* 248, 156), and also by heating dry *p*-amido-benzene sulphonic acid (1 mol.) with urea ($1\frac{1}{2}$ mols.) (Friedel, *C. R.* 112, 868). Pearly plates (from dilute alcohol), v. sol. water.—$BaA'_2 3aq$; monoclinic prisms, sol. Aq.

***o*-URAMIDO-BENZOIC ACID** $C_8H_8N_2O_3$ *i.e.* $NH_2.CO.NH.C_6H_4.CO_2H$. Formed from potassium cyanate and the hydrochloride of *o*-amido-benzoic acid (Griess, *J. pr.* [2] 5, 371; *B.* 11, 1730). HNO_3 yields only one di-nitro- derivative.

***m*-Uramido-benzoic acid** $C_8H_8N_2O_3$. S. 1 at 100°. S. (96 p.c. alcohol) ·72 at 16°. S. (ether) ·127 at 16°. Occurs in urine after a dose of *m*-amido-benzoic acid (E. Salkowski, *H.* 7, 113).

Formation.—1. By adding potassium cyanate to a boiling saturated solution of the sulphate of *m*-amido-benzoic acid (Menschutkin, *A.* 153, 84; *Z.* [2] 4, 275).—2. By fusing *m*-amido-benzoic acid with urea (Griess, *Z.* [2] 5, 312; *B.* 2, 47). 3. By boiling *m*-cyanamido-benzoic acid with HClAq (Traube, *B.* 15, 2122).

Properties.—Small prisms (containing aq), v. sl. sol. hot water. At 200° it yields $CO(NH.C_6H_4.CO_2H)_2$. On distilling *m*-uramido-benzoic acid (4 pts.) with P_2O_5 (1 pt.) *m*-amido-benzoic nitrile [54°] is formed (Griess, *B.* 8, 224). Boiling KOHAq splits it up into *m*-amido-benzoic acid, CO_2, and NH_3.

Salts.— $NH_4A'aq$. — KA'. — $CaA'_2 4aq$. — $PbA'_2 2aq$.—AgA': curdy pp., becoming crystalline.

Ethyl ether EtA'. [176°]. Formed from *m*-amido-benzoic ether and KCyO (Griess, *J. pr.* [2] 4, 293). Plates, sl. sol. hot water.

Amide $C_8H_9N_3O_2$. Formed from *m*-amido-benzamide and KCNO (Menschutkin). Scales (from water), decomposed by fusion, sl. sol. alcohol.

***p*-Uramido-benzoic acid** $C_8H_8N_2O_3$. Formed in like manner (Griess, *J. pr.* [2] 5, 369). Plates, almost insol. cold water, v. sl. sol. hot water, m. sol. hot alcohol. Yields some *p*-amido-benzonitrile [86°] on distilling with P_2O_5.—BaA'_2. Plates, v. e. sol. cold water.

Di-uramido-benzoic acid $C_9H_{10}N_4O_4$ *i.e.* $(NH_2.CO.NH)_2C_6H_3.CO_2H$. Formed by fusing di-amido-benzoic acid with urea (Griess, *B.* 2, 47). Small granules, v. sl. sol. hot water.—BaA'_2 (dried at 130°). Nodules, v. sol. hot water.

References.—AMIDO-, NITRO-, and OXY- URAMIDO-BENZOIC ACIDS.

URAMIDO-BENZOYL *v.* OXY-QUINAZOLINE.

***p*-URAMIDO-BENZYL-UREA** $C_9H_{12}N_4O_2$ *i.e.* $NH_2.CO.NH.C_6H_4.CH_2.NH.CO.NH_2$. [197°]. *p-ω-Di-uramido-toluene.* Formed by heating together *p*-amido-benzyl-amine hydrochloride (1 mol.), and KCNO (2 mols.) in aqueous solution (Amsel a. Hofmann, *B.* 19, 1289). Small needles. Sol. hot water.

URAMIDO-ISOBUTYRIC ACID *v.* ACETON-URAMIC ACID.

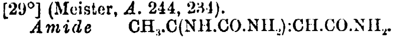
***o*-URAMIDO-CINNAMIC ACID** $C_{10}H_{10}N_2O_3$ *i.e.* $NH_2.CO.NH.C_6H_4.CH:CH.CO_2H$. Formed from *o*-amido-cinnamic acid and aqueous KCNO (Rothschild, *B.* 23, 3341). Sol. NH_3Aq and hot HClAq.

(β)-URAMIDO-CROTONIC ACID $C_5H_8N_2O_3$ *i.e.* $CH_3.C(NH.CO.NH_2):CH.CO_2H$. The ether is converted by NaOHAq into the salt NaA′, which crystallises in needles, v. sol. water; but on adding acids to this salt di-oxy-methyl-pyrimidine $C_5H_6N_2O_2$ is produced. Methyl-uracil is reconverted by NaOHAq into sodium uramido-crotonate (Behrend, *A.* 229, 5).

Ethyl ether EtA′. [166°]. Formed from acetoacetic ether and urea. Needles, v. sol. ether, m. sol. alcohol. Decomposed by warm HClAq into urea, acetone, CO_2, and alcohol. Alcohol forms $CH_3.C(NH.CO_2Et):CH.CO_2Et$ [29°] (Meister, *A.* 244, 234).

Amide $CH_3.C(NH.CO.NH_2):CH.CO.NH_2$. [131°]. Crystals (containing EtOH) (Meister).

Amido-uramido-crotonic acid. *Lactam.*


$C_5H_3(NH_2)N_2O_2$ *i.e.* $CO<\begin{matrix}NH.CMe\\NH.CO\end{matrix}>C.NH_2$ (?).

Amido-methyl-uracil. Methyl-uracil (*v.* DI-OXY-METHYL-PYRIMIDINE) is converted by Br in CS_2 into crystalline bromo-methyl-uracil $C_5H_5BrN_2O_2$, whence conc. NH_3Aq at 150° forms amido-methyl-uracil (Behrend, *A.* 231, 250). Satiny plates (from water), melting near 250°. Sol. alcohol. The hydrochloride is converted by potassium cyanate into oxy-methyl-xanthine $C_6H_8N_4O_3$ 2aq, crystallising from water in prisms.—B′HCl aq. Monoclinic crystals; $a:b:c = 1{\cdot}629:1:2{\cdot}345$; $\beta = 52°\ 57'$.—$B'_2H_2PtCl_6$ 2aq: needles, v. sol. water.

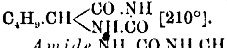
Acetyl derivative $C_5H_3(NHAc)N_2O_2\frac{1}{2}aq$. Formed from oxy-methyl-xanthine and Ac_2O at 170°. Thick trimetric prisms (from water). Decomposes near 210° without melting. Sol. alkalis and reppd. by acids.

URAMIDO-ETHANE SULPHONIC ACID $NH_2.CO.NH.CH_2.CH_2.SO_3H$. *Taurocarbamic acid.* Occurs in small quantity in urine after a dose of taurine (E. Salkowski, *B.* 6, 744, 1191). Formed by evaporating a solution of taurine with KCyO. Formed also by the action of bromine-water on ethylene-ψ-thio-urea (Gabriel, *B.* 22, 1142). Dimetric plates, v. sol. water, sl. sol. alcohol, insol. ether. Decomposed by baryta-water at 140° into CO_2, taurine, and NH_3.—BaA'_2: tables (from alcohol).—AgA′. Radiating tufts of crystals.

URAMIDO-HEXOIC ACID $C_7H_{14}N_2O_3$ *i.e.* $NH_2.CO.NH.CH(C_4H_9).CO_2H$. [200°]. Formed by boiling isobutyl-hydantoïn with baryta-water (Pinner a. Spilker, *B.* 22, 696). Needles, v. sol. alcohol and hot water.—BaA'_2: nodular groups of prisms.

Ethyl ether EtA′. [135°]. Formed by heating isobutyl-hydantoïn with KOH and EtBr. Needles, v. sol. alcohol and hot water.

Nitrile. $NH_2.CO.NH.CH(C_4H_9).CN$. Formed by heating the cyanhydrin of isovaleric aldehyde with urea (Pinner a. Lifschütz, *B.* 20, 2351). Oil, sol. alcohol and ether. On warming with HClAq it yields isobutyl-hydantoïn


$C_4H_9.CH<\begin{matrix}CO.NH\\NH.CO\end{matrix}$ [210°].

Amide $NH_2.CO.NH.CH(C_4H_9).CO.NH_2$. [170°]. Formed from the nitrile (1 pt.) and conc. H_2SO_4 (3 pts.) in the cold. Crystals, v. sol. water and alcohol.

URAMIDO-HIPPURIC ACID $C_{10}H_{11}N_3O_4$. Formed by fusing *m*-amido-hippuric acid with urea (Griess, *J. pr.* [2] 1, 235). Nodules, v. e. sol. hot water. Decomposed by boiling conc. HClAq into glycocoll and *m*-uramido-benzoic acid.—AgA′. Crystalline pp.

URAMIDO-NITRO-AMIDO-PHENOL $C_7H_8N_4O_4$ *i.e.* $C_6H_2(NO_2)(NH_2)(NH.CO.NH_2).OH$. Formed by reducing di-nitro-oxy-phenyl-urea with ammonium sulphide (Griess, *J. pr.* [2] 5, 1). Reddish-brown needles, sl. sol. hot water and alcohol.—B′HCl: white scales.—BaA'_2 $3\frac{1}{2}aq$: steel-blue needles, v. sol. hot. water. Boiling HClAq converts it into amidocarboxamidonitrophenol $C_7H_5N_3O_4$, which yields BaA'_2 *x*aq and B′HCl aq, and is reduced by tin and HClAq to diamidocarboxamidophenol $C_7H_7N_3O_2$, which yields B′HCl, crystallising in plates.

URAMIDO-DI-NITRO-PHENOL *v.* DI-NITRO-OXY-PHENYL-UREA.

***p*-URAMIDO-PHENYL-ACETIC ACID** $NH_2.CO.NH.C_6H_4.CH_2.CO_2H$. [174°]. Formed by boiling *p*-cyanamido-phenyl-acetic acid with HClAq (Traube, *B.* 15, 2122). Small crystals (containing $1\frac{1}{2}aq$), sol. water, alcohol, and ether.

α-Uramido-phenyl-acetic acid. *Ethyl ether* $NH_2.CO.NH.CHPh.CO_2Et$. [139°]. Formed by the action of aqueous KCyO on the hydrochloride of α-amido-phenyl-acetic ether (Kossel, *B.* 21, 4150). V. sol. alcohol and hot water.

Nitrile $NH_2.CO.NH.CHPh.CN$. [170°] Formed by heating the cyanhydrin of benzoic aldehyde with urea (Pinner a. Lifschütz, *B.* 20, 2351). Converted by acids into $C_9H_8N_2O_2$ [182°], crystallising in scales, v. sol. alcohol and hot water.

α-URAMIDO-PHENYL-CROTONIC ACID. *Nitrile* $CHPh:CH.CH(NH.CO.NH_2).CN$. [160°]. Formed by heating urea with the cyanhydrin of cinnamic aldehyde (Pinner a. Lifschütz, *B.* 20, 2351). Needles, v. sol. hot alcohol. Boiling HClAq converts it into di-oxy-styryl-pyrazole (*q.v.*).

Amide $CHPh:CH.CH(NH.CO.NH_2).CO.NH_2$. Formed from the nitrile and cold conc. H_2SO_4 (Pinner a. Spilker, *B.* 22, 692). Microcrystalline powder, decomposing at 210°–220° with evolution of NH_3. Sol. alcohol, sl. sol. hot water.

a-URAMIDO-PROPIONIC ACID $C_4H_8N_2O_3$ *i.e.* $CH_3.CH(NH.CO.NH_2).CO_2H$. *Lacturamic acid.* [155°]. Formed by evaporating a solution of alanine sulphate mixed with KCyO (Urech, *A.* 165, 99). Formed also by boiling lactyl-urea with baryta-water (Heintz, *A.* 169, 128). Prisms, sl. sol. cold water and alcohol, insol. ether.—BaA'_2aq (dried at 100°).—$PbA'2aq$.—AgA': needles, m. sol. water.

Nitrile $CH_3.CH(NH.CO.NH_2).CO_2H$. [106°] (Franchimont a. Klobbie, *R. T. C.* 7, 16).

Amide $CH_3.CH(NH.CO.NH_2).CO.NH_2$. [196°]. Small needles (from alcohol), sol. water.

URAMIDO-SUCCINIC ACID. Amic acid $NH_2.CO.CH_2.CH(NH.CO.NH_2).CO_2H$. [138°] (G.); [157°] (P.). *Succinuramide. Amido-succinuric acid.* S. 5·4 at 23°. Formed by evaporating the mixed solutions of asparagine KCyO (Guareschi, *G.* 7, 404; *B.* 10, 1747). Dextro-asparagine gives a lævo- compound, while lævo-asparagine gives a dextro- compound (Piutti, *B.* 19, 1693). Prisms, nearly insol. alcohol and ether. According to Piutti, the dextro- and lævo- compounds both melt at 157°.

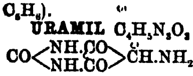
Reactions.—1. Decomposed by fusion, with formation of malyl-ureide $C_5H_7N_3O_3$ [230°–235°], which is also formed by heating urea with asparagine at 125° (Grimaux, *A. Ch.* [5] 11, 400) and crystallises from water in pointed rhombohedra.—2. Boiling HClAq (S.G. 1·12) forms malyl-ureidic acid $C_5H_6N_2O_4$, which is also got by heating aspartic acid with urea at 130°. Malyl-ureïdic acid crystallises in prisms [215°–220°], S. 25 at 100°, which yields BaA'_2aq and is converted by heating with bromine-water into $C_9H_6Br_6N_4O_6$, S. 3 at 100°, $C_9H_4Br_4N_4O_5$, S. ·25 at 100°, $C_9H_4Br_2N_4O_5$, which is v. sol. water, $C_8H_5BrN_4O_4$, S. c. 6 at 100°, and $C_4H_4Br_2N_2O_3$, S. 10 in the cold and c. 22 at 100°.

URAMIDO-THIO-FORMIC ACID *v.* THIO-ALLOPHANIC ACID.

DI-URAMIDO-TOLUENE *v.* URAMIDO-BENZYL-UREA.

DI-*p*-URAMIDO-DI-*o*-TOLYL-SULPHIDE [2:1:4] $S(C_6H_3Me.NH.CO.NH_2)_2$. *Thio-p-tolyl-di-urea.* [151°] (when containing benzene of crystallisation). Formed by heating the hydrochloride of di-*p*-amido-di-tolyl-sulphide with KCNO (Trehlar, *B.* 20, 669). Crystallises from benzene in white silky needles (containing C_6H_6).

URAMIL $C_4H_5N_3O_3$ *i.e.*



$CO<\begin{matrix}NH.CO\\NH.CO\end{matrix}>CH.NH_2$. *Dialuramide. Amido-barbituric acid. Amido-malonyl-urea. Murexan.* Mol. w. 143. Formed by boiling alloxantin with NH_4Cl (Liebig a. Wöhler, *A.* 26, 310; Grimaux, *C. R.* 87, 752) and by boiling ammonium thionurate with HClAq. Formed also by reducing nitro- or nitroso- barbituric acid with HIAq (Baeyer, *A.* 127, 223). It is also a product of the action of acids on murexide (Beilstein, *A.* 107, 183).

Properties.—Silky needles, sl. sol. hot water, insol. alcohol and ether. Sol. conc. H_2SO_4 and re-ppd. on dilution. Its alkaline solution turns red in air, forming purpurates; thus it is converted, in ammoniacal solution into murexide by boiling with air or HgO. Conc. HNO_3 forms alloxan. Bromine at 85° forms orange $C_4H_4BrN_3O_3$ (Mulder, *B.* 14, 1060).

URAMILIC ACID $C_8H_9N_5O_7$ (?). S. 14 in the cold; 33 at 100°. Formed by heating uramil with H_2SO_4 and water, or by evaporating ammonium thionurate with some H_2SO_4 (Liebig a. Wöhler, *A.* 26, 314; Gregory, *P. M.* 24, 187). Transparent, four-sided prisms, sl. sol. cold water. Converted by boiling conc. HNO_3 into nitro-barbituric acid.

URANATES *v.* URANIUM, OXYACIDS AND SALTS OF, p. 826.

URANIUM. U. At. w. 239 (not determined with very great accuracy). Mol. w. unknown. M.P. not determined accurately; between red heat and white heat. S.G. of fused U at $\frac{18°}{4°}$ = 18·685 (Zimmermann, *B.* 15, 851). S.H. at 100° = ·0276 (Z., *l.c.*). S.V.S. 12·8.

Historical.—In 1789 Klaproth prepared some compounds of a new element from *pitchblende*; to the characteristic element of these compounds he gave the name uranium, from *οὐρανός* = the heavens, in allusion to the planet *Uranus* which had been discovered a few years before (*Crell's A.* 1789 [2] 400). The compounds of U were examined by Richter (*Gehlen's A.* 4, 402), Buchholz (*Gehlen's A.* 4, 17, 134), Lecanu (*J. Ph.* 9, 141; 11, 279), Brande (*S.* 44, 1), Berzelius (*P.* 1, 359), and Arfvedson (*P.* 1, 245). In 1840, Péligot showed that the substance supposed till then to be U was really an oxide of U (*A. Ch.* [3] 5, 5); P. isolated the metal, and determined the at. w. to be 120. Mendeléeff in 1872 (*A. Suppl.* 8, 133; *cf. C. N.* 41, 39 [1880]) proposed to double the at. w. of U, making it 240; this proposal was completely justified by the determination of S.H. of pure U by Zimmermann in 1882 (*B.* 15, 851), and by the determination of the V.D. of UCl_4 and UBr_4 (Z., *A.* 216, 2 [1883]).

Occurrence.—Never uncombined. A few minerals containing compounds of U are found sparsely distributed and not in large quantities; the chief of these is *pitchblende*, which consists of U_3O_8 along with SiO_2 and oxides of Sb, As, Ca, Cu, Fe, Mg, V, &c. Carbonate, sulphate, phosphate, niobate, tantalate, and various other compounds of U are also found in varying quantities in several rare minerals (*v.* Zimmermann, *A.* 232, 300; Hidden a. Mackintosh, *Am. S.* [3] 38, 474; Hillebrand, *Am. S.* [3] 38, 329; 40, 384). Lockyer (*Pr.* 27, 49) stated that some of the lines in the emission-spectrum of U coincide with dark lines in the solar spectrum. Hutchins a. Holden (*P. M.* [5] 24, 325) think there is no trustworthy evidence in favour of the existence of U in the solar atmosphere.

Preparation.—1. A mixture of UCl_4, NaCl, and Na is strongly heated in a closed iron cylinder. Zimmermann (*A.* 116, 14) used a cylinder of soft iron with walls c. 3 centim. thick, bored from a larger cylinder (similar to that employed by Nilson a. Pettersson for preparing Be; *B.* 11, 383) fitted with a cap which could be screwed on tightly. He placed a layer of pure fused NaCl in the cylinder, then small pieces of Na (c. 3 to 4 pts. for 10 pts. UCl_4), then UCl_4 (which must be put into the cylinder as quickly as possible, as it is hygroscopic), and covered the whole with a layer of fused NaCl. Z. raised the cylinder to a white heat, kept it at that temperature for some time, cooled, and washed the contents with dilute alkali solution, and then with water. According to Z., the metal as thus prepared is quite pure (*v. infra*).—2. Moissan (*C. R.* 116, 347) obtained U, containing from 5 to 13·5 p.c. C, by mixing the oxide prepared by strongly heating $UO_2(NO_3)_2$ with excess of charcoal, compressing the mixture in a carbon crucible, imbedding this in MgO, and heating for 10–12 minutes in an electric furnace, using a current of 60 volts and 450 ampères.

UCl_4 is obtained by heating the nitrate $UO_2(NO_3)_2$ in air, mixing the oxide thus obtained (chiefly U_3O_8) with C, and heating in a stream of Cl (*v.* URANIUM TETRACHLORIDE, p. 823). The nitrate is obtained from *pitchblende* by powdering the mineral, washing with water, drying, and washing to remove S and As, dissolving in HNO_3Aq, evaporating to dryness, dissolving in water, filtering from Fe_2O_3, $PbSO_4$, &c., evaporating a little, and allowing to crystallise. The crystals of $UO_2(NO_3)_2$ thus obtained are purified by draining in a funnel, washing with a little cold water, drying in the air, dissolving in ether in a wide-mouthed bottle, crystallising by spontaneous evaporation, and re-crystallising from hot water; the crystals of $UO_2(NO_3)_2$ are then dissolved in water so as to form a conc. solution, $UO_2.C_2O_4$ is ppd. by adding $H_2C_2O_4Aq$ to this solution, the pp. is washed with boiling water, and then decomposed by heat, and the UO_2 thus produced is digested with conc. HClAq, washed, dissolved in HNO_3Aq, and the solution is crystallised (Péligot, *A. Ch.* [3] 5, 5; 12, 258; *cf.* Ebelmen, *A.* 43, 286; Wertheim, *J. pr.* 29, 209).

The oxide U_3O_8 used by Zimmermann (*v. supra*) for the preparation of UCl_4, from which pure U was obtained, was prepared by him as follows. A warm solution of commercial uranium hydroxide in HClAq was saturated with H_2S; after standing for some time the liquid was filtered off, NH_3Aq and $(NH_4)_2CO_3Aq$ were added in excess, the liquid was warmed and $(NH_4)_2SAq$ was added; after standing the liquid was filtered, saturated with HClAq, and boiled till CO_2 was removed, then mixed with NH_3Aq and $(NH_4)_2SAq$ and heated on the water-bath till most of the $(NH_4)_2S$ was removed; the pp. of UO_2 was collected, washed, and heated over the blowpipe; the U_3O_8 thus formed was dissolved in HNO_3Aq and the solution was crystallised; the crystals of $UO_2(NO_3)_2$ were dissolved in ether, the solution was poured off from insoluble substances, evaporated to dryness, and the residue was strongly heated; the U_3O_8 which remained was again dissolved in HNO_3Aq, and the crystals that formed on evaporation were dissolved in ether, and the ethereal solution was evaporated to dryness and the residue decomposed by heating.

Properties.—A lustrous, hard, silver-white metal; S.G. 18·685 at $\frac{13^\circ}{4^\circ}$ (Zimmermann, *B.* 15, 851); if UCl_4 is reduced by Na at a red heat, U is obtained as a greyish-black powder. S.H. at 100° = ·0276 (Z., *l.c.*). U is somewhat malleable, but cannot be hammered into thin plates. The emission-spectrum, obtained by the aid of electric sparks, shows only a few lines, the most marked being one in the yellow (Thalén, *A. Ch.* [4] 18, 239). For the fluorescence, phosphorescence, and absorption-spectra of U compounds *v.* Becquerel (*A. Ch.* [4] 27, 539), also Morton a. Bolton (*Am. Ch.* 3, 361, 401). U melts towards a white heat; according to Moissan (*C. R.* 116, 1429), the metal is volatilised by heating in an electric furnace using a current of 350 ampères and 75 volts. After long standing in the air the surface of U becomes covered with a steel-blue to black film of oxide; U that has been fused burns brilliantly when heated on Pt foil in the air; pulverulent U burns at 150°–170° in the air. U combines directly with Cl or Br, also with S; the metal dissolves in dilute H_2SO_4Aq or HClAq; it is not acted on by acetic acid, nor by KOHAq, NaOHAq, or NH_3Aq.

The at. w. of U has been determined (1) by determining U and Cl in UCl_4 (Péligot, *A. Ch.* [3] 5, 12 [1842]; Rammelsberg, *P.* 55, 318; 56, 125 [1842]); (2) by analyses of $UO_2.C_2O_4.H_2O$ (Ebelmen, *A. Ch.* [3] 5, 191 [1842]; Péligot, *A. Ch.* [3] 20, 341 [1846]); (3) by analyses of $UO_2(C_2H_3O_2)_2.2H_2O$ (Péligot, *l.c.*; Wertheim, *J. pr.* 29, 207); (4) by analyses of the double salt $UO_2.Na(C_2H_3O_2)_3$ (Wertheim, *l.c.*); (5) by transforming UO_2 into U_3O_8, and $UO_2.Na(C_2H_3O_2)_3$ into Na_2UO_4 (Zimmermann, *A.* 232, 117, 273 [1886]); (6) by determining S.H. of U (Zimmermann, *B.* 15, 851 [1882]); (7) by determining V.D.s of UBr_4 and UCl_4 (Z., *A.* 216, 2 [1883]).

The at. w. of U was formerly taken as c. 120; in 1872 Mendeléeff adduced reasons for doubling this value, based on a comparative study of the properties of compounds of U to which he was led by considering the periodic arrangement of the elements (*A. Suppl.* 8, 178; *C. N.* 41, 39). When the at. w. of U was taken as 120, the formulæ given to the chief oxides, chlorides, and salts of this element were UO, UCl_2, USO_4, &c.; U_3O_4; U_2O_3, UOCl, $UO_2(NO_3)$, &c.; and U was classed with the iron metals. Mendeléeff pointed out that U was very much heavier than the iron metals, that the oxide U_2O_3 did not form salts similar to those derived from Fe_2O_3, that the salts of UO, *i.e.* USO_4, $U(NO_3)_2$, &c., were not isomorphous with the salts of MgO, FeO, NiO, &c. Mendeléeff also drew attention to the existence of a chloride which would have to be represented as U_2Cl_5 if U = 120, and that this chloride was obtained by heating UCl_2 in H. Mendeléeff proposed to double the value then accepted for the at. w. of U, and, following on this, to write the formulæ of the chlorides, oxides, and salts as UCl_4, UO_2, $U(SO_4)_2$, &c.; U_3O_8; UO_3, UO_2Cl_2, $UO_2(NO_3)_2$, &c.; and UCl_5. It was pointed out that many of these formulæ are analogous to those of the corresponding compounds of Cr, Mo, and W; and it was shown that the properties of compounds of U more nearly resemble those of compounds of Cr, Mo, and W than of any other elements. Especial stress was laid by Mendeléeff on the acidic character of the highest oxide of U. Finally, Mendeléeff showed that an element with the properties of U, and an at. w. equal to c. 240, finds its proper place in Group VI., series 12, of the periodic arrangement of the elements. Mendeléeff suggested that the S.H. of pure U should be determined; that the V.D. of the volatile chloride should be found; that the action of H on the chloride then taken to be UCl_2 should be studied; that salts of the lower oxide (UO if U = 120, UO_2 if U = 240) should be examined, especially as regards their isomorphism with salts of ThO_2, SnO_2, ZrO_2, and TeO_2; that the crystalline forms of corresponding compounds of MoO_3, WO_3, and UO_3 (U = 240) should be studied, and that an especially thorough crystallographic examination should be made of the compounds $R_2UO_2F_4$; and that the physical properties of compounds of Cr, Mo, W, and U should be compared. Since the publication of Mendeléeff's memoir, the S.H. of U, and the V.D.s of UBr_4 and UCl_4 have been determined, the action of H on UCl_4 has been examined, and something has been done in the study of the crystalline forms of compounds of U, including those of the form $R_2UO_2F_4$; the results of all these investigations fully confirm the justness of Mendeléeff's view that the at. w. of U is c. 240, and that this element must be classed with Cr, Mo, and W. The exact value to be given to the at. w. of U has not been yet determined; Zimmermann's measurements gave 238·75 from the ratio $UO_2:U_3O_8$, and 238·67 from the ratio $UO_2Na(C_2H_3O_2)_3:Na_2UO_4$ (O = 15·96). The mol. w. of U is not known.

U is the last member of the even-series family of Group VI.; this family also contains, besides O, the elements Cr, Mo, —, and W. The chromium elements are both metallic and non-metallic in their chemical relations; they form oxides MO_3 that are acidic, and some of the lower oxides are basic. The oxide UO_2 forms some corresponding salts; a series of salts of the form UO_2X is also known, where $X = SO_4$, &c. Several series of uranates M_2UO_4, $M_2U_2O_7$, &c., are known. The haloid compounds are UX_3, UX_4, and UX_5. (For a comparison of the metals of the Cr family *v.* Chromium group of elements, vol. ii. p. 168; *cf.* Classification, vol. ii. p. 207.)

The atom of U is tetravalent in the gaseous molecules UBr_4 and UCl_4.

Reactions and Combinations.—1. Heated in ***air*** U is burnt to a voluminous deposit of U_3O_8 (perhaps containing also UO_2), which stops the further oxidation of the metal. Pulverulent U burns when heated in air to 150°–170°.—2. U burns brilliantly when heated in *chlorine*, forming UCl_4; heated in *bromine* to c. 240° part of the metal is changed to UBr_4.—3. Heated in ***sulphur*** vapour US_2 is produced.—4. It is generally said that U does not react with *water*; but, according to Moissan (*C. R.* 116, 347), the metal obtained by him by reducing the oxide by charcoal in an electric furnace decomposed water at the ordinary temperature; this specimen of U contained from 5 to 13·5 p.c. C.—5. U dissolves in *dilute sulphuric acid*, rapidly on warming, forming USO_4, and giving off H; pulverulent U dissolves in hot conc. H_2SO_4, giving off SO_2; the compact metal is scarcely acted on by conc. H_2SO_4.—6. U dissolves in *hydrochloric acid*, dilute or conc., rapidly on warming, forming a hyacinth-red solution of UCl_3, which goes green on shaking in air, and then contains UCl_4.—7. *Conc. nitric acid*, even when hot, scarcely acts on U that has been fused; the pulverulent metal is quickly oxidised by hot conc. HNO_3Aq to U_3O_8.—8. Several *metallic salts* in solution are reduced by U, with ppn. of the metals, *e.g.* $HgNO_3$, $AgNO_3$, $CuSO_4$, $SnCl_2$, $PtCl_4$, $AuCl_3$.

Detection and Estimation.—Uranyl salts ($UO_2.SO_4$, &c.) are formed by heating uranates with acids, also by the reactions of acids with UO_3, and also by oxidising uranous salts (salts of UO). K_4FeCy_6Aq gives a brownish-red pp. with uranyl salts, soluble in HClAq or in $(NH_4)_2CO_3Aq$; this reaction is said to be extremely delicate; H_2O_2Aq and alcohol give a brown pp. (Fairley, *C. N.* 62, 227); carbonates give yellow pps., soluble in excess, forming yellow liquids; NaOHAq or KOHAq forms yellow pps., NH_4ClAq does not interfere with the ppn., but in presence of sugar or tartaric acid pps. are not produced. Uranous salts are produced by reducing uranyl salts in solution by Zn and HClAq. After reduction the solutions give green pps. with KOHAq or NaOHAq, the pps. becoming brown and then yellow in the air; with $(NH_4)_2SAq$ green pps. are formed, quickly becoming dark green, and black on boiling; K_4FeCy_6Aq produces yellow-green pps. becoming red in the air (*v.* Zimmermann, *A.* 213, 285).

U is generally estimated as UO_2 or U_3O_8 (*v.* Zimmermann, *A.* 232, 209). Solutions may be reduced by Zn and H_2SO_4Aq, and then titrated with $KMnO_4Aq$, the quantity of O used corresponding with the change of UO_2 to UO_3 (Z., *l.c.*; *v.* also Bělohoubek, *J. pr.* 99, 231).

Uranium, arsenates of. A compound, probably $UO_2.As_2O_5.4aq$, is described by Rammelsberg (*P.* 59, 26). Werther (*J. pr.* 43, 321) describes $UO_2H_2AsO_4.3aq$, and various *double salts* of this compound with arsenates of Ca, Cu, and Na.

Uranium, bromides of. UBr_4 is formed by heating U_3O_8 mixed with C in Br vapour; and UBr_3 by heating UBr_4 in H. Zimmermann (*A.* 216, 5) failed to obtain a compound with more Br by heating UBr_4 with Br to 230° in a sealed tube.

Uranium tetrabromide UBr_4. (*Uranous bromide.*) Mol. w. 558. Prepared by strongly heating a mixture of U_3O_8 and sugar, mixing with sugar charcoal that has been heated to redness, placing the mixture in a tube, and heating it first in a stream of thoroughly dried CO_2, and then in Br vapour, and allowing to cool in CO_2; the Br used must be perfectly freed from Cl, HBr, and H_2O by distillation from KBr, MnO_2, and P_2O_5 (Zimmermann, *A.* 216, 2; Alibegoff, *A.* 232, 132; *cf.* Hermann, *J.* 1861. 260). UBr_4 forms black, fusible leaflets; volatile at red heat, giving a vapour with V.D. 281 (Z., *l.c.*); very hygroscopic; dissolves in water, with a hissing sound, forming a green liquid.

By evaporating a solution of $UO_2.xH_2O$ in HBrAq, Rammelsberg (*P.* 59, 12) obtained green crystals of hydrated UBr_4, probably $UBr_4.8H_2O$.

Uranoxybromides. (*Bromoxy-uranates.*) $UO_2Br_2.2MBr$ or $M_2UO_2Br_4$. By the reaction of HBrAq with K_2UO_4 and $(NH_4)_2UO_4$ respectively, Sendtner (*A.* 195, 325) obtained yellowish, hygroscopic tablets of the composition $M_2UO_2Br_4.2H_2O$, where M = NH_4 and K.

Uranium tribromide UBr_3. Mol. w. not determined. Obtained by Alibegoff (*A.* 233, 119; *cf.* Zimmermann, *A.* 216, 5) by passing dry H over molten UBr_4. Dark-brown needles; easily volatilised; not changed by continued heating in H; very hygroscopic; warmed in H_2S, in complete absence of air, forms U_2S_3.

Uranium, chlorides of. By heating U in Cl both UCl_5 and UCl_4 are produced; and by heating UCl_4 in H, UCl_3 is formed.

URANIUM PENTACHLORIDE UCl_5. Mol. w. not determined; formula probably molecular, from analogy of $MoCl_5$ and WCl_5.

Preparation.—1. By heating U in excess of Cl.—2. A slow stream of dry Cl is passed over a mixture of charcoal and any oxide of U, or UO_2Cl_2, heated to dull redness in a glass tube; dark-green octahedral crystals of UCl_4 are formed near the heated part of the tube, and in front of these needle-shaped crystals of UCl_5 are deposited, mixed with a loose brown powder, which is also UCl_5. If the stream of Cl is rapid, most of the UCl_5 is produced as a light-brown, mobile powder (Roscoe, *C. J.* [2] 12, 933).

Properties and Reactions.—UCl_5 crystallises in long, dark, needle-shaped forms; the crystals are lustrous, and reflect greenish light, in transmitted light they are dark ruby red. Both the crystals and the brown powder are very hygroscopic. Dissolves in water, with a hissing sound, forming a yellow-green liquid and giving off HCl. Decomposed to UCl_4 and Cl when heated, either alone or in CO_2 or Cl; decomposition begins at 120° in CO_2, and is complete at 235°. Heating in NH_3 probably produces a nitride (Roscoe, *l.c.*; no analyses given).

Combination.—A compound $UCl_5.PCl_5$ is described by Cronander (*J.* 1873. 222) as an amorphous, yellow solid; formed by heating UO_2 with excess of PCl_5 in a sealed tube for a long time.

URANIUM TETRACHLORIDE UCl_4. (*Uranous chloride.*) Mol. w. 380·48.

Preparation.—1. U is heated in Cl.—2. A mixture of charcoal and an oxide of U, or UO_2Cl_2, is heated in a slow stream of dry Cl (Péligot, *A.* 43, 258; *cf.* Roscoe, *C. J.* [2] 12, 933). The crystals that form nearest to the heated part of the tube are again heated in a stream of dry CO_2, whereby traces of UCl_5 are volatilised and removed (Zimmermann, *A.* 216, 8).—3. A solution of ammonium uranate in HClAq is reduced by Zn, and the solution is evaporated and crystallised. Arendt a. Knop (*C. C.* 1857. 164) reduced, by boiling the solution for 15 min. with Cu and a little $PtCl_4Aq$; they then filtered, saturated with H_2S, filtered, boiled off H_2S, and crystallised.

Properties and Reactions. — Dark-green, lustrous, regular octahedral crystals; volatilises at red heat, in complete absence of moisture, giving a red vapour (Péligot, *l.c.*) with V.D. 192 (Zimmermann, *l.c.*). Very deliquescent; fumes much in air, giving off HCl; dissolves in water, with a hissing sound, forming a green solution that is unchanged in air; gives green, amorphous UCl_4 by evaporation *in vacuo*, but is decomposed by evaporation in the air. When UCl_4Aq is dropped into boiling water all the U is ppd. as $UO_2.xH_2O$. Solution of UCl_4 reduces salts of Au and Ag to the metals, and $FeCl_3$ to $FeCl_2$, &c. By heating in dry H one-fourth of the Cl is removed and UCl_3 remains (Péligot, *A.* 43, 266). According to Péligot (*l.c.*), UCl_4 combines with several metallic chlorides to form double salts.

Uranoxychlorides. (*Chloroxyuranates.*) $UO_2Cl_2.2MCl.2aq$, or $M_2UO_2Cl_4.2aq$. Salts of this composition, $M = NH_4$ and K, are produced by the reaction of large excess of HClAq with uranates of NH_4 and K (Péligot, *A.* 43, 279). The K compound is also formed by acting on UO_2Cl_2 with excess of KClAq, and separating the KCl that crystallises with the $K_2UO_2Cl_4$ mechanically (Berzelius, *P.* 1, 366). The K compound forms thick plates (for crystalline measurements *v.* de la Provostaye, *A. Ch.* [3] 6, 165); easily loses water; gives off HCl at a little above 100°; melts at red heat, giving off Cl, and leaving UO_2 and KCl. The ammonium compound forms very deliquescent rhombohedra.

URANIUM TRICHLORIDE UCl_3. Mol. w. not determined. Obtained by Péligot (*l.c.*) by heating UCl_4 in dry H as long as HCl was given off. Also formed in solution by long-continued reduction of uranyl salts by Zn and HClAq (Zimmermann, *A.* 213, 300). A brownish-red solid; dissolves very readily in water, forming a red solution, which gives off H and becomes green (*v.* P., *l.c.*; Z., *l.c.*; also *A.* 216, 12).

Uranium, ferrocyanides of. Various compounds are described by Wyruboff (*A. Ch.* [5] 8, 444) and Atterberg (*Bl.* [2] 21, 355) as obtained by ppg. K_4FeCy_6Aq by solutions of salts of U. The following formulæ are given:

(1) $U_2FeCy_6.10aq$; (2) $U_2K_2FeCy_6.6aq$;
(3) $(UO_2)_3K_2(FeCy_6)_2.6aq$;
(4) $(UO_2)_5K_6(FeCy_6)_4.12aq$.

Uranium, fluorides of. Only one compound, UF_4, has been isolated with certainty.

URANIUM TETRAFLUORIDE UF_4. (*Uranous fluoride.*) Mol. w. not determined; formula probably molecular, from analogy of UBr_4 and UCl_4. Prepared by adding HFAq to U_3O_8, boiling, pouring off the yellow solution (which contains UO_2F_2), washing the green powder that remains, first on a filter and then by decantation, until free from HFAq, and drying at 100° (Smithells, *C. J.* 43, 125; *cf.* Bolton, *Z.* [2] 2, 353). The process of washing is very tedious, and occupies many days. UF_4 is a green powder; insol. in water and dilute acids; slowly dissolved by conc. acids; boiling NaOHAq produces UO_2. Heated in a Pt crucible with the lid on, a small quantity of a white, bulky sublimate is obtained; this sublimate is UO_2F_2 (Smithells, *l.c.*); the residue in the crucible is chiefly UO_2. Heated on Pt foil, UF_4 leaves U_3O_8 (S., *l.c.*).

Double salts.—Bolton (*l.c.*) obtained the compounds $UF_4.KF$ and $UF_4.NaF$—as green powders, insoluble in water and dilute acids, giving UO_2, KF (or NaF), and HF when heated to redness, in closed vessels—by the action of formic or oxalic acid on $UO_2F_2.3KF$ or $UO_2F_2.NaF$ (*v. infra*) in sunlight. These compounds may be called *uranofluorides*, and written KUF_5 and $NaUF_5$.

Uranium hexafluoride UF_6 was said by Ditte (*C. R.* 91, 115) to be formed by heating U_3O_8 with HFAq, evaporating the yellow liquid, and heating the crystals of $UF_6.8HF$ thus obtained; but Smithells (*C. J.* 43, 125) has shown that the substance obtained by evaporating the *solution formed by heating U_3O_8 with HFAq is* UO_2F_2 (*v.* URANIUM OXYFLUORIDE, p. 828).

Uranoxyfluorides. (*Fluoxy-uranates.*) These compounds may be regarded either as double salts of UO_2F_2 with alkali fluorides, or as salts derived from hypothetical acids $H_xUO_2F_y$. The compounds are formed by adding alkali fluorides to solutions of uranous nitrate, and crystallising under different conditions (*v.* Bolton, *Z.* [2] 2, 353; Baker, *C. J.* 35, 763). The compounds that have been isolated belong to several series: (1) $MF.UO_2F_2.x aq = MUO_2F_3.x aq$, where $M = Na$ and $x = 2$ and 4 (Bolton); (2) $3MF.UO_2F_2 = M_3UO_2F_5$, where $M = NH_4$ and K (Bolton; Baker); (3) $3KF.2UO_2F_2.2aq = K_3U_2O_4F_7.2aq$ (Baker); (4) $5KF.2UO_2F_2 = K_5U_2O_4F_9$ (Baker); (5) $3BaF_2.5UO_2F_2.2aq$ (Bolton). Two other series were described by Ditte (*C. R.* 91, 166), $4MF.UO_2F_2$ and $4MF.UOF_4.x aq$; but the experiments of Smithells (*C. J.* 43, 131) have shown that these compounds do not exist.

Uranium, haloid compounds of. U combines directly with Br and Cl, but not with I; no iodide, indeed, has been isolated. The haloid compounds of U belong to the form UX_3, where $X = Br$ or Cl; UX_4, where $X = Br$, Cl or F; and UX_5, where $X = Cl$. The compounds UBr_4 and UCl_4 have been gasified, and the formulæ are molecular. From the analogy of WCl_6 and $MoCl_5$ the formula UCl_5 is probably molecular; this compound decomposes to UCl_4 and Cl when heated, either alone or in CO_2 or Cl. From the analogy of $CrCl_3$ it may be supposed that UCl_3 and UBr_3 are molecular formulæ. No haloid compounds of U have been isolated corresponding with the chlorides of Cr, Mo, and W, M_xCl_{2x}. No haloid compounds of U are known containing each more than one halogen. Various oxyhaloid compounds, chiefly UO_2X_2, and compounds of these with alkali haloids, are known.

Uranium, hydroxides of, *v.* URANIUM, OXIDES AND HYDRATED OXIDES OF (*infra*); also URANIUM OXYACIDS, AND SALTS OF (p. 826).

Uranium, iodides of. No compound of U and I has been isolated. Hermann (*J.* 1861. 260) and Sendter (*Verbind. des Uraniums*, Erlangen, 1877) failed to obtain an iodide by heating a mixture of UO_2 and C in I vapour or in HI.

Uranium, nitride of, U_3N_4. A greyish-black powder; obtained by heating UCl_4 in NH_3, then mixing with NH_4Cl and heating for a long time in a stream of NH_3 (Uhrlaub, *Verbind. einiger Metalle mit Stickstoff*, Göttingen, 1859). Roscoe (*C. J.* [2] 12, 933) states that a nitride is formed by heating UCl_5 in NH_3, but no analyses are given.

Uranium, oxides and hydrated oxides of. When U is burnt in air the product is U_3O_8; by heating this oxide with reducers, or for a long time in a stream of N or CO_2, UO_2 is formed; UO_3 is produced by fusing U_3O_8 with $KClO_3$, also by heating $UO_2(NO_3)_2$; by adding H_2O_2Aq to $UO_2(C_2H_3O_2)_2Aq$ or $UO_2(NO_3)_2Aq$ a hydrate of UO_4 is obtained. Besides these four oxides, others, intermediate between UO_2 and UO_3, perhaps exist. No definite hydrate of UO_2 has been isolated; the pp. formed by adding NH_3Aq to UCl_4Aq, or to solution of a uranous salt ($U(SO_4)_2$, &c.), is either a hydrate, or a mixture of hydrates, of UO_2. A hexahydrate of U_3O_8 probably exists. Uranic acid is the monohydrate of UO_3. UO_2 dissolves in some acids to form corresponding salts; U_3O_8 is said to react with conc. H_2SO_4 or HClAq to form both uranous salts UX_2, and uranyl salts UO_2X, where X = a divalent acidic radicle. UO_3 interacts with several acids to form uranyl salts UO_2X^{II}; UO_3 also reacts as an acidic oxide with strong bases, forming uranates, di-uranates, &c., $M^I_2UO_4$, $M^I_2U_2O_7$, &c.

According to Guyard (*Bl.* [2] 1, 89), two oxides having the compositions UO and U_3O_4 exist; but the more accurate investigations of Zimmermann (*A.* 213, 301) showed that the substances examined by Guyard were not definite compounds. Péligot described a black oxide U_2O_5; Zimmermann (*A.* 232, 273) has shown that the substance is a mixture, in variable proportions, of UO_2 and U_3O_8.

URANIUM DIOXIDE UO_2. (*Uranous oxide.*) Mol. w. not known. This oxide was supposed to be the element U until 1840, when Péligot proved the presence of O in the substance (*A. Ch.* [3] 5, 5).

Formation.—1. By heating U_3O_8 with such reducing agents as H (Arfvedson, *P.* 1, 245), NH_4Cl and S (Hermann, *J.* 1861. 258), a little C (Buchholz, *Gehlen's Ann.* 4, 17, 134), oxalic acid (Wertheim, *J. pr.* 29, 211), &c.—2. By heating U_3O_8 for a long time in a stream of N or CO_2 (Zimmermann, *A.* 232, 283).—3. By strongly heating $UO_2.C_2O_4$ in absence of air (Berzelius, *P.* 1, 359), or in a stream of H (Péligot, *A. Ch.* [3] 5, 5; Ebelmen, *A. Ch.* [3] 5, 189).

Preparation.—A mixture of UO_2Cl_2 and excess of NaCl and NH_4Cl is strongly heated in absence of air; and the product is washed thoroughly with water, and dried (Wöhler, *A.* 41, 345; *cf.* Hillebrand, *Zeit. f. anorg. Chemie*, 3, 243). If air is not excluded during heating, some UO_3 is obtained (H., *l.c.*). This process gives UO_2 as a black crystalline powder. In place of using UO_2Cl_2, a solution of ammonium uranate in HClAq may be mixed with excess of NaCl and NH_4Cl, and evaporated to dryness, and the residue heated. By fusing any oxide of U with borax for 24 hours, and washing with water and then with dilute acetic acid, or dilute HClAq, Hillebrand (*l.c.* p. 249) obtained jet-black octahedra of UO_2 isomorphous with ThO_2.

Properties.—Prepared by heating $UO_2.C_2O_4$, UO_2 is a dark-brown, pyrophoric powder; if the temperature has been kept high the oxide is lustrous, reddish-black, and not pyrophoric; prepared by heating UO_2Cl_2 with NaCl and NH_4Cl, UO_2 forms black, non-pyrophoric, octahedral crystals. Péligot gave S.G. 10·15; according to Hillebrand (*l.c.*), the S.G. is nearly 11. UO_2 is insoluble in water, HClAq, and dilute H_2SO_4Aq; it dissolves in HNO_3Aq, and in conc. H_2SO_4 in presence of a little water. UO_2 is oxidised to U_3O_8 by heating in air.

Reactions.—1. Heated in *air* or *oxygen* U_3O_8 is produced; UO_2 burns brilliantly in the O-H flame (Clarke, *G. A.* 62, 353).—2. Heating in *chlorine* produces UO_2Cl_2; when mixed with *carbon* and heated in *chlorine*, UCl_5 and UCl_4 are formed. UBr_4 is produced by heating UO_2 mixed with *carbon* in *bromine* vapour.—3. U_3O_8 is formed by heating UO_2 in *water vapour*

(Regnault, *A. Ch.* [2] 62, 358).—4. Heating in vapour of *carbon disulphide* produces $U_3O_2S_4$ (Hermann, *J.* 1861. 258; H. Rose, *G. A.* 73, 139). UO_2 is said to be unchanged by heating in *hydrogen sulphide* (Arfvedson, *P.* 1, 245).—5. A solution of UO_2 in conc. *sulphuric acid* gives green crystals of $U(SO_4)_2$ on evaporation.

HYDRATES OF URANIUM DIOXIDE. No definite hydrate of UO_2 has been isolated; NH_3Aq produces a reddish-brown pp. when added to UCl_4Aq or solution of a uranous salt, this pp. becomes black on boiling; when washed with air-free water and dried *in vacuo* it forms black, coherent lumps. A black pp. is also produced by dropping UCl_4Aq into boiling water. These black pps. contain UO_2; they are probably hydrates of this oxide. The name *uranous hydroxide* is often given to the pp. obtained by either of the processes described; the pp. dissolves in dilute H_2SO_4Aq, HNO_3Aq, and HClAq.

URANOSO-URANIC OXIDE U_3O_8. (*Olive-green oxide of uranium. Uranyl uranate* $UO_2.2UO_3$.) Mol. w. not known.

Occurrence.—In combination with SiO_2, and oxides of Sb, As, Ca, Cu, Fe, Mg, &c., in *pitchblende.*

Preparation.—U, or a decomposable U compound, *e.g.* $UO_2(NO_3)_2$, is heated in the air and then in a stream of O, and is allowed to cool in O (*v.* Zimmermann, *A.* 232, 283). For a method of preparing U_3O_8 from *pitchblende v.* URANIUM, *Preparation of* (p. 821).

Properties.—A dark olive-green powder, sometimes almost black, but always showing a green streak when rubbed on unglazed porcelain (Z., *l.c.*). S.G. 7·2 (Karsten, *S.* 65, 394); 7·31 (Ebelmen, *J. pr.* 27, 385). S.H. ·07979 (Donath, *B.* 12, 742). Insoluble in water; slightly soluble in dilute HClAq or H_2SO_4Aq; soluble in HNO_3Aq, also in H_2SO_4 with a little water.

Reactions.—1. Gives off O when heated in *air* or in an *indifferent gas*; the final product of heating in N or CO_2 is UO_2 (Zimmermann, *A.* 232, 283).—2. Reduced to UO_2 by heating with *hydrogen, carbon, sulphur, potassium,* or *sodium.* 3. Heated in vapour of *carbon disulphide* $U_3O_2S_4$ is formed.—4. Heated with *conc. sulphuric acid,* or with *hydrochloric acid* to 180°–200°, gives both uranous and uranyl sulphates, or chlorides; reacting as $UO_2.2UO_3$ (Z., *A.* 232, 287).—5. *Silver nitrate* solution is slowly reduced to Ag (Isambert, *C. R.* 80, 1087).

HYDRATE OF URANOSO-URANIC OXIDE. By adding NH_3Aq to UCl_4Aq and allowing the pp. to oxidise in the air, and drying *in vacuo* over H_2SO_4, Rammelsberg (*P.* 55, 319) obtained a greenish-black solid which may have been a hydrate of U_3O_8; one determination of water only is given which agrees fairly with $U_3O_8.6aq$.

URANIUM TRIOXIDE UO_3. (*Uranic oxide. Uranic anhydride. Uranyl oxide* $(UO_2)O$.) Mol. w. not known. This oxide is obtained by carefully heating the hydrate $UO_3.H_2O$ (*v. infra*) to 300° (Ebelmen, *A. Ch.* [2] 5, 199); to 250°, temperature being gradually raised (Jacquelin, *Ph. C.* 1845. 183). The oxide is also formed by heating $UO_2.CO_3.2(NH_4)_2CO_3$ to 300° (E., *l.c.*). The preparation of UO_3 may be conducted by heating $UO_2(NO_3)_2$ in a Pt basin until decomposition begins, then transferring to glass tubes and heating these in an oil-bath to 250° so long as acid fumes are given off.

UO_3 is a chamois-yellow powder. S.G. 5·02 to 5·26 (Brauner a. Watts, *P. M.* [5] 11, 60). Ebelmen (*l.c.*) described UO_3 obtained by heating $UO_2.CO_3.2(NH_4)_2CO_3$ as a sealingwax-red powder. When UO_3 is heated to redness it gives off O and U_3O_8 remains (E., *l.c.*; *cf.* Read, *C. J.* 65, 313 [1894]); the oxide seems to be somewhat volatile at the temperature of a porcelain oven (Elsner, *J.* 1866. 35).

UO_3 reacts with many acids as a basic oxide, but the salts formed are always basic salts of the forms $UX_6.2UO_3$, where X = the radicle of a monobasic acid, and $UX_3.2UO_3$ where X = the radicle of a dibasic acid. It is customary to write the formulæ of these basic salts as $UO_2.X^I_2$ and $UO_2.X^{II}$, and to call them *uranyl* salts (UO_2 = uranyl); thus $\frac{U(NO_3)_6.2UO_3}{3} = UO_2(NO_3)_2$, and $\frac{U(SO_4)_3.2UO_3}{3} = UO_2(SO_4)$.

UO_3 behaves towards strong bases as an acidic oxide, forming uranates M_2UO_4, and diuranates $M_2U_2O_7$, &c.; these salts are generally formed by fusing U compounds with bases and O, and by ppg. uranyl salt solutions by strong bases. When KOHAq, NaOHAq, NH_3Aq, BaOAq, or CaOAq is added to a solution of a uranyl salt, *e.g.* to $UO_2(NO_3)_2Aq$, the pp. consists of a uranate of the metal of the base. Alkali carbonates ppt. alkali uranates, but the pps. contain also CO_2; the pps. dissolve in excess of the alkali carbonates forming double carbonates of uranyl and the alkali metal, *e.g.* $UO_2.CO_3.2(NH_4)_2CO_3$. Addition of alkali or alkali carbonate to solutions of uranyl salts containing other metallic salts causes ppn. of a uranate of the metal of the salt present, generally mixed with alkali uranate (*cf.* URANIUM, OXYACIDS, AND SALTS THEREOF, p. 826).

By adding KOHAq to a cold solution of UCl_4 or $UO_2(NO_3)_2$, and dialysing, Graham (*T.* 1861. 213) obtained a solution, free from acid and alkali, which he regarded as a loose compound of sugar and UO_3, and which he called *sucrate of peroxide of uranium.*

HYDRATES OF URANIUM TRIOXIDE. Pure hydrates of UO_3 are not obtained by ppg. uranyl salt solutions by alkalis (*v. supra*); but according to Ebelmen (*A. Ch.* [3] 5, 199) $UO_3.xH_2O$ is produced by boiling an aqueous solution of $UO_2.CO_3.2(NH_4)_2CO_3$ until a yellow pp. is formed, and allowing this pp. to stand for a long time. By the continued action of sunlight on $UO_2(C_2O_4)$ in presence of water, $UO_3.xH_2O$ is said to be formed; after washing and drying in the air, the solid has the composition $UO_3.2H_2O$; and after drying *in vacuo* the composition is $UO_3.H_2O$ (E., *l.c.*). Berzelius (*B. J.* 24, 118) obtained $UO_3.H_2O$ by heating $UO_2(NO_3)_2$ on a sand-bath until acid fumes ceased to be given off, washing the residue with boiling water, and drying in air. The same hydrate is said to be formed by heating U_3O_8 with $KClO_3$ until fusion begins, boiling out with water, and drying in air (Drenkmann, *J.* 1861. 256). The best method of preparing $UO_3.H_2O$ seems to be that given by Malaguti (*A. Ch.* [3] 9, 463), viz. boiling a solution of $UO_2(NO_3)_2$ in absolute alcohol as long as a reaction proceeds, washing the yellow solid that separates with water, and drying in air or *in vacuo*; $EtNO_3$, N_2O_3, C_2H_4O, and $H.CO_2H$ are formed in the reaction.

$UO_3.H_2O$ is described as a yellow powder; S.G. 5·93 at 15° (Malaguti, *l.c.*); reddens litmus paper; when hot it absorbs CO_2 from the air; heated to 250°–300° water is given off and UO_3 remains (Ebelmen, *l.c.*; Jacquelin, *A. Ch.* [3] 5, 199); heated to redness gives off O and leaves U_3O_8. $UO_3.H_2O$ is generally called *uranic acid*; *v.* Uranium oxyacids, and salts thereof (*infra*).

Uranium peroxide. By adding $UO_2(NO_3)_2Aq$ to a mixture of H_2O_2Aq and a large excess of H_2SO_4Aq, and allowing to stand for a considerable time, Fairley (*C. J.* 31, 13[illegible] [1877]) obtained a small quantity of a heavy, crystalline, almost white pp., which when dried (? in air, or at 100°) had the composition UO_4. By adding dilute H_2O_2Aq to solution of $UO_2(NO_3)_2$ or $UO_2(C_2H_3O_2)_2$, free from acids, Fairley (*l.c.* p. 127) obtained a yellowish-white pp., which when dried by pressure between filter paper, had the composition $UO_4.4H_2O$, and when dried at 100° the composition $UO_4.2H_2O$.

Zimmermann (*A.* 232, 273 [1886]) failed to obtain the tetrahydrate $UO_4.4H_2O$; according to him the dihydrate $UO_4.2H_2O$ is very hygroscopic, and begins to decompose at 115°. Alibegoff also obtained only $UO_4.2H_2O$; he failed to prepare the anhydrous oxide UO_4 (*A.* 233, 123 [1886]).

Hydrated uranium peroxide, dried at 100°, is a yellowish-white powder; decomposed by heat, giving off O and leaving much U_3O_8; reacts with alkali solutions to give $UO_3.xH_2O$, and a solution from which alkali *peruranate* $2M_2O.UO_6.8aq$, crystallises (Fairley, *l.c.*; *v. Peruranates* under Uranium oxyacids, and salts thereof, p. 827).

Uranium oxyacids, and salts thereof. $UO_3.H_2O = H_2UO_4$ reacts with strong bases as an acid, forming uranates $M^I_2UO_4$; di-uranates $M^I_2U_2O_7$ are also known, and a few tri- and hexa-uranates. A few peruranates are derived from hydrated uranium peroxide $UO_4.xH_2O$. The compounds of UO_2X_2 with MX (X = Br, Cl, or F) may be regarded as bromoxy-, chloroxy-, and fluoxy-uranates. The substance known as *uranium red* is perhaps $UO_2.ONH_4.SNH_4$, *i.e.* the ammonium salt of an oxythio-uranic acid (*v.* Uranium oxysulphides, p. 828).

Uranic acid H_2UO_4. This compound is obtained as a yellow powder, which reddens litmus paper, and is decomposed to UO_3 and H_2O at 250°–300°, and to U_3O_8 and O at a higher temperature, by boiling a solution of $UO_2(NO_3)_2$ in absolute alcohol, washing the solid that separates with water, and drying in air or *in vacuo*. (For other methods of preparation, and more details *v.* Hydrates of uranium trioxide, p. 825.) The salts of H_2UO_4 are prepared indirectly.

Uranates, di-uranates, &c. Salts derived from H_2UO_4; salts derived from the hypothetical acids $H_2U_2O_7$, $H_2U_3O_{10}$, $H_2U_6O_{19}$ are also known.

URANATES. Salts of the composition $M^I_2UO_4$ and $M^{II}UO_4$. These salts are prepared by ppg. solutions of uranyl salts by bases in solution, or by adding alkali solution to a mixture of a uranyl salt and a metallic oxide in solution; also, in many cases, by oxidising U_3O_8 or UO_2 in presence of a base or a salt of a base. The uranates are insoluble in water, and are not readily decomposed by heat except the ammonium salt. Carson a. Norton (*Am.* 10, 219) have pointed out that analyses of uranates always show considerable differences between the percentages of U found and calculated; they have found the same anomaly in analyses of uranates of ammonium and several ammonium derivatives, such as $NEtH_3$, NEt_2H_2, &c.

Ammonium uranates. The pure salt does not seem to have been isolated. An impure uranate containing c. 90 p.c. UO_3 ($(NH_4)_2UO_4$ requires 84·66 p.c. UO_3) is obtained by adding NH_3Aq to a solution of a uranyl salt (Péligot); it is a yellow powder, which loses H_2O and NH_3 above 100°, very slightly soluble in water, and insol. NH_3Aq (Arfvedson, *P.* 1, 245). An impure salt is also obtained by adding NH_4ClAq or $(NH_4)_2SO_4Aq$ to boiling Na_2UO_4Aq, as long as NH_3 and CO_2 are given off, washing the pp., and drying at a low temperature (Anthon, *D. P. J.* 156, 211). Heated to redness gives U_3O_8; many of the compounds of U are prepared from ammonium uranate.

Potassium uranate K_2UO_4. Prepared by heating 6 g. U_3O_8 with $HClAq$ and HNO_3Aq, adding 4 g. KCl and 16 g. NH_4Cl, evaporating to dryness, heating very strongly until the fused mass is orange-yellow, and washing with water (Zimmermann, *A.* 213, 290). The salt is said to be formed also by strongly heating UO_2HPO_4 (obtained by ppg. a uranyl salt by a phosphate) with K_2SO_4 (Grandeau, *A. Ch.* [6] 8, 223). Orange-yellow, rhombic tablets; insol. water, cold or hot; easily sol. acids (Zimmermann, *l.c.*).

Sodium uranate Na_2UO_4. Prepared by fusing U_3O_8 with NaCl and Na_2CO_3, or with NaCl with gradual addition of $NaClO_3$, and washing with water; resembles K_2UO_4 (Zimmermann, *l.c.*).

Lithium uranate Li_2UO_4 has been prepared similarly to K_2UO_4; it is said to be decomposed by hot water (Z., *l.c.*). Uranates of Ba, Ca, and Sr—MUO_4—are said by Ditte (*C. R.* 95, 988) to be formed by heating the chlorides of these metals with U_3O_8.

DI-URANATES. Salts of the composition $M^I_2U_2O_7$ and $M^{II}U_2O_7$. The formulæ may also be written $M^I_2UO_4.UO_3$ and $M^{II}UO_4.UO_3$.

Barium di-uranate BaU_2O_7. Formed by ppg. $UO_2(C_2H_3O_2)_2Aq$ by BaOAq (Berzelius, *P.* 1, 359); also by heating to redness $UO_2.Ba(C_2H_3O_2)_4$ (Wertheim, *J. pr.* 29, 207). A yellowish-red powder.

Calcium di-uranate CaU_2O_7. Formed, according to Ditte (*C. R.* 95, 988), by strongly heating U_3O_8 with $Ca(ClO_3)_2$; a yellowish-green solid.

Copper di-uranate CuU_2O_7. This salt is said to be formed, as a green crystalline powder, by fusing $Cu(UO_2.PO_4)_2.8aq$, with Na_2CO_3, and washing with water (Debray, *A. Ch.* [8] 61, 451).

Lead di-uranate PbU_2O_7. Formed by digesting $UO_2(C_2H_3O_2)_2Aq$ with freshly ppd. $PbCO_3$ (Wertheim, *J. pr.* 29, 207); also by adding NH_3Aq to a mixture of $UO_2(NO_3)_2Aq$ and $Pb(NO_3)_2Aq$ (Arfvedson, *P.* 1, 258). A yellowish-red powder, becoming green when heated; strongly heated in H, gives a pyrophoric mixture of Pb and UO_2.

Potassium di-uranate $K_2U_2O_7$. Formed by melting together UO_3 and K_2CO_3 and washing with water; also by strongly heating $UO_2.K_2(CO_3)_2$ or $UO_2.K(C_2H_3O_2)_3$ (Berzelius, *P.* 1, 359). A yellowish-red powder.

Silver di-uranate $Ag_2U_2O_7$. Obtained by adding amorphous K_2UO_4 to molten $AgNO_3$, and washing with ice-cold water (Alibegoff, *A.* 232, 129; 233, 117, 143). Also by strongly heating $UO_2.Ag(C_2H_3O_2)_3$ (Wertheim, *J. pr.* 29, 221; *cf.* Rammelsberg, *P.* 59, 10). An amorphous, yellow-red solid; easily sol. acids; decomposed by hot water (Alibegoff, *l.c.*).

Sodium di-uranate $Na_2U_2O_7$. 6aq. Obtained by ppg. uranyl salts by NaOHAq (Patera, *J. pr.* 51, 125; *cf.* Stolba, *Fr.* 3, 74). Loses water of crystallisation over H_2SO_4. A light-yellow to darkish-yellow powder. Known commercially as *uranium yellow* (*v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 893).

Di-uranate of strontium SrU_2O_7 is said also to exist (Ditte, *C. R.* 95, 988).

TRI-URANATES. The only salt that has been isolated is *sodium tri-uranate* $Na_2U_3O_{10}$; it is prepared by fusing $UO_2(SO_4)$ with NaCl, and boiling out with water. This salt forms yellow leaflets resembling mosaic gold; S.G. 6·912; hygroscopic; insol. water, sol. acids (Drenkmann, *J.* 1861. 255).

HEXA-URANATES. The *potassium salt*, $K_2U_6O_{19}$. 6aq, is described as a yellow microscopically crystalline powder, which loses all water at 300°–400°; prepared by melting $UO_2(SO_4)$ with KCl (Drenkmann, *J.* 1861. 255).

PER-URANATES. By adding excess of alkali and H_2O_2Aq to solutions of uranyl salts, Fairley (*C. J.* 31, 134) obtained salts which may be formulated as $M^I{}_4UO_8$. $x$aq and $M^I{}_2R^{II}UO_8$. $x$aq where $M = NH_4$, K, or Na, and $R = UO_2$.

Ammonium-uranyl peruranate $(NH_4)_2(UO_2)UO_8$. 8aq. The formula may also be written $(NH_4)_2O.U_2O_9$. 8aq, or $(NH_4)_2O.UO_3.UO_6$. 8aq, or, regarding the compound as a double peroxide of U and NH_4, as $2UO_4.(NH_4)_2O_2$.8aq. The salt is prepared by adding excess of NH_3Aq and H_2O_2Aq to a solution of a uranyl salt and ppg. by alcohol; it is an orange-yellow solid, readily soluble in water. The quantity of $KMnO_4$ in solution decolourised shows that the ratio of U to 'peroxide oxygen' in the salt is U:3O.

Potassium per-uranate K_4UO_8. 10aq. This salt may also be looked on as a double peroxide of U and K ($UO_4.K_4O_4$.10aq), or as $2K_2O.UO_6$. 10aq. It is prepared by adding alcohol to a solution obtained by treating $UO_2(NO_3)_2$Aq with KOHAq and excess of H_2O_2Aq, and rapidly drying the orange-yellow pp. by pressure in filter paper. The salt rapidly absorbs CO_2 from the air and loses O; it is easily decomposed by heat, giving off H_2O and O. Experiments showed that the ratio of U to 'peroxide oxygen' is U:3O.

Sodium peruranate Na_4UO_8. 8aq. The formula may also be written $UO_4.Na_4O_4$. 8aq or $2Na_2O.UO_6$. 8aq. The salt is prepared by dissolving 'ordinary uranic hydrate,' or UO_4. $x$aq, in excess of NaOHAq along with excess of H_2O_2Aq, allowing to crystallise if conc. solutions are used, or ppg. by a little alcohol if dilute solutions are used, and drying by pressure in filter paper. Poleck (*B.* 27, 1051 [1894]) obtained this salt by adding sodium superoxide to solution of a salt of U. The salt is golden-yellow and lustrous; it slowly absorbs CO_2 from the air, and gives off O. When heated, alone or in CO_2, it gives off 3O; it also loses 3O in contact with acidified $KMnO_4$Aq or other unstable O compounds. The ratio of U to 'peroxide oxygen' is U:3O as measured by the quantity of $KMnO_4$ decolourised by a solution of the salt.

Sodium-uranyl per-uranate $Na_2(UO_2)UO_8$. 6aq. The formula may also be written $Na_2O.U_2O_9$. 6aq or $Na_2O.UO_3.UO_6$. 6aq; or, regarding the compound as a double peroxide of U and Na, as $2UO_4.Na_2O_2$. 6aq. The salt is prepared similarly to Na_4UO_8. 8aq, but using only the minimum quantity of NaOHAq required for solution, and adding alcohol, when it separates as a red oil which slowly crystallises to a red solid. The quantity of $KMnO_4$ in solution decolourised by a solution of the salt showed that the ratio of U to 'peroxide oxygen' is U:3O.

Uranium, oxybromide of, UO_2Br_2. (*Uranyl bromide.*) In preparing UBr_4, by heating a mixture of U_3O_8 and C in Br vapour, Hermann (*J.* 1861. 260) obtained a yellow, easily volatile sublimate, which was probably an oxybromide. By heating UO_2 with Br and water, also by dissolving UO_3 in HBrAq, a colourless liquid is obtained, which on evaporation gives yellow needles of the *hydrated oxybromide* UO_2Br_2. 7aq (Sendtner, *A.* 195, 325). This compound combines with NH_4Br and KBr to form $UO_2Br_2.2MBr$ (*v.* URANOXYBROMIDES, p. 822).

Uranium, oxychloride of, UO_2Cl_2. (*Uranyl chloride.*) Formed by strongly heating UO_2 in Cl; a yellow, crystalline solid, easily fused, but volatilised only at a high temperature; heated with K forms UO_2 and KCl (Péligot, *A. Ch.* [3] 5, 5). By dissolving $UO_3.H_2O$ in HClAq, also by oxidising UCl_4 by HNO_3Aq, and evaporating, yellowish-green crystals of $UO_2Cl_2.xH_2O$ are obtained (Klaproth, *Crell's A.* 1789 [2]. 387).

By dissolving UO_2Cl_2 in ether and evaporating, Regelsberger (*A.* 227, 119) obtained yellow needles of the compound $UO_2Cl_2.2Et_2O$.

UO_2Cl_2 forms compounds with NH_4Cl and KCl of the form $2MCl.UO_2Cl_2$ (*v.* URANOXYCHLORIDES, p. 823).

UO_2Cl_2 combines with NH_3 to form $UO_2Cl_2.xNH_3$, where $x = 2$, 3, and 4. The first of these compounds, $UO_2Cl_2.2NH_3$, is formed by passing dry NH_3 into UO_2Cl_2 dissolved in ether, drying the voluminous yellow pp. that forms, and then placing it *in vacuo* over H_2SO_4 until all ether is removed; the second compound, $UO_2Cl_2.3NH_3$, is formed by the action of NH_3 on $UO_2Cl_2.2NH_3$; and a mixture of $UO_2Cl_2.3NH_3$ and $UO_2Cl_2.4NH_3$ is produced by passing NH_3 over solid UO_2Cl_2. When strongly heated in air these compounds give off all NH_3 and Cl and leave U_3O_8; heated out of contact with air they give UO_2 (Regelsberger, *A.* 227, 119). The three compounds are called by R. *uranylammonium chlorides*, and their formulæ are written $UO_2(NH_3Cl)_2$, $UO_2(NH_3Cl)(NH_2.NH_3Cl)$, and $UO_2(NH_2.NH_3Cl)_2$. Water reacts thus:—

(1) $3UO_2(NH_3Cl)_2 + 3H_2O =$
$(NH_4)_2U_2O_7 + UO_2Cl_2 + 4NH_4Cl$;

(2) $UO_2(NH_4Cl)_2 + 2H_2O = UO_2(OH)_2 + 2NH_4Cl$; the second reaction takes place quickly with warm water.

Uranium, oxyfluoride of, UO_2F_2. (*Uranyl fluoride.*) This compound is produced by boiling U_3O_8 with HFAq, filtering off UF_4 (*v.* URANIUM TETRAFLUORIDE, p. 823), and evaporating the filtrate; it is also formed, in small quantities, by heating UF_4 in a closed Pt crucible. The compound differs according to the method of preparation (Smithells, *C. J.* 43, 125).

a-Oxyfluoride. About 1 gram UF_4 is heated in a Pt crucible with the lid on, temperature being raised as quickly as possible; after five minutes the crucible is allowed to cool, the light, bulky sublimate is removed, and the crucible is again heated for five minutes, and these processes are repeated several times (S., *l.c.* p. 129). This form of UO_2F_2 is a very bulky, light, white, crystalline solid; it is very soluble in water, forming a yellow liquid; heated in air it is gradually changed to U_3O_8.

β-Oxyfluoride. U_3O_8 is treated with boiling HFAq in a leaden vessel, the yellow solution is poured off from green UF_4, heated until the excess of HF is driven off, and allowed to evaporate; evaporation may be completed over H_2SO_4 and CaO *in vacuo*; the residue is dried at 100° (S., *l.c.* p. 130). This form of UO_2F_2 is a yellow saponaceous mass; in one instance the preparation had a semi-crystalline appearance, forming yellow, lustrous scales; it is very soluble in water or alcohol; heated on Pt foil U_3O_8 is formed; heated in a closed crucible it is slowly decomposed, giving UO_2. β-UO_2F_2 probably forms a compound with HF; by evaporating a solution of U_3O_8 in HFAq over H_2SO_4 and CaO until the weight was constant, Smithells (*l.c.* p. 131) obtained a substance which gave results on analyses agreeing fairly with the formula $UO_2F_2.HF.H_2O$.

A solution in water of either form of UO_2F_2 mixed with KFAq and KHF_2Aq, and evaporated, gives the quadratic fluoxy-uranate $K_3UO_2F_5$ (S., *l.c.* p. 130–1). For the compounds of UO_2F_2 with MF *v.* URANOXYFLUORIDES (p. 824).

Ditte (*C. R.* 91, 115) gave the formula UOF_4 to the sublimate obtained by heating, in a closed Pt crucible, the solid that remained when U_3O_8 was treated with boiling HFAq. Ditte said that this solid was UO_2F_2; Smithells (*l.c.*) has, however, shown that the solid obtained by the method used by Ditte is UF_4, and that the sublimate formed by heating this is a-UO_2F_2.

Uranium, oxysulphides of. Two compounds probably exist.

URANIUM OXYSULPHIDE $U_2O_2S_4$. This composition was given by Hermann (*J.* 1861. 258) to a dark, greyish-black solid, obtained by heating UO_2, U_3O_8, or NH_4 uranate to redness in vapour of CS_2. Dissolves in conc. HClAq; burns when heated in air (*cf.* H. Rose, *G. A.* 73, 139).

URANYL SULPHIDE $(UO_2)S$. A brown solid, obtained by ppg. an ammoniacal solution of a uranyl salt by cold $(NH_4)_2SAq$, and quickly washing with conc. alcohol. Probably not obtained pure, as it quickly decomposes; water produces $UO_3.xH_2O$; at 40°–50° it is changed to UO_2 and S (Remelé, *P.* 124, 114; Zimmermann, *A.* 204, 204). $(UO_2)S$ is somewhat sol. water or dilute alcohol; dissolved by conc. HClAq, giving UCl_4 and S; dissolved by $(NH_4)_2SAq$, only in presence of $(NH_4)_2CO_3Aq$ (Zimmermann, *l.c.*), forming a brown liquid.

Uranium black. By allowing $(UO_2)S$ to stand in contact with freshly prepared $(NH_4)_2SAq$, in absence of air, a dull black amorphous powder is obtained. This solid dissolves in mineral acids, giving off traces of H_2S; it dissolves partly in warm $(NH_4)_2CO_3Aq$, but not in warm $(NH_4)_2SAq$, nor in caustic alkali solutions; heated in a tube to c. 270° it gives off a very little NH_3 and H_2O. Zimmermann (*A.* 204, 204) gives the formula U_7O_{10} to uranium black, neglecting (as impurities) the traces of NH_3 and S which the substance contains.

Uranium red. By allowing $(UO_2)S$ to stand for 24–48 hours in contact with cold $(NH_4)_2SAq$, exposed to air, a deep-red solid is obtained; soluble in dilute mineral acids, with separation of S and evolution of H_2S; gives off NH_3, S, and H_2O when heated to 150° and, at above 200°, leaves U_3O_8 (Zimmermann, *l.c.*). According to Z., the formation of this red substance takes place only when $(NH_4)_2S_2O_3$ is present in the $(NH_4)_2SAq$ used; $(NH_4)_2S_2O_3$ is formed by the action of the air. Z. gives to uranium red the composition $U_5S(NH_4)_2O_9 = UO_2.ONH_4.SNH_4.2U_2O_3$ (*cf.* Patera, *J. pr.* 51, 122; Remelé, *P.* 124, 158; Hermann, *J.* 1861. 14).

Uranium, salts of. Two classes of salts are formed by treating oxides of U with acids; UO_2 forms corresponding salts, UX_2 when X = the radicle of a dibasic acid, and UX_4 when X = the radicle of a monobasic acid; UO_3 forms salts $(UO_2)X$ when X = the radicle of a dibasic acid, and $(UO_2)X_2$ when X = the radicle of a monobasic acid. The salts UX^I_4 and UX^{II}_2 are called *uranous salts*; and $(UO_2)X^I_2$ and $(UO_2)X^{II}$ are called *uranyl salts*. (For reactions of the two classes of salts *v.* URANIUM, *Detection and estimation* of, p. 822.) Besides the normal salts, a large number of basic salts of both classes is known, and also many double salts.

The chief *uranous salts* are *arsenates*, *phosphates*, and *sulphites*. The chief *uranyl salts* are *arsenates*, *bromate*, *double carbonates*, *chromates*, *hypophosphite*, *iodate*, *nitrates*, *oxalate*, *phosphates*, *phosphite*, *selenates*, *selenites*, *sulphates*, and *sulphites* (*v.* NITRATES, SULPHATES, &c.).

Uranium, sulphides of. When U is burnt in vapour of S, the disulphide US_2 is formed; by passing H_2S over heated UBr_3 the sesquisulphide U_2S_3 is produced; and by heating U_2S_3 in H the monosulphide US is obtained. The mol. w. of none of these is known.

URANIUM DISULPHIDE US_2. Prepared by heating U in vapour of S (Péligot, *P.* 54, 122; *cf.* Zimmermann, *A.* 216, 18); also by heating UCl_4 to redness in H_2S (Hermann, *J.* 1861. 258). A dark greyish-black powder; becomes crystalline when fused with borax; oxidises slowly in air, rapidly on heating. Easily soluble in conc. HClAq (Hermann, *l.c.*).

URANIUM SESQUISULPHIDE U_2S_3. A stream of dry H_2S, perfectly free from air, is passed over heated UBr_3 as long as HBr is given off. Grey-black solid, forming pseudomorphs of UBr_3; decomposes in air, giving off H_2S; burns when heated in air; scarcely acted on by HClAq or dilute HNO_3Aq; decomposed violently by conc. HNO_3 (Alibegoff, *A.* 233, 117).

Uranium monosulphide US. A black, amorphous powder; obtained by passing dry H over U_2S_3, kept at a red heat, for c. 40 hours, until H_2S is no longer given off. Similar in properties to U_2S_3 (Alibegoff, *A.* 233, 135).

Uranium thio-acids, salts of. No thio- acid, nor salt of a thio- acid, of U has been definitely isolated. *Uranium red* (*v. supra*, p. 828) may perhaps be an ammonium oxythionate of U.

M. M. P. M.

URANOXYBROMIDES *v.* p. 822, under Uranium tetrabromide.

URANOXYCHLORIDES *v.* p. 823, under Uranium tetrachloride.

URANOXYFLUORIDES *v.* p. 824, under Uranium tetrafluoride.

URANYL COMPOUNDS, compounds of the radicle UO_2; *v.* Uranyl ammonium chlorides (p. 827), Uranyl bromide (p. 827), Uranyl chloride (p. 827), Uranyl fluoride (p. 828), Uranyl salts (p. 828), Uranyl sulphide (p. 828).

URAZOLE. A name given by Pinner (*B.* 20, 2358) to di-oxy-triazole, which may be represented as $\begin{matrix}NH.C(OH)\\ N{=}C(OH)\end{matrix}\!\!\geqslant\!N$ or $\begin{matrix}NH.CO\\ NH.CO\end{matrix}\!\!>\!NH$.

UREA CH_4N_2O, *i.e.* $CO(NH_2)_2$. *Carbamide.* Mol. w. 60. [132°] (Lubavin, *B.* 3, 305). S.G. 1·323 (Schröder, *B.* 12, 562). S. (alcohol) 20 in the cold; 100 at 78°. H.C.v. 152,500. H.C.p. 152,200 (Stohmann a. Langbein, *J. pr.* [2] 44, 387); 160,900 (Berthelot a. Petit, *C. R.* 109, 759; 110, 887). H.F. 80,800.

Occurrence.—In the urine of mammalia, especially in that of flesh-eaters (Fourcroy a. Vauquelin, *A. D.* 1799). Occurs in small quantity in blood, muscle, chyle, and lymph of mammalia (Wurtz, *C. R.* 49, 52; Poisseuille a. Gobley, *J.* 1859, 612; Verdeil a. Dollfus, *A.* 74, 214; Munk, *Pf.* 11, 100; Pickard, *C. R.* 83, 1179; 87, 533; Gréhant a. Quinquand, *C. R.* 108, 1092; Garrod, *Pr.* 53, 478). Constitutes about 30 p.c. of the solid substance of the vitreous humour of the eye (Millon, *C. R.* 26, 119; *A.* 66, 128). Occurs also in saliva (Rabuteau, *J.* 1873, 877), in cow's milk (Lefort, *Z.* 1866, 190; Vogel, *J.* 1867, 932), and in other animal secretions.

Formation.—1. By evaporating a solution of ammonium cyanate (Liebig a. Wöhler [1828], *B. J.* 12, 266; *P.* 12, 253; 15, 619; *A.* 38, 108). 2. By adding a little NHO_3 to an ethereal solution of cyanamide (Cannizzaro a. Cloëz, *A.* 78, 230) or by the action of dilute (50 p.c.) H_2SO_4 on cyanamide (Baumann, *B.* 6, 1373).—3. From $COCl_2$ and dry NH_3 (Regnault, *A. Ch.* [2] 69, 180; Natanson, *A.* 98, 287), guanidine and NH_4Cl being formed at the same time (Fenton, *C. J.* 35, 793).—4. By heating carbonic ether with NH_3Aq at 180°.—5. By heating ammonium carbamate at 140° (Basaroff, *J. pr.* [2] 1, 283).—6. By passing an alternating electric current through a solution of ammonium carbamate (Drechsel, *J. pr.* [2] 22, 481).—7. By electrolysis of ammonia solution using carbon electrodes (Millot, *Bl.* [2] 46, 243).—8. By passing a mixture of NH_3 and CO_2 through a red-hot tube (Dexter, *Am.* 4, 35).—9. Formed by passing air charged with NH_3 and vapour of benzene over a red-hot helix of platinum wire (Herroun, *C. J.* 39, 471). Acetylene, but not ethylene, may be substituted for benzene.—10. By heating ammonium thiocarbamate $NH_2.CO.SNH_4$, or by shaking it with water and $PbCO_3$.—11. By the action of aqueous $KMnO_4$ on thio-urea (Maly, *M.* 11, 277).—12. By the action of $KMnO_4$ on KCy in acid solution (Baudrimont, *J.* 1880, 393).—13. By the action of NH_3Aq and H_2S on copper fulminate (Gladstone, *A.* 66, 2).—14. By heating oxamide with HgO (Williamson, *Mémoires du Congrès scientif. de Venise*, A.D. 1847).—15. By oxidation of uric acid.—16. By the action of $KClO_3$ and HCl on guanine (Strecker, *A.* 118, 159).—17. By boiling guanidine with baryta (Baumann, *B.* 6, 1376).—18. By boiling biguanide sulphate or phenyl-biguanide sulphate with baryta (Emich, *M.* 12, 11).—19. By the action of baryta on arginin (Schulze a. Likiernik, *B.* 24, 2701).—20. By boiling creatin with baryta.—21. A product of oxidation of proteïds by $KMnO_4$ (Béchamp, *A. Ch.* [3] 48, 348; *C. R.* 70, 866; Ritter, *Bl.* [2] 16, 32). Staedeler (*J. pr.* 72, 251) and Loew (*J. pr.* [2] 2, 289) failed to obtain urea in this manner. Dreschel (*B.* 23, 3097) obtained urea from albumen by electrolysis, but not by oxidation.

Preparation.—1. Urine, concentrated by evaporation, is treated with nitric or oxalic acid, and the ppd. nitrate or oxalate of urea is decomposed by $CaCO_3$.—2. A solution of potassium cyanate mixed with ammonium sulphate is evaporated on a water-bath to dryness, and the residue extracted with alcohol.—3. A mixture of dry K_4FeCy_6 (28 pts.) and MnO_2 (14 pts.) is heated till sticky on an iron plate. A cold aqueous extract of the mass is mixed with $(NH_4)_2SO_4$ (20·5 pts.), evaporated to dryness, and extracted with alcohol (Liebig).—4. Dry K_4FeCy_6 (8 pts.) is fused with K_2CO_3 (3 pts.) and PbO (15 pts.) added to the melted mass. The cooled mixture is dissolved in water, mixed with $(NH_4)_2SO_4$ (8 pts.) evaporated, and extracted with alcohol (Clemm, *A.* 66, 382). Any K_4FeCy_6 left can be removed by $FeSO_4$.—5. Lead cyanate is digested with $(NH_4)_2SO_4$ (J. Williams, *C. J.* 21, 64).—6. From NH_3Aq, COS, and lead carbonate (Schmidt, *B.* 10, 193).—7. By the action of $(NH_4)_2SO_4$ on KCyO obtained by heating dry K_4FeCy_6 with $K_2Cr_2O_7$; the yield being 25 p.c. of the weight of ferrocyanide (C. A. Bell, *C. N.* 32, 99).—8. A stream of dry NH_3 gas is passed through phenyl-carbonate (from phenol-sodium and $COCl_2$), melted in a water-bath, and the melt is then poured into hot water; the aqueous solution after separation from the phenol is evaporated to crystallisation (Hentschel, *B.* 17, 1286).

Properties.—Dimetric crystals, v. e. sol. water, m. sol. cold alcohol, insol. $CHCl_3$, nearly insol. ether. Sublimes at 130°. *In vacuo* it distils at 135° (Bourgeois, *Bl.* [3] 7, 45). Urea is not attacked by pure HNO_3 (Franchimont, *R. T. C.* 6, 217).

Reactions.—1. When heated alone at 150°–170° it yields NH_3, cyanuric acid and biuret; at 140° it yields ammelide.—2. Decomposed into CO_2 and NH_3 by heating with water in sealed tubes above 100°, by boiling with potash, lime, or magnesia, by warming with conc. H_2SO_4, by evaporating with lead acetate, and by the action of ozone (Gorup-Besanez, *A.* 125, 207) in presence of free alkali. CaO produces cyanamide (Emich, *M.* 10, 330). A 8 p.c. HCl solution decomposes 4 p.c. of the urea in 24 hours. NaOHAq of the same strength has less effect. Cold water does not decompose urea (Berthelot a. André, *Bl.* [2] 47, 840).—3. *Alcoholic potash* forms, on heating in sealed tubes, cyanic acid, NH_3, and water (Haller, *Bl.* [2] 45, 705).—4. Urea hydrochloride at 145° yields NH_4Cl and cyanuric acid (De Vry, *A.* 61, 249).—5. *Chlorine* passed over melted urea forms HCl, nitrogen, NH_4Cl, and cyanuric acid (Wurtz, *A.* 64, 307).—6. *Hypochlorous acid, hypochlorites, chlorine-water*, and *hypobromites*, set free nitrogen, *e.g.* $CON_2H_4 + 3HOCl = CO_2 + 3HCl + 2H_2O + N_2$.—7. *Nitrous acid* added to a hot solution forms CO_2 and nitrogen: $CON_2H_4 + N_2O_3 = CO_2 + 2H_2O + 2N_2$. Nitrous acid (2 mols.) when added to a cold solution of urea (1 mol.) reacts as follows: $2CON_2H_4 + N_2O_3 = (NH_4)_2CO_3 + 2N_2 + CO_2$ (Claus, *B.* 4, 140).—8. Neutral $KMnO_4$ has no action in the cold, and acts but slowly at 100°. In acid solutions $KMnO_4$ gives off nitrogen (1 vol.) and CO_2 (2 vols.) (Béchamp, *J.* 1856, 696; *cf.* Wanklyn a. Gamgee, *C. J.* 21, 25).—9. *Bromine* added gradually to an alcoholic solution of urea forms NH_4Br, cyanuric acid, and nitrogen. In sealed tubes Br gives NH_4Br and cyamelide (Smolka, *M.* 8, 64).—10. Heating with P_2O_5 forms cyanic and cyanuric acids, ammelide, cyamelide, and NH_3 (Weltzien, *A.* 107, 219).—11. Yields cyanamide on warming with Na (Fenton, *C. J.* 41, 262).—12. Conc. HNO_3 reacts thus: $CON_2H_4 + 2HNO_3 = CO_2 + N_2O + NH_4NO_3 + H_2O$ (Franchimont, *R. T. C.* 2, 96; 3, 219).—13. P_2S_5 forms crystalline $C_2H_8N_3PS_2O_2$, which yields $C_2H_7AgN_3PS_2O_2$ and $C_2H_5Ag_3N_3PS_2O_2$, and gives off PH_3 on warming (Kutschig, *M.* 9, 406).—14. *Zinc-dust* at a red heat forms $ZnCy_2$, ammonia, and hydrogen (Aufschläger, *M.* 13, 272). 15. CS_2 at 100° forms COS and ammonium sulphocyanide. With alcohol and CS_2 the products are mercaptan, CO_2, and ammonium sulphocyanide (Ladenburg, *Z.* [2] 5, 253; *B.* 1, 273; 2, 271; Fleury, *A.* 123, 144).—16. *Alcohols* in sealed tubes form carbamic ethers and alkyl allophanates (Cahours, *C. R.* 76, 1387).—17. Boiling Ac_2O forms acetamide and diacetamide (Hofmann, *B.* 14, 2733).—18. $ZnEt_2$ forms CON_2H_2Zn, which is reconverted into urea by water (Gal, *Bl.* [2] 39, 648).—19. *Oxalic ether* at 135°-170° forms oxamide, allophanic ether, and alcohol (Grabowski, *A.* 134, 115). *Oxamic ether* forms, on fusion, oxaluramide (Carstanjen, *J. pr.* [2] 9, 143).—20. *Methylamido-acetic acid* (sarcosine) forms methyl-hydantoïn on fusion (Huppert, *B.* 6, 1278).—21. *Aniline* at 150°-170° gives NH_3 and di-phenyl-urea (Baeyer, *A.* 131, 251).—22. *Aniline sulphonic acid* at 120° gives $NH_2.CO.NH.C_6H_4.SO_3H$ (Ville, *Bl.* [3] 6, 6).—23. *Biguanide sulphate* forms, on heating, ammeline, NH_3 and $(NH_4)_2SO_4$ (Smolka a. Friedreich, *M.* 10, 95).—24. Heated with *acetone* and $ZnCl_2$ or P_2O_5 at 110°-140° it gives *s*-tri-methyl-pyridine and a base $C_{18}H_{19}N$ [119°]; (320°) (Riehm, *A.* 238, 22). This base forms hard monoclinic crystals, with metallic ring; its solutions fluoresce. It gives $B'_2H_2PtCl_6$: [225°].—25. Heated with *acetyl-acetone* (1 mol.), urea (2 mols.) forms $CH_2(CMe:N.CO.NH_2)_2$, which crystallises from alcohol [200°] (Combes, *Bl.* [3] 7, 790). The same body is formed, together with $CH_2{<}\begin{smallmatrix}CMe:N\\CMe:N\end{smallmatrix}{>}CO$ [198°], by adding HClAq or H_2SO_4 to an alcoholic solution of urea and acetyl-acetone (Evans, *J. pr.* [2] 46, 352; 48, 499).—26. *Benzoyl-acetone* forms, in like manner, $Bz.CH_2.CMe:N.CO.NH_2$ [191°] and $CH_2{<}\begin{smallmatrix}CMe:N\\CPh:N\end{smallmatrix}{>}CO$ [227°] (Evans, *J. pr.* [2] 46, 352; 48, 509).—27. *Acetoacetic ether* (2 mols.) and NaOEt (2 mols.) form in the cold $C_{13}H_{22}N_2O_7Na_2$ [c. 165°] (Ernert, *A.* 258, 361). Acetoacetic ether in alcoholic solution forms uramido-crotonic acid (*q. v.*).—28. *Urea* reacts with aldehydes in the cold. In aqueous solution a diureïde $R.CH(NH.CO.NH_2)_2$ is usually formed, while solid urea forms triureïdes. On warming with excess of aldehyde, di- and tri-ureïdes yield tetra- and hexa-ureïdes (H. Schiff, *A.* 151, 186). These ureïdes are sparingly soluble neutral solids, and are split up by warming with acids into the parent substances. Benzoic aldehyde forms benzylidene-di-urea (*q. v.*), while *o*-oxy-benzoic aldehyde forms $C_6H_4(OH).CH(NH.CO.NH_2)_2aq$, which is converted by acetoacetic ether in alcohol into $C_6H_4(OH).CH:N.CO.N:CMe.CH_2.CO_2Et$ [200°], $C_6H_4(OH).CH:N.CO.NH.CMe:CH.CO_2Et$ [204°], and $C_6H_4{<}\begin{smallmatrix}CH:N.CO\\O.CH:CMe\end{smallmatrix}{>}NH$, which decomposes between 260° and 270° (Biginelli, *B.* 24, 2963). Acroleïn forms $(CON_2H_4)_2 3C_3H_4O$, which chars at 250° (Lüdy, *M.* 10, 295). *o*-Nitro-benzoic aldehyde forms nitro-benzylidene-di-urea $C_6H_4(NO_2).CH(NH.CO.NH_2)_2$ aq [200°]. In like manner cuminic aldehyde in alcohol forms the di-ureïde $C_3H_7.C_6H_4.CH(NH.CO.NH_2)_2$ [176°] (Biginelli, *B.* 24, 2964), and cinnamic aldehyde forms $Ph.CH:CH.CH(NH.CO.NH_2)_2$ [172°], and compounds melting at 116° and 212°.—29. *Chloral* added to conc. aqueous solutions of urea forms $(C_2HCl_3O)CON_2H_4$ [150°], v. e. sol. hot water, and $(C_2HCl_3O)_2CON_2H_4$ [190°] nearly insol. hot water, both compounds being crystalline (Jacobsen, *A.* 157, 246). Chloral cyanhydrin at 105° forms the very stable crystalline $C_3H_3Cl_2N_3O$ (Pinner a. Fuchs, *B.* 10, 1069).—30. *Benzene sulphonic chloride* at 100° forms colourless crystals of $C_6H_5SON_4H_7C_2O_2$ aq (Elander, *Bl.* [2] 34, 207). Naphthalene (α)-sulphonic chloride acts similarly.—31. *Cinnamoyl chloride* forms $C.H_8(NH.CO.NH.C_9H_8.NH.CO.NH_2)_2$ [184°] (Biginelli, *B.* 24, 2965).—32. $ClCH_2.OH$ forms methylene-urea, which is split up by hot dilute H_2SO_4 into formic aldehyde and urea (Von Hemmelmayr, *M.* 12, 89).—33. *Trichlorolactic acid* and a little water form, on heating, acetylene-urea $C_4H_6N_4O_2$ (Pinner, *B.* 17, 1997).—34. *Hexa-chloro-acetone* (2 mols.) heated with urea (1 mol.) at 150° forms $CO:N_2H_2(C_2Cl_3O)_2$, crystallising from alcohol in hexagonal plates (Cloëz, *A. Ch.* [6] 9, 145).

Detection.—Urea gives, in conc. solution, crystalline pps. with nitric and oxalic acids. Urea dissolved in amyl alcohol is completely ppd. by an ethereal solution of oxalic acid (Brücke, *M.* 3, 195). Musculus (*C. R.* 78, 132) filters putrid urine, dries the filter at 35°, and employs it as a test for urea, which it converts into ammonium carbonate. A conc. aqueous solution of furfuraldehyde followed by a drop of HClAq (S.G. 1·10) colours a crystal of urea violet (Schiff, *B.* 10, 774). *o*-Nitro-benzoic aldehyde added to an alcoholic solution of urea forms, on warming, a white pp. of *o*-nitro-benzylidene-di-urea [200°]. When present in small quantities this compound may be detected by resolving into the parent substances by boiling with very dilute H_2SO_4, and then adding a little phenylhydrazine solution, which produces a red colour (Lüdy, *M.* 10, 295). Mercuric nitrate gives a white pp. with solutions of urea. The various methods of estimating urea may also be employed for its detection.

Estimation. — Hypobromite method. Urea is mixed with NaOH (100 g. in 250 c.c. water) to which bromine (25 g.) has been added, and the nitrogen collected and measured (Knop, *Fr.* 9, 226; Hüfner, *J. pr.* [2] 3, 1; Dupré, *C. J.* 31, 534; Simpson a. O'Keefe, *C. J.* 31, 838; Russell a. West, *C. J.* 27, 749; Eykman, *R. T. C.* 3, 125; Schleich, *J. pr.* [2] 10, 263; Colquhoun, *C. N.* 67, 123; Camerer, *Zeit. Biol.* 29, 239). When this method is applied to urine it must be remembered that uric acid gives off 48 p.c. and creatinin 37 p.c. of its nitrogen in this way (Falck, *Fr.* 21, 300). Nevertheless, the quantity of nitrogen evolved is 8 p.c. less than the calculated amount (R. a. W.). Using Knop's solution, ammonia, urea, and oxamide give off 93, 92·3, and 75 p.c. of their nitrogen as gas (Foster, *C. J.* 35, 470; 35, 119). In the case of urea and oxamide the 'suppressed' nitrogen is present as cyanate and as nitrate (Fauconnier; Luther, *H.* 13, 500). The amount of 'suppressed' nitrogen is less in dilute than in concentrated solutions (Hüfner, *H.* 1, 350; *cf.* Pflüger a. Bohland, *Pf.* 38, 325; 39, 1, 143), and is greatly diminished by the addition of 1 to 5 p.c. acetoacetic ether (Jacoby, *Fr.* 24, 318). According to Duggan (*Am.* 4, 47), if bromine is added to a solution of urea in NaOHAq the yield of nitrogen is 99·4 p.c. of the theoretical amount. In estimating urea in urine Pflüger (*Fr.* 26, 117) adds HClAq (1 c.c.) to urine (10 c.c.), ppts. various nitrogenous bodies by phosphotungstic acid, neutralises the filtrate with lime and then adds an equal volume of conc. NaOHAq and, after allowing to stand for some time, decomposes with Knop's hypobromite. Frothing of albuminous urine can be avoided by first shaking with a pilule of fat (Méhu, *J. Ph.* [5] 15, 607). Hamburger (*R. T. C.* 2, 181) introduced a volumetric method of employing hypobromite, but Pflüger a. Schenck (*Pf.* 37, 399) consider the method to be untrustworthy. E. Salkowski adds two drops of HCl to urine (2·5 c.c.) diluted with 5 or 10 volumes of water until the air is expelled from the flask, then adds the hypobromite, continues boiling, and collects the nitrogen. Fenton (*C. J.* 33, 300) recommends the use of sodium hypochlorite, which was first proposed by E. W. Davy (A.D. 1854). In this case free NaOH must not be present, though excess of Na_2CO_3 may be present.

Mercuric nitrate method. Urea is completely ppd. by a solution of $Hg(NO_3)_2$. The white pp. is not decomposed, and therefore not turned yellow by Na_2CO_3. Urine (2 vols.) is mixed with a solution (1 vol.) prepared from saturated solutions of baryta (2 vols.) and $Ba(NO_3)_2$ (1 vol.); filtered through a dry filter from the ppd. sulphate and phosphate and 15 c.c. (equivalent to 10 c.c. urine) of the filtrate are titrated with standard mercuric nitrate till a drop taken out gives a yellow pp. with Na_2CO_3 (Liebig, *A.* 85, 370). Assuming the compound $CON_2H_4 2HgO$ to be formed, 1 pt. urea should ppt. 7·2 pts. HgO, but in practice 7·72 pts. of the latter are required. A solution of 71·48 g. mercury in HNO_3 diluted to 1 litre is equivalent to ·01 g. urea per c.c. If the urine contains more than 2 p.c. urea the titration gives too low results; in this case the urine must be diluted. When mercuric nitrate is added to a solution of urea nitric acid is set free. Liebig recommended the addition of Na_2CO_3 from time to time to keep the liquid neutral. Pflüger (*Fr.* 19, 375) proceeds as follows: During the titration, after each addition of $Hg(NO_3)_2$ a drop is placed in contact with a little pasty $NaHCO_3$. Long before the titration is ended, a yellow colour is seen between the two drops, but disappears on mixing them together. When the yellow colour is permanent, the titration is near its end; at this point the solution is neutralised by Na_2CO_3, and the titration continued till a permanent yellow colour is got on mixing the drops. Should the entire liquid become yellow on adding Na_2CO_3, a fresh quantity of urea solution must be taken and the operation be repeated with greater speed. The presence of over 1 p.c. NaCl in urine interferes with the titration when Na_2CO_3 is used as indicator, the final reaction not being sharp. Since $NaHCO_3$ does not ppt. $HgCl_2$, when the bicarbonate is used as indicator the titration may proceed as if NaCl were absent, subtracting the amount of $Hg(NO_3)_2$ that is converted into $HgCl_2$ by the chloride (Rautenburg, *A.* 133, 55; Pfeiffer, *Fr.* 24, 475; Pflüger, *Fr.* 27, 120). It is, however, better to ppt. the chlorides by $AgNO_3$ and titrate in the usual way.

Barium carbonate method. The solution is heated with $BaCl_2$ and NH_3Aq in sealed tubes at 220°–240° and the ppd. $BaCO_3$ weighed (Bunsen, *A.* 65, 375). Before applying this method to urine other substances which might form $BaCO_3$ must be ppd. by phosphotungstic acid (Pflüger a. Bleibtreu, *Fr.* 28, 377).

Kjeldahl's method. Nitrogen in urea may be estimated by Kjeldahl's method. 5 c.c. urine are heated with H_2SO_4 (10 c.c.), and Nordhausen H_2SO_4 (10 c.c.) until no more water or gas comes off, and the liquid is clear yellow. After cooling, water (200 c.c.) and NaOH are added and NH_3 distilled off. In the case of urine it must be remembered that about 13 p.c. of the nitrogen is, on an average, combined in substances other than urea (Pflüger, *Pf.* 35, 454; 40, 533; Camerer, *Z. B.* 24, 306).

Other methods. Urea may also be estimated by fermentation and determination of ammonia set free (Miquel, *C. R.* 111, 501).

Campani (*G.* 17, 137) proposes to decompose urea by nitrous acid, and pass the CO_2 into a solution of lime-water of known strength, and titrate with oxalic acid.

Cazeneuve and Hugouneng (*Bl.* [2] 48, 82) heat urea with a large excess of water and titrate the resulting ammonium carbonate.

Riegler (*F.* 33, 49) decomposes urea with Millon's reagent and measures the mixture of N and CO_2 evolved.

Mörner a. Sjöqvist (*Fr.* 30, 388) add 5 c.c. of a saturated solution of $BaCl_2$ containing 5 p.c. baryta to 5 c.c. urine and then add 100 c.c. of a mixture of 97 p.c. alcohol (2 pts.) and ether (1 pt.). After 24 hours the liquid is filtered, the pp. washed with 50 c.c. alcohol-ether, and the filtrate and washings evaporated at 50° to 25 c.c., MgO and some water added, and the evaporation continued as long as NH_3 comes off. The urea is then determined by Bunsen or Kjeldahl's method (Bödtker, *H.* 17, 140).

Salts.—$B'HCl$. Very deliquescent crystalline mass, formed from urea and dry HCl. Decomposed by water into urea and HCl. At 140° it yields NH_4Cl and cyanuric acid.—$B'HNO_3$. Small plates, sl. sol. water and alcohol, v. sl. sol. HNO_3.—$B'_2H_2C_2O_4$. S. 4·4 at 15°. S. (alcohol of S.G. ·833) 1·65. Monoclinic tables; $a:b:c = 1:·564:·491$; $\alpha = 82° 10'$ (Loschmidt, *Sitz. W.* 51, ii. 7, 384). V. sol. hot water. Ppd. from its aqueous solution by oxalic acid.—$B'H_2C_2O_4$aq (Lubavin, *A. Suppl.* 8, 83).—$B'HAuCl_4$aq: orange-red prisms or needles, v. sol. water, alcohol, and ether.—B'_2HAuCl_4: yellow needles, v. sol. hot water (Heintz, *A.* 202, 264).—$B'_2H_2PtCl_6$2aq. Yellow, deliquescent tables, v. sol. water and alcohol, insol. ether (Heintz, *A.* 198, 91).—$B'H_3PO_4$. Large crystals, v. sol. water and alcohol, sl. sol. ether (Lehmann, *Buchn. Rep.* 15, 224; Schmeltzer a. Birnbaum, *Z.* [2] 5, 206). Its solution does not ppt. $MgSO_4$.—$B'_3 2H_3PO_4$. Its aqueous solution gives a crystalline pp. of cyanuric acid on heating.

Tri-chloro-acetate $B'C_2HCl_3O_2$. Plates (from alcohol) (De Clermont, *J.* 1873, 536).—The fumarate $B'_2C_4H_4O_4$, maleates $B'C_4H_4O_4$ and $B'_2C_4H_4O_4$, malate $B'C_4H_6O_5$, gallate $B'C_7H_6O_5$, and succinate $B'_2C_4H_6O_4$ [145°], all crystallise in monoclinic forms (Loschmidt, *Sitz. W.* 52, ii. 238). The parabanate $B'C_3H_2N_2O_3$ and tartrate $B'_2C_4H_6O_6$ are trimetric.—The citrate $B'_2C_6H_8O_7$ is triclinic (L.). An acid tartrate $B'2C_4H_6O_6$ and an acid citrate $B'C_6H_8O_7$ have been prepared (Hlasiwetz, *J.* 1856, 698).—Cyanurate $B'C_3N_3H_3O_3$. Monoclinic crystals.—Picrate $B'C_6H_3N_3O_7$ [142°] (Smolka, *M.* 6, 920). S. 1·9 at 18·5°. S. (95 p.c. alcohol) 3 at 18°. Slender yellow needles (from alcohol). Tri-chloro methane sulphinate $B'CCl_3.SO_2H$. [96°–100°]. Thin prisms (McGowan, *J. pr.* [2] 33, 220).

Compounds with metallic oxides.—$B'_2 3Ag_2O$ (Liebig). Formed by adding moist Ag_2O to a solution of urea. Grey powder composed of slender needles. According to Mulder (*B.* 6, 1019), the yellow pp. got by adding NaOH to a solution of urea mixed with $AgNO_3$ is $CON_2H_2Ag_2$. It combines with iodine, forming $CON_2H_2Ag_2I$, a greenish mass, darkened by light (Tafel a. Enoch, *B.* 23, 1554).—B'_2HgO. Got by adding $Hg(NO_3)_2$ to a solution of urea mixed with KOH. White pp.—$B'_2 3HgO$. White pp. formed by adding $HgCl_2$ to a solution of urea and $HgCl_2$, changes to a yellow granular powder on boiling with water.—$B'HgO$. Formed by adding $Hg(NO_3)_2$ to a warm solution of urea (Dessaignes, *A.* 82, 232; Liebig, *A.* 85, 289).

Compounds with metallic salts.—$B'AgNO_3$. Prisms. Yields silver cyanate on boiling with water.—B'_2PdCl_2. Ppd. by adding a solution of $PdCl_2$ to one of urea (Drechsel, *J. pr.* [2] 20, 469).—$B'NaCl$aq. [60°–70°]. Formed by evaporation of a solution of urea and NaCl. Deliquescent prisms. Alcohol extracts urea from the compound.—$B'NaNO_3$aq. Prisms (from water).—$B'NH_4Cl$. Deliquescent crystals.—$B'_3(NH_4Cl)_2HCl$. Formed by dissolving urea in bleaching-powder solution (Beckmann, *A.* 91, 367). Large plates, sol. alcohol mixed with ether.—$B'_4Mg(NO_3)_2$ (Werther, *J. pr.* 35, 5).—$B'_6Ca(NO_3)_2$.—B'_2ZnCl_2. Very deliquescent crystals (Neubauer a. Kerner, *A.* 101, 337).—$B'CdCl_2$. Needles.—$B'_2Hg(NO_3)_2 3HgO$. Granular powder formed by mixing warm dilute solutions of urea and mercuric nitrate. At the moment of formation the pp. is flocculent.—$B'_2Hg(NO_3)_2 2HgO$. Formed by pouring mercuric nitrate into a solution of urea as long as a pp. is produced, and keeping the whole at 40° to 50° for some time (Liebig). Six-sided laminæ.—$B'_2Hg(NO_3)_2HgO$. Formed by adding an acid solution of mercuric nitrate to a solution of urea nitrate. Crusts of small tabular crystals (Liebig, *A.* 85, 296).—$B'HgCl_2$. Flat crystals, v. sl. sol. cold water (W.).—$B'_{12}Cr_8O_{21}$ 3aq. Formed by the action of water on the product of the action of CrO_2Cl_2 on urea (W. J. Sell, *Pr.* 33, 267; 45, 321). Olive-green needles (from hot water). $PtCl_4$ added to its solution in hot water ppts. silky green needles of $B'_{12}Cr_2Cl_6(PtCl_4)_3$ 2aq. The chromate treated with $PbCl_2$ forms lead chromate and a liquid from which gaseous HCl ppts. green prisms of $B'_{12}Cr_2O_6$ 6aq, the aqueous solution of which heated with Ag_2SO_4 gives dark-green prisms of $B'_{12}Cr_2(SO_4)_3$ 10aq. In a similar way green prisms of $B'_{12}Cr_2(NO_3)_6$ may be got.—$B'_{12}Cr_6Cl_2O_{11}$ 2aq. Green monoclinic crystals, got from the product of the action of CrO_2Cl_2 on urea by crystallising from conc. HClAq (1 vol.) diluted with water (9 vols.). By treatment with water it is split up into $B'_{12}Cr_8O_{21}$ and $B'_{12}Cr_2Cl_6$. By treatment with conc. HClAq (1 vol.) and water (6 vols.) it is converted into the salts $B'_{12}Cr_6Cl_6O_{12}$ 3aq.—$B'_{12}Cr_5O_{12}$ 4aq.—$B'_{12}Cr_2Br_6$ 6aq.—$B'_{12}Cr_2Cl_6$ $6HgCl_2$.—$B'_{12}Cr_4(C_2O_4)_6$ 4aq.—$B'_{12}Cr_2I_{18}$.—$B'_{12}Cr_2(SO_4)_3I_6$.—$B'_{12}Cr_2(CO_3)_2I_4$.—$B'_{12}Cr_2(CO_3)_2I_6$.—$B'_{12}Cr_2Br_{18}$. Bronze-yellow tables, giving off bromine in air.—B'_2CuCl_2. Small blue crystals.

Formyl derivative $NH_2.CO.NH.CHO$. [159°]. H.F. 13,400 (Matignon, *C. R.* 112, 1367). Formed by boiling urea with conc. formic acid (Geuther, *Z.* [2] 4, 300). Crystals, v. sol. water, being decomposed into urea and formic acid.

Acetyl derivative $C_3H_6N_2O_2$ *i.e.* $NH_2.CO.NHAc$. *Acetureide.* Mol. w. 102. [214°]. H.F. −200 (M.). S. (alcohol) 1 in the cold; 10 at 78°. Formed by boiling urea with AcCl or Ac_2O (Zinin, *A.* 92, 405; G.; Zande, *R. T. C.* 8, 235). Got also by the action of $KMnO_4$ on methyl-uracil (Behrend, *A.* 229, 29). Four-sided needles (from alcohol). Slowly but completely decomposed by pure HNO_3 with evolution of CO_2 (1 vol.) and N_2O (2 vols.) (Franchimont, *R. T. C.* 6, 215). It is not ppd. by $Hg(NO_3)_2$.

Di-acetyl derivative $CO(NHAc)_2$. [153°]. A product of the action of $COCl_2$ on acetamide at 50° (Schmidt, *J. pr.* [2] 5, 63).

Formed also from mercuric fulminate and AcCl (Scholl, *B.* 23, 3515). Needles (from alcohol), sl. sol. cold water.

Chloro-acetyl derivative $NH_2.CO.NH.CO.CH_2Cl$. Formed from chloro-acetyl chloride and urea (Jazukovitch, *Z.* 1868, 234; Tommasi, *C. R.* 76, 640). Thin needles (from alcohol). Begins to melt at 160°.

Tri-chloro-acetyl derivative $NH_2.CO.NH.CO.CCl_3$. [150°]. Crystals (from alcohol) (De Clermont, *J.* 1874, 798; Meldola a. Tommasi, *C. J.* 1874, 404; Cloez, *A. Ch.* [6] 9, 219). Nearly insol. hot water.

Bromo-acetyl derivative $NH_2.CO.NH.CO.CH_2Br$. Needles (from dilute alcohol) (Baeyer, *A.* 130, 156). Pure HNO_3 gives off CO_2 (1 vol.) and N_2O (2 vols.) (Franchimont, *R. T. C.* 6, 218).

Tri-bromo-acetyl derivative $NH_2.CO.NH.CO.CBr_3$. [148°]. Formed by the action of Br on an aqueous solution of di-bromo-barbituric acid (Baeyer). Crystals, v. sol. hot alcohol. Yields crystalline $B'_2Ba(OH)_2$ $x$aq, v. e. sol. water.

Cyano-acetyl derivative $NH_2.CO.NH.CO.CH_2Cy$. [200°–210°] (Mulder, *B.* 12, 466). Crystalline.

Butyryl derivative $NH_2.CO.NHC_4H_7O$. [176°]. Formed from urea and butyryl chloride (Moldenhauer, *A.* 94, 101). Plates.

Isovaleryl derivative $C_6H_{12}N_2O_2$. [191°]. Minute prisms, v. sl. sol. water.

Carbonyl derivative $CO(NH.CO.NH_2)_2$. Formed by heating urea with $COCl_2$ at 100° (E. Schmidt, *J. pr.* [2] 5, 39; Emich, *M.* 10, 347). Powder composed of minute crystals, v. sl. sol. cold water and alcohol. Decomposed by heat into NH_3 and cyanuric acid. Boiling KOH also produces cyanuric acid.—$B'HgO$: crystalline powder, insol. water.

Succinyl derivative $C_4H_4O_2(NH.CO.NH_2)_2$. Formed by heating urea (2 mols.) with succinyl chloride (1 mol.) at 65° (Conrad, *J. pr.* [2] 9, 301). Colourless powder, v. sl. sol. hot water.

Methyl-malonyl derivative $CHMe{:}C_2O_2{:}N_2H_2CO$. [192°]. Formed by heating methyl-malonic acid with urea and $POCl_3$ (Franchimont a. Klobbie, *R. T. C.* 7, 22). Pointed plates, v. sol. water and alcohol.

Benzoyl derivative $NH_2.CO.NHBz$. [c. 200°]. S. (alcohol) 1 in the cold; 4 at 78°. Formed by heating urea with BzCl or Bz_2O at 150° (Zinin, *A.* 92, 404; Geuther, *Z.* [2] 4, 299). Four-sided plates (from alcohol), insol. ether).

Di-benzoyl derivative $CO(NHBz)_2$. [210°] (S.); [197°] (H.). A product of the action of $COCl_2$ on benzamide at 165° (E. Schmidt, *J. pr.* [2] 5, 58). Formed also by heating guanidine carbonate with Bz_2O at 100° (Creath, *B.* 7, 1739), and by treating mercuric fulminate with BzCl (Hollemann, *R. T. C.* 10, 72; *B.* 23, 2998, 3742). Needles (from alcohol), sl. sol. water. Aniline at 180° gives NH_3, benzamide, benzanilide, and *s*-di-phenyl-urea.

u-Di-benzoyl derivative $NH_2.CO.NBz_2$. [c. 197°]. Formed by heating sodium benzoyl-cyanamide NaBzN.CN with BzCl, followed by boiling alcohol (Buddéus, *J. pr.* [2] 42, 97). White needles.

m-Nitro-benzoyl derivative $NH_2.CO.NH.CO.C_6H_4.NO_2$ [1:3]. Plates (Griess, *B.* 8, 222).

m-Amido-benzoyl derivative $C_8H_9N_3O_2$. Formed by boiling the preceding body with aqueous ammonium sulphide (G.). Needles (from water), decomposing at 200°. — $B'HCl$ aq: needles.—$B'_2H_2PtCl_6$.

(β)-Naphthoyl derivative $NH_2.CO.NH.CO.C_{10}H_7$. [215°]. Formed from naphthoyl chloride and urea (Vieth, *A.* 180, 319). Minute needles, m. sol. alcohol, v. sl. sol. benzene.

Di-(β)-naphthoyl urea [286°] (Ekstrand, *B.* 20, 1353). Needles.

Lactyl derivative v. Lactyl-urea.

Glycollyl derivative v. Hydantoïn.

Reference.—Oxy-urea.

UREA CARBOXYLIC ACID *v.* Allophanic acid.

UREA CHLORIDES. A name sometimes used to denote alkyl-carbamic chlorides X.NH.CO.Cl.

URECHITIN $C_{28}H_{42}O_8$. Occurs, together with urechitoxin, in the leaves of *Urechites suberecta*, growing in Jamaica (Bowrey, *C. J.* 33, 252). Crystallises from alcohol in needles (containing $x$aq), tastes bitter. It is very poisonous (*Pr.* 27, 309). Nearly insol. water, m. sol. ether. Appears to be a glucoside. Conc. H_2SO_4 forms a yellow liquid, turning red, and finally purple, especially in presence of an oxidising agent.

Urechitoxin $C_{13}H_{20}O_5$. Bitter poison, split up by acids into sugar and urechitoxetin.

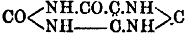
UREÏDES. Compounds obtained by elimination of water between urea and an acid or an aldehyde. Many of them may be represented as amides in which NH_2 is replaced by $NH.CO.NH_2$.

BIURET *v.* vol. i. p. 517.

URETHANE *v.* Carbamic ether.

ISURETINE *v.* Formamidoxim.

URIC ACID $C_5H_4N_4O_3$ *i.e.*



$$\mathrm{CO}\left<\begin{array}{l}\mathrm{NH.CO.C.NH}\\ \mathrm{NH{-\!-\!-}C.NH}\end{array}\right>\mathrm{CO}$$

(Medicus, *A.* 175, 243; Fischer, *B.* 17, 329, 1776). Mol. w. 168. S.G. 1·87. H.C.p. 461,400 (Berthelot, *C. R.* 110, 887; Matignon, *C. R.* 110, 1267); 462,500 (Stohmann, *J. pr.* [2] 44, 390). H.C.v. 462,700 (M.). H.F. 148,100 (M.). S. ·002 at 0°; ·006 at 20°; ·0625 at 100° (Blarez a. Denigès, *C. R.* 104, 1847; *cf.* Garrod, *Pr.* 35, 63).

Occurrence.—In urine and in urinary calculi (Scheele, A.D. 1776; Liebig a. Wöhler, *A.* 26, 241; Horbaczewski, *M.* 12, 221). About ·5 g. is daily excreted in human urine. Uric acid occurs in urine of carnivora, herbivora (Mittelbach, *H.* 12, 463), and of birds. Serpent's urine is chiefly composed of acid ammonium urate. A considerable quantity occurs in the blood of gouty subjects, and sodium urate is deposited as 'chalk-stones.' Very small quantities are normally present in the liver, lungs, brain, and blood. It occurs in the green gland of the fresh-water crayfish (Griffiths, *Pr.* 38, 187). Urea, glycocoll, leucine, and aspartic acid given to fowls appear in the urine as uric acid (Jaffé a. Meyer, *B.* 10, 1930; Knierim, *B.* 10, 1930).

Synthesis.—1. By rapidly heating glycocoll (1 pt.) with urea (10 pts.) to 230° (Horbaczewski, *B.* 15, 2678; *M.* 3, 796; 6, 356).—2. By heating urea with tri-chloro-lactic acid or its amide (Horbaczewski, *M.* 8, 201, 584).—3. By preparing methyl-uracil from acetoacetic ether and urea; converting methyl-uracil into nitro-uracil carboxylic acid by treatment with fuming HNO_3; boiling the carboxylic acid with water, and reducing the resulting nitro-uracil to amido-uracil, and finally to isobarbituric acid by means of tin and HClAq; oxidising the isobarbituric acid to isodialuric acid; and heating the isodialuric acid (1 pt.) with urea (1 pt.) and H_2SO_4 (6 pts.) (Behrend a. Roosen, *A.* 251, 235).—4. By fusing urea (4 g.) with cyano-acetic acid (1 g.) (Formánek, *B.* 24, 3419).

Preparation.—1. Serpent's urine is dissolved in boiling KOHAq, filtered, and the uric acid ppd. by HCl or dilute H_2SO_4. If the uric acid is much coloured a little $KMnO_4$ or $K_2Cr_2O_7$ (Gibbs, *Am. S.* [2] 48, 215) should be added to the boiling alkaline solution before ppn.—2. Guano is boiled with borax (1 pt.) and water (120 pts.), and the solution of sodium urate thus obtained ppd. by HCl.—3. Guano is extracted with dilute HClAq, and the residue dissolved in conc. H_2SO_4 and ppd. by water.

Properties.—White anhydrous scales (by ppn.). When slowly deposited from dilute solutions (*e.g.* urine) it separates as large crystals (containing 2aq). Nearly insol. water, insol. alcohol and ether. Sol. conc. H_2SO_4 and reppd. by water. Its solution in hot H_2SO_4 deposits on cooling a deliquescent compound of uric acid with H_2SO_4. Uric acid is m. sol. glycerin, hot NaOAc, and sodium phosphate. Lithium carbonate (1 pt.) dissolved in water (90 pts.) can dissolve uric acid (4 pts.). Aqueous K_2CO_3 also dissolves uric acid.

Reactions.—1. Decomposed by *heat*, without fusion, yielding HCy and a sublimate of cyanuric acid, ammonium cyanate, urea, and ammonium carbonate, and leaving a carbonaceous residue. 2. *Water* at 180° forms mycomelic acid (Hlasiwetz, *A.* 103, 211).—3. *Potash-fusion* yields NH_3 and potassium oxalate, carbonate, and cyanate.—4. *Chlorine* and *bromine* in presence of water yield alloxan, urea, and parabanic acid (Hardy, *A. Ch.* [4] 2, 372). Alloxan is also produced by iodine, by HNO_3, and by MnO_2 and H_2SO_4.—5. Boiling with water and PbO_2 yields allantoïn. Allantoïn is also produced by *ozone* (Gorup-Besanez, *A.* 110, 94), alkaline K_3FeCy_6, $KMnO_4$ (Claus, *B.* 7, 226), and MnO_2 and water. 6. Pure HNO_3 decomposes uric acid in the cold, with evolution of CO_2 (14 vols.), N_2O (24 vols.), and nitrogen (4 vols.) (Franchimont, *R. T. C.* 6, 222). 7. KNO_2 and HOAc yield urinilic acid (Sokoloff, *Z.* [2] 5, 78) and stryphnic acid (Gibbs, *Am. S.* [2] 48, 215).—8. HIAq at 165° forms glycocoll, NH_4I, and CO_2 (Strecker, *Z.* [2] 4, 215).—9. Exposed to the air in alkaline solution it yields oxonic and uroxanic acids.—10. A dilute solution of sodic urate absorbs oxygen from the air at 35° according to the equation $C_5H_4N_4O_3 + O + 2H_2O = C_5H_8N_4O_6$ (uroxanic acid). Uric acid in dilute NaOH solution is completely decomposed by 35 days' digestion at 35° (Nencki a. Sieber, *J. pr.* [2] 26, 18). 5 g. uric acid dissolved in 200 c.c. water and 20 g. potash disappeared in 5 days. However, if no oxygen be present the uric acid is not affected.—11. In fermenting urine uric acid is completely split up into CO_2 and NH_3 (Sestini, *G.* 20, 133).

Detection.—Uric acid may be recognised by its insolubility in water and HClAq, by its crystalline character under the microscope, and especially by the murexide reaction. When evaporated with HNO_3 on a water-bath it leaves an orange residue, which is coloured violet-red by ammonia and violet-blue by potash. A solution of uric acid in aqueous Na_2CO_3 produces a dark-brown spot of reduced silver when added to paper moistened with $AgNO_3$ (Schiff, *A.* 109, 65). Uric acid (1 mol.) reduces boiling Fehling's solution, forming a pp. of Cu_2O (1 mol.) (W. Müller, *J. Th.* 1881, 73). In presence of KOH uric acid dissolves CuO, forming a blue solution, which slowly deposits white cuprous urate. The compound $C_5H_4N_4O_3Cu_2O$ is ppd. when an alkaline solution of uric acid is treated with Fehling's solution and hydroxylamine hydrochloride (Balke, *J. pr.* [2] 47, 546). Uric acid evaporated with a little dilute HNO_3 gives a blue colour on shaking with H_2SO_4 and benzene containing thiophene (Denigès, *J. Ph.* [5] 18, 161).

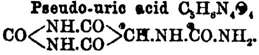
Estimation in urine.—1. Urine (500 c.c.) is concentrated, HCl is added, and after twenty-four hours the pp. is collected and weighed. Uric acid may be separated from xanthine by ppn. with conc. H_2SO_4 (Horbaczewski, *H.* 18, 341; *cf.* Wulff, *H.* 17, 634).—2. Urine (200 c.c.) is mixed with conc. Na_2CO_3Aq (10 c.c.), and after an hour conc. NH_4ClAq (20 c.c.) added. After forty-eight hours the pp. is collected, washed with HCl (1 pt. of S.G. 1·123), diluted with water (10 pts.), the washings allowed six hours to deposit any dissolved uric acid, the combined pps. washed with alcohol and dried at 110° (Salkowski, *Fr.* 16, 373). Uric acid may also be ppd. as ammonium urate by saturating urine with solid NH_4Cl (30 g. to 100 c.c.) (Hopkins, *Pr.* 52, 93).—3. Fresh urine is mixed with very dilute (·15 p.c.) NaOHAq, filtered from phosphates, and diluted to S.G. 1·010. To 300 c.c. of this solution is added 50 c.c. of magnesia mixture [$MgSO_4$ 7aq (1 pt.), NH_4Cl (2 pts.), NH_3Aq (4 pts. of S.G. ·924), and water (8 pts.)]. The pp. is filtered off, and 175 c.c. of the filtrate mixed with ·5 g. $CaCO_3$ and 5 c.c. of a 3 p.c. solution of $AgNO_3$. The pp. is washed and dried, and a nitrogen estimation made by Kjeldahl's method (Camerer, *Z. B.* 26, 84; *cf.* Salkowski, *Pf.* 5, 319).—4. Urine (25 c.c.) is mixed with $NaHCO_3$ (1 g.), and NH_3Aq (2 to 3 c.c.), and ammoniacal $AgNO_3$ (1 to 2 c.c. of a solution of 5 g. $AgNO_3$ in 100 c.c. water, to which NH_3Aq is added till the ppd. Ag_2O is just re-dissolved). The pp. is collected, washed, dissolved in HNO_3, and the silver determined volumetrically by the sulphocyanide method (Haycraft, *Fr.* 25, 167; 30, 648). This method is liable, according to Salkowski (*H.* 14, 31) and Gossage (*Pr.* 44, 384), to an error which may amount to 60 p.c. The error is partly due to variations in composition of the silver urate, and partly to presence of bodies of the xanthine group (Deroide, *Bl.* [3] 7, 363). *V.* also Herrmann, *H.* 12, 496; Czapek, *H.* 12, 502).—5. In a solution containing not more than ·0125 p.c. of uric acid 1 c.c. of decinorma permanganate is reduced by ·0074 g. uric acid (Blarez a. Denigès, *C. R.* 104, 789).—6. By treat ment with a standard iodine solution in presence of alkali (Kreidl, *M.* 14, 109).

Salts.—$(NH_4)HA''$. S. ·06 at 15°. Slender needles.—$(NH_4)_3HA''_2$.—$(NH_4)_4H_2A''_3$ (Maly, *J.* 1863, 621).—K_2A''. S. 3 at 16°. Small needles.—KHA''. S. ·13 at 20°. Amorphous.—Na_2A'' aq. S. 1·5. Nodules.—$NaHA''$ ½aq (dried at 100°). Crystalline powder. S. ·09 at 15°; ·8 at 100°. Occurs as an amorphous urinary deposit.—$LiHA''$. S. ·27 at 20; ·9 at 40°; 2·5 at 100° (Schilling, *A.* 122, 241).—BaA''aq (dried at 100°). Granular pp. S. ·013 in the cold.—$BaH_2A''_2$ 2aq (dried at 100°). Amorphous, insoluble powder (Behrend a. Roosen, *A.* 251, 250).—CaA''. S. ·066 in the cold; ·07 at 100°.—$CaH_2A''_2$ 2aq. S. ·15 in the cold; ·37 at 100°. More sol. KClAq.—SrA'' 2aq. Minute stellate groups of needles. S. ·023 in the cold; ·055 at 100°.—$SrH_2A''_2$ 2aq.—$MgH_2A''_2$ 6aq. S. ·03 in the cold; ·6 at 100°.—$PbH_2A''_2$ (dried at 100°). Insol. water.—PbA'' (dried at 100°).—Cu_2A'' aq.—$Cu_3A''_2(OH)_2$ 4aq: green pp.

Reference.—METHYL-URIC ACID.

Iso-uric acid $C_5H_4N_4O_3$. Formed by boiling cyanamide (1 pt.) with an aqueous solution of alloxantin (2 pts.) (Mulder, *B.* 6, 1236; 7, 1633). Powder, almost insol. water. Oxidised by boiling with I and water. Its solution in K_2CO_3 reduces $AgNO_3$.

Pseudo-uric acid $C_5H_6N_4O_4$ *i.e.*



$$CO\!\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle\!CH.NH.CO.NH_2$$

Formed by the action of KCyO on uramil (Baeyer, *A.* 127, 3), and by heating uramil with urea at 180° (Grimaux, *Bl.* [2] 31, 535). White crystalline powder composed of small prisms, v. sl. sol. water. HNO_3 yields alloxan. Boiled with water and PbO_2 it yields oxalic acid, but no allantoïn. H_2SO_4 at 150° forms xanthinine.—$(NH_4)HA''$ aq.—KHA''aq: scales.—$NaHA''$ 2aq: groups of prisms, v. sol. hot water.—BaA'' 5aq: groups of slender needles.

URINILIC ACID $C_8H_7N_7O_6$. Formed by the action of KNO_2 and HOAc on uric acid (Sokoloff, *Z.* 1869, 78). Prisms (from water).—K_2HA'''. Prisms, v. e. sol. water. $Ca_3A'''_2$. Crystalline pp. insol. water and HOAc.—$Sr_3A'''_2$.—$Ba_3A'''_2$.—$CdHA'''$ 3aq.—$CuHA'''$ 4aq. Slender red needles.—Ag_2HA'''. Pp.—Ag_3A'''. Gelatinous pp. quickly blackening in light.

UROBILIN.

Occurrence.—Often in urine (Jaffé; Disqué, *H.* 2, 271; *C. C.* 1878, 711; Eikholz, *J. Physiol.* 14, 326). In bile, especially of the mouse.

Preparation.—Urine containing urobilin is ppd. by lead acetate and sub-acetate until the absorption band at F is removed. The pp. is extracted with alcohol, acidified with HCl or H_2SO_4, filtered, diluted with water, and extracted with chloroform.

Properties.—A red amorphous, shiny substance. Prepared as above it contains HCl or H_2SO_4, as the case may be. Its spectrum exhibits a dark band at F, destroyed by NH_3, but on adding NaOH another band near the red is formed (MacMunn, *Pr.* 30, 250; 31, 26, 206; *v.* also HYDROBILIRUBIN, this vol. p. 273.

Detection and estimation in urine: Jolles, *H.* 18, 545; Studensky, *C. C.* 1893, ii. 668.

UROCANINIC ACID $C_{12}H_{12}N_4O_4$. [213°]. Occurs in dog's urine (Jaffé, *B.* 7, 1669; 8, 811). Prisms (containing 4aq), v. sol. hot water, insol. alcohol and ether. Decomposed by fusion into CO_2 and **urocanine** $C_{11}H_{10}N_4O$, an amorphous base yielding $B'H_2PtCl_6$.—$HA'2HCl$: needles, v. e. sol. water.—$HA'2HNO_3$: crystalline pp. insol. dilute HNO_3, v. sol. water.—$HA'H_2SO_4$. Minute needles and plates.

UROCHLORALIC ACID $C_8H_{11}Cl_3O_7$ (?) [142°]. S. (ether) ·4. Found in the urine after administration of chloral (Von Mering a. Musculus, *B.* 8, 662; *H.* 6, 483; Külz, *C. C.* 1881, 486). Silky needles, v. e. sol. water and alcohol. Decomposed by boiling dilute H_2SO_4 into tri-chloro-ethyl alcohol and glycuronic acid $C_6H_{10}O_7$.—NaA'.—KA'.—BaA'_2: satiny plates (from ether-alcohol).

UROFUSCOHÆMATIN *v.* this vol. p. 274.

UROLEUCIC ACID $C_9H_{10}O_5$. [133·5°]. An acid occurring in human urine which darkens on addition of alkalis (Kirk, *Brit. Med. Journ.* [1888] 2, 232). Crystals. Its solution is ppd. by $Pb(OAc)_2$ and gives a transient green colour with very dilute $FeCl_3$. $FeCl_3$ colours the crystals red.

UROMELANIN $C_{18}H_{43}N_7O_{10}$. A black substance which separates on treating urine with H_2SO_4 or HClAq in presence in air (Thudichum, *J. pr.* 104, 257; *C. R.* 106, 1803; Plosz, *H.* 8, 89; Udranski, *H.* 11, 537; 12, 32; this vol. p. 274). It yields $C_{18}H_{40}AgN_7O_8$ (Thudichum).

URONITROTOLUOLIC ACID $C_{13}H_{15}NO_9$. Occurs in urine of dogs after a dose of *o*-nitro-toluene (Jaffé, *H.* 2, 47). Very deliquescent. Asbestos-like mass, v. e. sol. water and alcohol. Decomposed by dilute H_2SO_4 into *o*-nitro-benzyl alcohol and a syrupy acid. **Salts.** — BaA'_2: crystalline powder, v. e. sol. water, insol. alcohol.—$CO(NH_2)_2HA'$ 2½aq. [149°]. Needles, v. e. sol. water, sl. sol. cold alcohol.

UROROSEÏN *v.* this vol. p. 274.

UROSULPHINIC ACID $C_5H_4N_4SO_2$. Formed by heating thio-uramido-barbituric acid (1 pt.) with H_2SO_4 (2 pts.) at 160° (Nencki, *B.* 4, 724; 5, 45). Nodules (from hot HClAq). Its K salt crystallises in needles, m. sol. cold water.

UROXANIC ACID $C_5H_8N_4O_6$. Formed by leaving a solution of uric acid (5 g.) in water (200 c.c.) containing KOH (20 g.) to stand for 5 days at 35°, neutralising by HOAc, filtering, and evaporating (Nencki a. Sieber, *J. pr.* [2] 24, 504; *cf.* Städeler, *A.* 78, 286; 80, 119; Strecker, *A.* 155, 177; Mulder, *B.* 8, 1291). Tetrahedra, sl. sol. cold water, insol. alcohol. Decomposed by boiling water into CO_2, urea, and allanturic acid.—K_2A''3aq. Four-sided pearly plates, v. sol. hot water.—CaA'' 4aq.—BaA'' 5aq.—PbA'' ½aq. Insol. water.—Ag_2A'': flocculent pp., turned red by light.

URSONE $C_{30}H_{48}O_3$ 2aq. [265°] (Gintl, *M.* 14, 255). Occurs in the leaves of the red bear-berry (*Arctostaphylos Uva-ursi*) (Trommsdorff, *Ar. Ph.* [2] 80, 273; Hlasiwetz, *J. pr.* 66, 123). Needles, insol. water, acids, and alkalis, sl. sol. alcohol and ether. Conc. H_2SO_4 added to its solution in Ac_2O gives a red colour, changing through blue to green. Does not react with hydroxylamine or phenyl-hydrazine. Reduced by HI and P at 360° to $C_{15}H_{24}$ (256°–267°).

Acetyl derivative [264°].

Benzoyl derivative [214°].

URUSHIC ACID $C_{14}H_{18}O_2$. S.G. ^{25} ·985. Occurs in urushi or Japanese lacquer (Yoshida, *C. J.* 43, 472). Dark, pasty mass, v. sol. benzene and ether, insol. water. Br in CS_2 forms $C_{14}H_{12}Br_6O_2$. HNO_3 forms $C_{14}H_{16}(NO_2)_2O_2$, which forms FeA'_3. Chromic acid mixture forms oxy-urushic acid $C_{14}H_{18}O_3$.—PbA'_2 (dried at 100°). [110°-115°]. Flocculent pp.—$FeH_9A'_{12}$ 2aq.—$FeH_3A'_6$. Deep-black pp.

USNETIC ACID $C_9H_{10}O_3$. [178°]. Occurs in small quantity, together with usnic acid, in the lichen *Usnea barbata* (Hesse, *B.* 10, 1326). Flat prisms (from alcohol), v. sol. ether. $FeCl_3$ colours its alcoholic solution bluish-violet. Bleaching-powder does not colour its alkaline solution. Is perhaps identical with decarbusnin.

USNIC ACID $C_{18}H_{16}O_7$ (Salkowski; Paterno) or $C_{19}H_{16}O_8$ (Hesse), or $C_{18}H_{18}O_7$ (Stenhouse a. Groves, *C. J.* 39, 234). *Carbusnic acid.* [195·4° cor.]. S. (ether) ·3 at 20°. Occurs in the lichens *Usnea barbata*, *Usnea florida*, *Zeora sordida* (Knop, *A.* 49, 103; Rochleder a. Heldt, *A.* 48, 12; Thomson, *A.* 53, 252; Stenhouse, *Pr.* 18, 222; *A.* 68, 97, 114; 155, 51; Hesse, *A.* 117, 343; Paterno, *G.* 8, 225; Salkowski, *B.* 8, 1459). Sulphur-yellow monoclinic crystals, sl. sol. alcohol, v. sol. hot ether and benzene. Does not yield betorcin when heated. Conc. H_2SO_4 forms **usnolic acid** $C_{27}H_{24}O_{10}$ [213°] crystallising in small yellowish prisms (Stenhouse a. Groves, *C. J.* 39, 236). When it is heated with an alcoholic solution of aniline it yields the anilide $C_{18}H_{15}O_6(NHPh)$, crystallising from alcohol in pale-yellow plates [171°], and forming in KOHAq a yellow solution from which HCl ppts. $C_{23}H_{23}NO_6$ [171°].

Salts.—$NaC_{18}H_{17}O_8$ 2aq (Spica, *G.* 12, 432). Pale-yellow, silky needles.—$KC_{19}H_{15}O_8$ 3aq or $KC_{18}H_{17}O_8$ 3aq. Pale-yellow plates (from 50 p.c. alcohol) (Hesse, *B.* 10, 1325).—$KC_{19}H_{15}O_8$ aq or $KC_{18}H_{17}O_8$ aq. Yellow prisms (from 93 p.c. alcohol).—CuA'_2: green pp.

Decarbusneïn $C_{17}H_{18}O_6$. [175°]. Formed by heating usnic acid (1 pt.) with alcohol (3⅓ pts.) at 150° (Paterno, *G.* 12, 234). Yellow, silky needles, sol. hot alcohol, sl. sol. water and ether. Not coloured by $FeCl_3$. Not attacked by AcCl. Reduces warm ammoniacal $AgNO_3$. Boiling KOHAq in absence of air splits it up into HOAc and **decarbusnic acid** $C_{15}H_{16}O_5$, which crystallises from alcohol in lemon-yellow prisms [199°] and yields, when boiled with Ac_2O, two acetyl derivatives $C_{15}H_{15}AcO_5$ [148°] (isomeric with decarbusneïn) and $C_{15}H_{14}Ac_2O_5$ [131°].

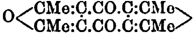
Pyrousnic acid $C_{12}H_{12}O_5$ (P.); $C_9H_8O_4$ (Salkowski, *B.* 8, 1461). [197°]. Formed, together with pyrousnetic acid, by boiling usnic acid (2 pts.) with KOH (5 pts.) and water (5 pts.) in an atmosphere of hydrogen (Paterno, *G.* 13, 313; 12, 242). Shining scales (from ether), v. sol. alcohol, sl. sol. ether. Its alkaline solution absorbs oxygen from the air, turning green and ultimately brown. Reduces ammoniacal $AgNO_3$ readily. Ac_2O yields an acetyl derivative [205°]. Alcohol and HCl form an ether [147°]. Pyrousnic acid is split up on dry distillation in a current of H into CO_2 and **usneole** $C_{11}H_{12}O_3$, which crystallises from alcohol in yellow prismatic tablets [176°] and is converted by AcCl into a di-acetyl derivative [142°].

Pyrousnetic acid $C_{14}H_{14}O_6$ *i.e.* $C_{13}H_{13}O_4(CO_2H)$. [186°]. Formed by boiling usnic acid (10 pts.) with KOH (25 pts.) and water (25 pts.) for 15 minutes (Paterno, *G.* 12, 238). Colourless plates or needles (from alcohol). Ac_2O yields $C_{14}H_{13}AcO_6$ [168°]. When heated in a current of H, pyrousnetic acid is split up into CO_2 and **usnetole** $C_{13}H_{14}O_4$, which crystallises from dilute alcohol in yellowish needles [179°].

(β)-Usnic acid *v.* CLADONIC ACID.

UVIC ACID *v.* PYROTRITARIC ACID.

UVINONE $C_{14}H_{12}O_4$ *i.e.*



$O\left<\begin{matrix}CMe:C.CO.C:CMe\\CMe:C.CO.C:CMe\end{matrix}\right>O$ (?) [247°]. Formed, to the extent of 2 p.c., by distilling pyrotritaric acid (Dietrich a. Paal, *B.* 20, 1086). Yellow needles (by sublimation), sol. HOAc, v. sl. sol. alcohol. Conc. H_2SO_4 forms a solution with green fluorescence. Br at 100° forms crystalline $C_{12}H_4Br_8O_4$.

UVITIC AICD $C_9H_8O_4$ *i.e.* $C_6H_3Me(CO_2H)_2$ [1:3:5]. *Mesidic acid.* Mol. w. 180. [288°]. H.C.v. and p. 928,900. H.F. 193,100 (Stohmann, *J. pr.* [2] 40, 128). Formed, together with uvitonic acid, by boiling pyruvic acid with baryta-water (Finck, *A.* 122, 184). Formed also by oxidation of mesitylene or mesitylenic acid (Fittig a. Von Furtenbach, *Z.* [2] 4, 1; *A.* 147, 295), by oxidation of di-methyl-ethyl-benzene (Wroblewsky, *A.* 192, 217), and by heating $C_6H_2Me(SO_2NH_2)(CO_2H)_2$ with conc. HClAq at 230° (Hall a. Remsen, *Am.* 2, 136). Slender needles (from water), v. sl. sol. hot water, m. sol. alcohol and ether. Yields toluene on heating with soda-lime (Baeyer, *Z.* [2] 4, 119). The Ca salt heated with lime yields *m*-toluic acid (Böttinger a. Ramsay, *A.* 168, 255). Chromic acid mixture oxidises it to trimesic acid.

Salts.—K_2A'': plates (from alcohol), v. sol. water.—BaA″ aq.—CaA″ aq.—Ag_2A''. Nearly insol. cold water.

Ethyl ether Et_2A''. [35°]. Crystalline.

References.—AMIDO-, BROMO-, NITRO-, and OXY-UVITIC ACID.

Isouvitic acid *v.* CARBOXY-PHENYL-ACETIC ACID.

Uvitonic acid *v.* METHYL-PYRIDINE-DICARBOXYLIC ACID.

VALERAL *v.* VALERIC ALDEHYDE.

VALERAL-DI-ACETONAMINE *v.* *Pentylidene di*-ACETONAMINE.

VALERALDINE $C_{15}H_{31}NS_2$. *Thiovaleraldine.* [41°]. Formed by the action of H_2S on isovaleric aldehyde ammonia suspended in water (Beissenhirtz, *A.* 90, 109; Parkinson, *A.* 90, 119). Formed also from thio-isovaleric aldehyde and dry NH_3 (Schröder, *B.* 4, 468). Plates (from ether), with powerful smell, sol. alcohol, insol. water.—B'HCl. Needles, sol. water.

VALERCREATININ *v.* METHYL-GUANIDO-VALERIC ACID.

VALERIAN OIL. An essential oil obtained from the root of *Valeriana officinalis*. It contains a terpene $C_{10}H_{16}$ (156°) $[\alpha]_D = -21°$, a camphene, borneol $C_{10}H_{18}O$, di-bornyl oxide $(C_{10}H_{17})_2O$ (285°–290°), formyl-, acetyl-, and valeryl-borneol, and a little valeric acid (Gerhardt, *A. Ch.* [3] 7, 275; Pierlot, *A. Ch.* [3] 56, 291; Bruylants, *J. Ph.* [4] 27, 349; *B.* 11, 452; Haller, *C. R.* 103, 151; Oliviero, *C. R.* 117, 1096).

***n*-VALERIC ACID** $C_5H_{10}O_2$ *i.e.* $CH_3.CH_2.CH_2.CH_2.CO_2H$. Mol. w. 102. (186° cor.). S.G. $\frac{0}{0}$ ·9562 (Zander, *A.* 224, 65); $\frac{15}{15}$ ·9446; $\frac{25}{25}$ ·9375 (Perkin); $\frac{20}{4}$ ·9298 (Brühl). C.E. (0°–10°) ·00098 (Z.). S. 3·5 at 16°. S.V. 130·0 (Z.). M.M. 5·513 at 13·6°. $\mu_\beta = 1·4093$. $R_\infty = 43·16$ (Brühl). H.F. 137,800 (Stohmann, *J. pr.* [2] 49, 99). Occurs in crude wood vinegar (Grodzki a. Krämer, *B.* 11, 1358).

Formation.—1. By saponifying its nitrile (*n*-butyl cyanide) (Lieben a. Rossi, *A.* 159, 58; *G.* 1, 239).—2. By oxidation of *n*-amyl alcohol (L. a. R.).—3. By the action of metallic silver on a mixture of EtI and *β*-iodopropionic acid (W. von Schneider, *Z.* [2] 5, 343).—4. By oxidising *a*-oxy-*n*-caproic acid (Erlenmeyer, *B.* 9, 1840).—5. By heating *β*-acetyl-propionic acid with HI and P at 200° (Kehrer a. Tollens, *A.* 206, 233).—6. By reducing *β*-acetyl-propionic acid with sodium-amalgam (Wolff, *A.* 208, 110).—7. By heating *n*-propyl-malonic acid at 180° (Juslin, *B.* 17, 2504; Furth, *M.* 9, 308).—8. By fermentation of calcium lactate (Fitz, *B.* 13, 1309; 14, 1084). 9. By heating the lactone of *γ*-oxy-*n*-valeric acid with HIAq and P at 240° (Fittig, *A.* 226, 346).—10. A product of oxidation of castor oil by dilute HNO_3 (Wahlforss, *B.* 22 Ref., 438).

Properties.—Liquid, smelling like butyric acid.

Salts.—KA'. Plates (from alcohol).—CaA'_2aq. S. 10·267 at 0°; 8·144 at 60°. Least soluble at 60°–70° (F.);—$CaA'_2 1\frac{1}{2}$aq (Schorlemmer, *A.* 161, 270).—BaA'_2. S. 21·693 at 0°; 23·076 at 80°.—MnA'_2aq.—CuA'_2: minute green needles. More sol. cold than hot water.—ZnA'_2. S. 2·6 at 25°.—AgA'. S. ·229 at ·3°; ·641 at 70·5°.

Methyl ether MeA'. (127·3°). S.G. $\frac{0}{0}$ ·9097 (G.); $\frac{20}{4}$ ·8795. C.E. (0°–10°) ·00106. S.V. 149·1 (Gartenmeister, *A.* 233, 273). $\mu_\beta = 1·3997$. $R_\infty = 50·7$.

Ethyl ether EtA'. Mol. w. 130. (144·7° cor.). S.G. $\frac{0}{0}$ ·8939 (G.); $\frac{20}{0}$ ·8765 (Lieben a. Rossi, *A.* 165, 117); $\frac{20}{4}$ ·8661 (Brühl). S.V. 174·3. C.E. (0°–10°) ·00111. $\mu_\beta = 1·402$. R_∞ 58·03 (B.).

n-Propyl ether PrA'. (167·5°). S.G. $\frac{0}{0}$ ·8888. C.E. (0°–10°) ·00106 (G.). S.V. 197·8.

n-Butyl ether C_4H_9A'. (185·8°). S.G. $\frac{0}{0}$ ·8847. C.E. (0°–10°) ·00101. S.V. 222·1.

n-Amyl ether $C_5H_{11}A'$. Mol. w. 172. (203·7°). S.G. $\frac{0}{0}$ ·8812 (G.); $\frac{20}{4}$ ·8568 (Brühl). C.E. (0°–10°) ·00097. S.V. 245·8. μ_β 1·417. R_∞ 80·48.

n-Hexyl ether $C_6H_{13}A'$. (223·8°). S.G. $\frac{0}{0}$ ·8797. C.E. (0°–10°) ·00096. S.V. 272·0.

n-Heptyl ether $C_7H_{15}A'$. (243·6°). S.G. $\frac{0}{0}$ ·8786. C.E. (0°–10°) ·00090. S.V. 297·4.

n-Octyl ether $C_8H_{17}A'$. (260·2°). S.G. $\frac{0}{0}$ ·8784. C.E. (0°–10°) ·00088. S.V. 322·6.

Amide $C_4H_9.CO.NH_2$. Mol. w. 101. [116°]. Pearly plates (Weidel a. Ciamician, *B.* 13, 69). V. sol. water, alcohol, and ether.

Nitrile $C_4H_9.CN$. *n-Butyl cyanide.* (140°). S.G. ^{0} ·816 (Lieben a. Rossi, *A.* 158, 171). Formed, together with amylamine, by allowing a mixture of hexoic amide (1 mol.) and bromine (2 mols.) to run into a 10 p.c. solution of NaOH (Hofmann, *B.* 17, 1410).

Isovaleric acid $(CH_3)_2CH.CH_2.CO_2H$. *Isopropyl-acetic acid.* (176° cor.). S.G. $\frac{15}{15}$ ·9336; $\frac{25}{25}$ ·9261 (Perkin); $\frac{20}{20}$ ·931 (E. a. H.). M.M. 5·635 at 16°. S. 4·24 at 20°.

Vapour tension: Richardson, *C. J.* 49, 767.

Heat of neutralisation: Gal a. Werner, *Bl.* [2] 46, 801.

Occurs in the fat of *Delphinum Phocæna* (Chevreul [1817], *Corps gras*, pp. 99, 209), in valerian root (Grote, *B. J.* 11, 225; Trommsdorff a. Ettling, *A.* 4, 229; 6, 176), in the root of *Angelica Archangelica* (Meyer a. Zenner, *A.* 55, 328), in the root of *Athamanta Oreoselinum*, in the bark of the alder tree, in the berries and bark of the Guelder rose (*Viburnum Opulus*) (Moro, *A.* 55, 330), in the root of *Viburnum prunifolium* (Allen, *Ph.* [3] 11, 413), and in oil of geranium (O. Jacobsen, *A.* 157, 232). A valeric acid occurs in rosin oil (Lwoff, *B.* 20, 1017) and in yolk of wool (suint) (Buisine, *Bl.* [2] 48, 639).

Formation.—1. By oxidation of inactive fermentation amyl alcohol (Dumas a. Stas, *A.* 33, 156; 35, 143; Erlenmeyer a. Hell, *A.* 160, 257; Pedler, *C. J.* 21, 74).—2. By boiling its nitrile with alcoholic potash (E. a. H.; Schmidt a. Sachtleben, *A.* 193, 87).—3. Together with the active acid by oxidation of leucine (amido-hexoic acid) (E. a. H., *cf.* Neubauer, *A.* 106, 59).—4. By heating isopropyl-malonic acid at 180° (*B.* 11, 596).—5. By oxidising di-methyl-allyl-carbinol, treating the resulting $CMe_2(OH).CH_2.CO_2H$ with HI, and reducing the *β*-iodo-valeric acid so formed by means of 3 p.c. sodium-amalgam applied in an acid solution (Schirokoff, *J. pr.* [2] 23, 286).—6. By the action of KOH or HClAq on *Athamantin* (Schnedermann a. Winckler, *A.* 51, 324).—7. By putrefactive fermentation of proteïds (Iljenko, *A.* 63, 269).—8. By the action of CrO_3 on gelatin and albumen (Schlieper, *A.* 59, 7; Guckelberger, *A.* 64, 71).—9. From isopropyl-aceto-acetic ether (Frankland a. Duppa, *A.* 145, 84).—10. By distilling isopropyl-malonic acid (Conrad a. Bischoff, *A.* 204, 151).—11. A product of distillation of colophony (Renard, *A. Ch.* [6] 1, 253).

Preparation.—1. *Isoamyl alcohol* is oxidised by less than the calculated quantity of $KMnO_4$ in the cold. Some acetic acid is formed, but this can be got rid of by distilling a dilute solution of the acids, for valeric acid passes over in the first quarter of the distillate, the acetic acid remaining behind (Duclaux, *C. R.* 105, 171).—2. By oxidising isoamyl alcohol (1,000 c.c.) with $K_2Cr_2O_7$ (1000 g.) dissolved in water (3,500 c.c.) by adding in the cold H_2SO_4 (1,400 g.) mixed with water (800 g.). The resulting isoamyl isovalerate is saponified by potash (Pierre a. Puchot, *A. Ch.* [4] 29, 229).—3. By distilling valerian root with dilute phosphoric acid, neutralising the distillate with Na_2CO_3, and decomposing the resulting Na salt by H_2SO_4. In purifying valeric acid use may be made of the fact that the acid forms crystalline acid salts with K and Na (Lescœur, *Bl.* [2] 27, 104).

Properties.—Liquid, inactive to light. Its smell is powerful and unpleasant. Sl. sol. water. Separated from aqueous solution by $CaCl_2$. Volatile with steam. Mixes with alcohol and ether. It is set free from its salts by mineral acids, by HOAc, by oxalic, tartaric, citric, and malic acids, but not by butyric acid. When conc. valeric acid is added to a solution of cupric acetate, anhydrous cupric valerate separates in oily drops, which soon change to a greenish-blue crystalline powder of the hydrated salt; butyric acid would at once give a crystalline pp. (Larocque a. Huraut, *J. Ph.* [3] 9, 430).

Reactions.—1. *Oxidised* by chromic acid mixture at 20° to acetic acid and CO_2.—2. Boiling dilute HNO_3 forms nitro-valeric acid, methyl-malic acid, and a little di-nitro-propane (when prepared from valerian) or di-nitro-butane (when prepared from isoamyl alcohol) (Bredt, *B.* 14, 1782; 15, 2319; *cf.* Dessaignes, *A.* 79, 374).—3. Dilute alkaline $KMnO_4$ forms $CMe_2(OH).CH_2.CO_2H$.—4. Electrolysis of the K salt in conc. solution yields octane $C_2H_4Pr_2$ (Kolbe, *A.* 69, 259).—5. Passed through a *red-hot tube* it yields ethylene, propylene, butylene, and other hydrocarbons (Hofmann, *C. J.* 3, 121).—6. The Ca salt yields di-isobutyl ketone on distillation by itself, valeric aldehyde on distillation with calcium formate, and methyl isobutyl ketone on distillation with calcium acetate.

Salts.—NH_4A'. V. sol. water and alcohol.—$(NH_4)H_2A'_3$.—KA'. Deliquescent crystalline mass. S. (alcohol) 26 at 20°. [140°].—LiA'$\frac{1}{2}$aq. Nodules.—TlA'. V. sol. water.—$CaA'_2$3aq: needles (Barone, *A.* 165, 120; Schmidt a. Sachtleben, *A.* 193, 87; Schirokoff, *J. pr.* [2] 23, 286). S. 18·4 at 0° (Sedlitzky, *M.* 8, 563).—$CaA'_2$4aq.—$CaA'_2$5aq.—BaA'_2. Triclinic plates. S. 94 at 18°. S. (alcohol) 3·3 at 20°.—BaA'_2aq.—$BaA'_2$2aq.—SrA'_2.—$MnA'_2$2aq.—$ZnA'_2$2aq. Crystalline.—ZnA'_2. S. 1 in the cold. S. (80 p.c. alcohol) 1·7 in the cold; S. (ether) ·2 in the cold; ·5 at 35° (Wittstein, *J.* 1847, 557).—$ZnA'_2$12aq.—$ZnA'_2$3aq.—$ZnA'_2 2NH_3$ (Lutschak, *B.* 5, 30).—CuA'_2. Green crystalline pp.—CuA'_2aq.—$Bi_6A'_4(OH)_8O_3$ (Schucht, *Ar. Ph.* [3] 2, 97).—FeA'_3.—$FeA'_2(OH)$.—$Fe_2A'_4(OH)_2$.—PbA'_2: easily fusible laminæ.—$Pb_3A'_2O_2$. Groups of needles, sl. sol. water.—AgA'. S. ·177 at 0° (Sedlitzky); ·185 at 20° (Erlenmeyer).

Methyl ether MeA'. (116°). S.G. $\frac{0}{4}$ ·9007. C.E. (0°–10°) ·001174. S.V. 149·6 (Elsässer, *A.* 218, 315); 148·3 (R. Schiff, *A.* 220, 334). S.H. (21°–45°) ·491 (Kopp). Smells like bananas.

Ethyl ether EtA'. (134°). (E.); (135° cor.) (Perkin). S.G. $\frac{0}{4}$ ·8851 (E.); $\frac{15}{15}$ ·8714; $\frac{25}{25}$ ·8632 (P.). C.E. (0°–10°) ·001034. S.V. 173·4 (E.); 173·0 (S.). M.M. 7·615 at 18°. Oil, sol. alcohol. Smells like rennet apples and water-mint (Pierre a. Puchot, *A. Ch.* [4] 29, 234). Converted by sodium into oxy-decoic acid, ethyl ethoxy-decoate (Hantzsch, *A.* 249, 64), an acid $C_{20}H_{34}O_3$ [c. 127°] (295°), and other bodies (Greiner, *Z.* [2] 2, 460; Wanklyn, *C. J.* 17, 371; Geuther a. Greiner, *J.* 1865, 319).

n-Propyl ether PrA'. (156°). S.G. $\frac{0}{4}$ ·8809. C.E. (0°–10°) ·000997. S.V. 197·5 (Elsässer); 196·8 (Schiff).

Isopropyl ether PrA'. (142°). S.G. ^{0} ·870; ^{17} ·854 (Silva, *A.* 153, 136).

Di-chloro-propyl ether $C_3H_5Cl_2A'$. (245°) at 737 mm. S.G. ^{11} 1·149. Formed from epichlorhydrin and isovaleryl chloride (Truchot, *A.* 138, 298).

Isobutyl ether C_4H_9A'. (169°) (Elsässer, *A.* 218, 328); (173°) (P. a. P.). S.G. $\frac{0}{4}$ ·8736 (E.). ^{0} ·8884 (P. a. P.). C.E. (0°–10°) ·001027. S.V. 223·4 (E.).

Isoamyl ether $C_5H_{11}A'$. (188°) (Kopp; R. Schiff, *A.* 234, 344); (196°) (Balard); (190°) (Balbiano, *J.* 1876, 348); (194°) (Kahlbaum). S.G. ^{0} ·870 (Balbiano). S.V. 244·5. V.D. 6·1. Smells, when dissolved in alcohol (7 pts.), like apples.

Octyl ether $C_8H_{17}A'$. (250°). S.G. ^{12} ·862 (Zincke, *A.* 152, 6).

Cetyl ether $C_{16}H_{33}A'$. [25°]. (280°–290°) at 202 mm. S.G. ^{22} ·852 (Dollfus, *A.* 131, 283).

Allyl ether C_3H_5A'. (154°). Oil (Cahours a. Hofmann, *A.* 108, 296).

Glyceryl derivative v., GLYCERIN.

Chloride $Pr.CH_2.COCl$. (114°) at 726 mm. S.G. $\frac{20}{4}$ ·9887. μ_β 1·4213. R_∞ 49·14. Liquid, easily decomposed by water (Béchamp, *C. R.* 42, 224; Brühl, *A.* 203, 24).

Bromide C_5H_9OBr. (143°). Liquid.

Iodide C_5H_9OI. (168°) (Cahours, *C. R.* 44, 1252).

Anhydride $(C_5H_9O)_2O$. Mol. w. 186. (215°) (Chiozza, *A.* 84, 106). Converted by hydrated BaO_2 into the oily peroxide $(C_5H_9O)_2O_2$ (Brodie, *Pr.* 12, 655).

Aceto-valeric anhydride $(C_5H_9O).OAc$. (147°–160°) (Autenrieth, *B.* 20, 3187).

Amide $C_4H_9.CONH_2$. [128°] (Letts, *B.* 5, 669; Hofmann, *B.* 15, 982); [135°] (Schmidt a. Sachtleben, *A.* 193, 102). (231°). Silky plates, v. sol. water and alcohol.

Anilide $C_4H_9.CO.NHPh$. [115°] (Chiozza, *A. Ch.* [3] 39, 201; Kelbe, *B.* 16, 1200; *cf.* Dumas, *C. R.* 25, 475, 658; Dessaignes, *A.* 68, 333). Sl. sol. hot water, v. sol. alcohol and ether.

Nitrile $Pr.CH_2.CN$. *Isobutyl cyanide.* Mol. w. 83. (129°) (R. Schiff, *B.* 19, 567). S.G. ^{0} ·823. V.D. 2·89. Formed by heating ammonium valerate or valeramide with P_2O_5 (Dumas, Malaguti a. Leblanc, *C. R.* 25, 658). Occurs among the products of oxidation of gelatin and caseïn by chromic acid mixture (Schlieper, *A.* 59, 15; Guckelberger, *A.* 64, 72), of the action of chlorine on leucine (Schwanert, *A.* 102, 228), and of the action of conc. HNO_3 on castor oil (Hell a. Kitrosky, *B.* 24, 980). Formed also, together with valeramide, by heating valeric acid with potassium sulphocyanide (Letts, *B.* 5, 669). It is also got by the action of cold Ac_2O on the oxim of valeric aldehyde (Dollfus, *B.* 25, 1915). Prepared by digesting isobutyl iodide with KCy and alcohol (Erlenmeyer a. Hell, *A.* 160, 266). Liquid, smelling like almonds, dissolving in about four times its volume of water

Sodium converts it, on heating, into **cyanbutine** $C_{15}H_{27}N_3$, crystallising in stellate groups of needles, which yield B'HCl and $B'_2H_2PtCl_6$, and is converted by nitrous acid into $C_{15}H_{26}(OH)N_2$ [89°] (E. von Meyer, *J. pr.* [2] 37, 407).

Active valeric acid $CHMeEt.CO_2H$. *Methyl-ethyl-acetic acid. Hydrotiglic acid.* (177° i.V.). S.G. $\frac{24}{175}$ ·938 (Saur). S.V. 129·1 (Lossen, *A.* 254, 60). Occurs in the essential oil from the fruit of *Angelica Archangelica* (R. Müller, *B.* 14, 2476).

Formation.—1. By oxidation of isoamyl alcohol.—2. By reducing tiglic acid with HI and P (Schmidt a. Berendes, *A.* 191, 117).—3. By heating methyl-ethyl-malonic acid (Bischoff a. Conrad, *A.* 204, 151).—4. From methyl-ethyl-acetoacetic ether (Saur, *A.* 188, 257).—5. By reducing angelic acid (Schmidt, *A.* 208, 261).—6. By reducing bromo-hydro-tiglic acid (Pagenstecher, *A.* 195, 121).—7. By the action of NaOEt and EtI on propionyl-propionic acid (Israel, *A.* 231, 219).—8. By oxidation of the corresponding aldehyde (Lieben a. Zeisel, *M.* 7, 56).

Properties.—The acid obtained by synthetic methods is inactive, but when obtained by oxidation of active amyl alcohol it is dextrorotatory, but is mixed with inactive isovaleric acid. By oxidation of an amyl alcohol $[\alpha]_D = -4·4°$ Guye and Chavanne (*C. R.* 116, 1454) obtained a valeric acid (174°), $[\alpha]_D = +13·6°$, S.G. $\frac{22}{22}$ ·938. By oxidation of an amyl alcohol $[\alpha]_D = -5·2°$ at 22° Rogers (*C. J.* 63, 1130) got a valeric acid (175°), S.G. $\frac{22}{22}$ ·936, $[\alpha]_D = +13·9°$ at 22°. Methyl-ethyl-acetic acid can be separated from isopropyl-acetic acid through the greater solubility of its silver salt. Dilute $KMnO_4$ oxidises methyl-ethyl-acetic acid to $CMeEt(OH).CO_2H$.

Salts.—CaA'_2 5aq: needles. S. (of CaA'_2)).—BaA'_2: gummy mass.—ZnA'_2. Needles, ore sol. cold than hot water.—CuA'_2: bluish-een, crystalline pp.—AgA': groups of needles. 1·13 at 20° (C. a. B.); 1·11 at 1° (Sedlitzky, . 8, 568).

Ethyl ether EtA'. (133·5° i.V.). S.G. $\frac{1}{0}$ ·8695.

Nitrile $C_5H_{11}N$. (125°). S.G. ^{0} ·8061. ormed by adding Na and EtI to a solution of cetonitrile in benzene (Hanriot a. Bouveault, *l.* [2] 51, 173). Liquid.

Valeric acid $CMe_3.CO_2H$. *Tri-methyl-acetic cid.* [35°]. (163·5° i.V.). S.G. ^{50} ·905. S. 2·2 ; 20°. *Heat of neutralisation*: Gal a. Werner, *l.* [2] 46, 801. Formed by heating its nitrile ith alcoholic potash or conc. HClAq at 00° (Butleroff, *A.* 165, 322; 170, 151; 173, 355; . 5, 478). Formed also by action of CrO_2 on inacolin (Friedel a. Silva, *B.* 6, 146, 826) and n tri-methyl-pyruvic acid (Glücksmann, *M.* 10, 77). Monometric crystals. Does not yield a romo- derivative on heating with Br, either lone or in presence of P (Reformatzky, *B.* 23, 596).

Salts.—NaA' 2aq. Prisms, v. sol. water.—$H_2A'_2$. Needles, m. sol. water.—CaA'_2 5aq.—aA'$_2$ 4aq. S. 7 at 1°.—SrA'_2 5aq.—BaA'_2 5aq. . 34 at 2° (Landau, *M.* 14, 707).—MgA'_2 8aq. -ZnA'_2 aq. S. (of ZnA'_2) 1·7 at 20°. The cold aturated solution becomes filled on warming with a solid salt, which dissolves up again on cooling.—PbA'_2.—$PbHA'_3$: needles.—CuA'aq: greenish pp.—AgA'. S. 1·1 at 1°; 1·27 at 27° (Stiassny, *M.* 12, 599).

Methyl ether MeA'. (101°) (Butleroff).

Ethyl ether EtA'. (118·5° i.V.). S.G. ^{0} ·875.

Tert-butyl ether C_4H_9A'. (135° i.V.).

Amyl ether $CMe_3.CH_2A'$. (165°) (Tissier, *Bl.* [2] 24, 558).

Chloride $CMe_3.COCl$. (106°).

Anhydride $(CMe_3.CO)_2O$. (190°).

Amide $CMe_3.CO.NH_2$. [154°]. (212°). Formed by heating the ammonium salt in sealed tubes at 230° (Franchimont a. Klobbie, *R. T. C.* 6, 238). Long needles. Decomposed by pure HNO_3 (S.G. 1·53), with evolution of N_2O.

Methylamide $CMe_3.CO.NHMe$. [91°]. (204°).

Dimethylamide $CMe_3.CO.NMe_2$. (186°).

Ethylamide $CMe_3.CO.NHEt$. [49°]. (204°).

Diethylamide $CMe_3.CO.NEt_2$. (203°). S.G. ^{15} ·891.

Nitrile $CMe_3.CN$. *Tert-butyl cyanide.* [16°]. (106°). Formed, together with a **polymeride** (160°), by the action of tert-butyl iodide on dry potassio-mercuric cyanide below 5° (Butleroff, *A.* 170, 151; Freund a. Lenze, *B.* 23, 2866; 24, 2161). Crystalline mass with pungent smell. On heating with aniline hydrochloride it yields phenyl-valeramidine, which forms an oxalate [192°]. Hydroxylamine forms the amidoxim $CMe_3.C(NH_2):NOH$ [116°].

References.—Amido-, Bromo-, Chloro-, Iodo-, Nitro-, Nitroso-, and Oxy- valeric acids.

***n*-VALERIC ALDEHYDE**

$CH_3.CH_2.CH_2.CH_2.CHO$. (103°). S.G. ^{11} ·819. Formed by distilling calcium *n*-valerate with calcium formate (Lieben a. Rossi, *A.* 159, 70; Zander, *A.* 224, 81).

Isovaleric aldehyde $(CH_3)_2CH.CH_2.CHO$. *Valeral.* Mol. w. 86. (92·5°). S.G. $\frac{15}{15}$ ·8041; $\frac{25}{25}$ ·7981 (Perkin, *C. J.* 45, 477). μ_β 1·3934. R_∞ 40·66 (Brühl). V.D. 43·06 (calc. 43) (Schröder, *B.* 4, 400, 468). S.V. 118·5. Formed by oxidation of isoamyl alcohol (Dumas a. Stas, *A. Ch.* [2] 73, 145; Parkinson, *A.* 90, 114; Kolbe a. Guthrie, *A.* 109, 296). Formed also by distilling calcium iso-valerate with calcium formate (Limpricht, *A.* 97, 370), by the distillation of isovalerates (Chancel, *A.* 60, 318; Ebersbach, *A.* 106, 262; Schmidt, *B.* 5, 600), by oxidation of gluten (Keller, *A.* 72, 34) and castor oil (Arzbächer, *A.* 73, 202), and by the action of SO_3 on leucine (Schwanert, *A.* 102, 226).

Properties.—Neutral oil, with pungent fruity odour. Polymerises on keeping. Mixes with alcohol and ether. On heating with ammonium sulphocyanide it yields a dark-red liquid, sol. alcohol, ether, and HOAc (Brodsky, *M.* 8, 37). Alkaline sodium nitroprusside gives a violet-red colour, destroyed by HOAc (Von Bitto, *A.* 267, 376). Combines with sodium bisulphite, forming $(C_5H_{10}O)NaHSO_3$.

Reactions.—1. Readily oxidised to valeric acid.—2. *Chlorine* forms mono- and di- chloro-valeric aldehydes, and, at 140°, oily $C_{10}H_{12}Cl_4O$ (204°), which is converted by alcoholic soda into $C_{10}H_{10}Cl_4O$ (209°).—3. PCl_5 forms $C_5H_{10}Cl_2$.—4. *Potash-fusion* gives valeric acid.—5. Heating with *lime* forms isoamyl alcohol, calcium valerate and other bodies (Fittig, *A.* 117, 68).—6. *Sodium-amalgam* and water slowly form isoamyl alcohol (Wurtz, *A.* 134, 201).—7. *Sodium* forms isoamyl alcohol, sodium valerate, decyl alcohol $C_{10}H_{22}O$ (203°), an oil $(C_{10}H_{18}O)_n$ (250°–290°), the compound $C_{20}H_{38}O_3$, and the acid $C_{10}H_{18}O_2$ (Borodin, *Z.* 1864, 353; *B.* 5, 480).—8. KOH at 0° produces an oily polymeride, lighter than water, not capable of combining with $NaHSO_3$, and yielding isovaleric aldehyde and the compounds $C_{10}H_{18}O$ and $C_{20}H_{38}O_3$ on distillation (Borodin, *B.* 6, 982). This polymeride, left in contact with Na_2CO_3Aq, often forms needles of $C_{20}H_{42}O_5$ [70°].—9. Heating with KOH forms the aldehyde $C_{10}H_{18}O$ and a compound $C_{20}H_{38}O_3$ (260°–290°). S.G. ·90.—10. Heating with *zinc* at 180° forms decenoic aldehyde $C_{10}H_{18}O$ (190°), S.G. ^{0} ·862 (Riban, *C. R.* 75, 96; Kekulé, *A.* 162, 77) and other products.—11. $ZnEt_2$ produces the oil $(C_{10}H_{18}O)_n$ in large quantity (Beilstein a. Rieth, *A.* 126, 242). $ZnMe_2$, followed by water, forms methyl-isobutyl-carbinol (Kuvsinoff, *J. R.* 1887, 204).—12. Dry K_2CO_3 at 50° forms an oily polymeride, which is reconverted at 180° into the aldehyde. Boiling with K_2CO_3 yields $C_{10}H_{18}O$ (*v. supra*), $C_{20}H_{38}O_3$ (265°–270°), and $C_{15}H_{28}O_2$ (235°–240°) (Gäss a. Hell, *B.* 8, 369).—13. Dry K_2CO_3 added to moist isovaleric aldehyde forms, after some days, crystals of a polymeride [84°], which is reconverted at 108° into the original aldehyde (Bruylants, *B.* 8, 414).—14. PH_4I forms a compound $(C_5H_{10}O)_4PH_4I$, crystallising from ether in plates [119°], converted by cold potash into $(C_5H_{10}O)_3PH_4.OH$, crystallising in prisms [125°], insol. water (De Girard, *A. Ch.* [6] 2, 33; *C. R.* 94, 215).—15. On heating with *hypophosphorous acid* in an atmosphere of hydrogen the compound $(C_5H_{10}O)_2H_3PO_2$ [160°] is formed. It yields BaA'_2 aq (Ville, *C. R.* 109, 71).—16. AcCl at 100° combines, forming chloro-amyl acetate $C_4H_9.CHCl.OAc$ (Maxwell Simpson, *Pr.* 27, 120). 17. *m-Amido-benzoic acid* forms $C_{12}H_{15}NO_2$ [c. 230°].—18. Dry HCl forms $(C_4H_9.CHCl)_2O$ (180°) (Bruylants, *B.* 8, 414).—19. Conc. NH_3Aq forms isovaleric aldehyde-ammonia $C_4H_9.CH(NH_2)OH$ 7aq [58°] (Erdmann, *A.* 130, 211; Petersen, *A.* 132, 158; Ljubavin, *B.* 6, 1460), which yields, on allowing its alcoholic solution to stand, or on boiling with potash, the oily 'trioxyamylamine' $C_{15}H_{33}NO_3$, forming B'HCl [113°] and $B'_2H_2PtCl_6$. $AgNO_3$ reacts with isovaleric aldehyde-ammonia, forming $(C_5H_{11}N)_2AgNO_3$ and $(C_5H_{11}N)_3AgNO_3$ (Goldschmidt, *B.* 11, 1200; Mixter, *J.* 1878, 438).—20. Alcoholic NH_3 at 150° forms valeritrine, hydrovaleritrine, and other bodies. Valeritrine $C_{15}H_{27}N$ is a very unstable liquid (250°–260°), yielding $B'HHgCl_3$ [88°], $B'_2H_2PtCl_6$, and $B'C_6H_3N_3O_7$ [130°]. Hydrovaleritrine $C_{15}H_{29}N$ or $C_{15}H_{31}N$ is a liquid, yielding crystalline B'HCl: S. 2·87 at 22°, not melted at 180° (Ljubavin, *B.* 6, 565).—21. H_2S passed into an aqueous solution forms thiovaleric aldehyde $C_5H_{10}S$ [69°]. An isomeride (115°) is got, together with a polymeride [94·5°], by heating isovaleric aldehyde with sulphur at 250° (Barbaglia, *B.* 13, 1574; 17, 2654; *G.* 11, 95; 16, 426).—22. CS_2 and NH_3Aq form carbovaleraldine $C_{11}H_{22}N_2S_2$ (Schröder, *B.* 4, 469; Mulder, *A.* 168, 237), which melts at 109° (Guareschi, *A.* 222, 311).—23. $NH_2.CS.OEt$ and HCl form $C_5H_{10}(NH.CS.OEt)_2$ [108°] (Bischoff, *B.* 7, 1078).—24. H_2Se passed into an aqueous solution of valeric aldehyde forms $C_5H_{10}Se$ [56·5°].—25. *Acetone* and dilute NaOH yield $PrCH_2.CH{:}CH.CO.CH_3$ (180°) (Barbier a. Bouveault, *C. R.* 118, 198).

Oxim $C_4H_9.CH{:}NOH$. Mol. w. 101. (163°). S.G. $\frac{20}{4}$ ·8934 (*in vacuo*). μ_D 1·437 (Petraczek, *B.* 16, 829; Trapesonzjanz, *B.* 26, 1428). It is a *syn*- oxim, because it yields valeronitrile when mixed with Ac_2O and ether (Dollfus, *B.* 25, 1915).

Isovaleric orthaldehyde. *Amylidene glycol.*

Acetyl derivative $C_4H_9.CH(OAc)_2$. (195°). Formed by heating isovaleric aldehyde with Ac_2O at 200°.

Benzoyl derivative $C_4H_9.CH(OBz)_2$. [111°]. (264°). Formed by heating the aldehyde with Bz_2O at 260° (Guthrie a. Kolbe, *A.* 109, 298).

Di-methyl ether $C_4H_9.CH(OMe)_2$. (124°). S.G. ^{10} ·852. Formed from isovaleric aldehyde (2 vols.), MeOH (5 vols.), and HOAc (1 vol.) (Alsberg, *J.* 1864, 486).

Di-ethyl ether $C_4H_9.CH(OEt)_2$. (168°). S.G. ^{12} ·835. Formed in like manner.

Di-isoamyl ether $C_4H_9.CH(OC_5H_{11})_2$. (c. 248°). S.G. ^{7} ·849.

Ethyl isoamyl ether $C_4H_9.CH(OEt)(OC_5H_{11})$. (c. 205°). S.G. ^{12} ·875. Formed by the action of Na on an ethereal solution of isovaleric ether (Greiner, *Z.* 1866, 465).

Valeric aldehyde $CHMeEt.CHO$. (91°). Formed by reducing tiglic aldehyde with iron and HOAc (Herzig, *M.* 3, 123; Lieben a. Zeisel, *M.* 7, 56), and by warming $CH_2{:}CH.CHEt.OH$ with dilute (1 p.c.) H_2SO_4 (Kondakoff, *J. R.* 20, 154).

Valeric aldehyde $CMe_3.CHO$. [3°]. (75°). S.G. ^{18} ·7927 (Tissier, *Bl.* [2] 24, 558).

Di-isovaleric aldehyde *v.* DECENOIC ALDEHYDE.

Reference.—DI-BROMO-, CHLORO-, IODO-, and OXY- VALERIC ALDEHYDE.

VALEROGUANAMINE $C_7H_{13}N_5$ *i.e.* $\left.\begin{array}{r}\mathrm{PrCH_2.C{:}N.C(NH)}\\ \mathrm{NH.C(NH)}\end{array}\right>\mathrm{NH}$. *Butylguanamine.* [173°]. Formed by heating guanidine isovalerate (Bandrowski, *B.* 9, 240; Haaf, *J. pr.* [2] 43, 76). Flat plates (from water). Weak base.—B'HCl: needles, v. sol. water.—$B'H_2SO_4$.—$B'AgNO_3$.

VALEROLACTIDE *v.* OXY-VALERIC ACID.

VALEROLACTONE *v.* OXY-VALERIC ACID.

VALERONE *v.* DI-ISOBUTYL KETONE.

VALERONITRILE *v.* *Nitrile* of VALERIC ACID.

VALEROVALERIC ACID *v.* VALERYL-VALERIC ACID.

DIVALERYL $C_{10}H_{18}O_2$ *i.e.* $C_4H_9.CO.CO.C_4H_9$. (270°–280°). Formed by the action of Na on valeryl chloride (Brühl, *B.* 12, 315). Oil.

VALERYL-ACETOPHENONE *v.* PHENYL BUTYL METHYLENE KETONE.

VALERYL CHLORIDE *v.* *Chloride* of VALERIC ACID.

VALERYL-CYANAMIDE *v.* CYANIC ACIDS.

VALERYLENE *v.* PENTINENES and also BROMO- and DI-CHLORO-VALERYLENE.

VALERYLENE TETRABROMIDE *v.* TETRA-BROMO-PENTANE.

VALERYLENE HYDRATE *v.* PENTENYL ALCOHOL.

VALERYLENE HYDROCHLORIDE *v.* CHLORO-AMYLENE.

VALERYL-VALERIC ACID. *Ethyl ether* $C_{12}H_{22}O_3$ *i.e.* $CH_2Pr.CO.CHPr.CO_2Et$. (206°) at 722 mm. Formed by the action of sodium on isovaleric ether (Greiner, *Z.* 1866, 461; Wohlbruck, *B.* 20, 2335). Oil, sol. alcohol and ether.

VALYLENE C_5H_6. Mol. w. 66. (50°). A product of the action of alcoholic potash on valerylene dibromide (Reboul, *A.* 135, 372). Liquid, with odour of garlic and prussic acid. Ammoniacal Cu_2Cl_2 ppts. yellow C_5H_5Cu, which yields the pure hydrocarbon on treatment with dilute HClAq. Bromine at 0° forms crystalline $C_5H_6Br_4$. Ammoniacal $AgNO_3$ yields a white pp. of C_5H_5Ag.

VANADATES *v.* VANADIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 851.

VANADIC ACIDS *v.* VANADIUM OXYACIDS, p. 851.

VANADIUM. V. At. w. 51·2. Mol. w. not known. Melts at a very high temperature; probably higher than m.p. of Mo, which does not melt at 1700°–1800° (Moissan, *C. R.* 116, 1225). S.G. 5·5 at 15° (Roscoe, *T.* 1869. 679). For emission-spectrum, obtained by using electric sparks, *v.* Thalén (*A. Ch.* [4] 18, 243)

Historical.—In 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapan in Mexico (*G. A.* 71, 7); to this metal he gave the name *erythronium*, but at a later time he thought the metal was only impure chromium. In 1830 Sefström found a new element in the bar-iron and refinery slags where iron-ore from Taberg in Sweden was smelted (*P.* 21, 43); this element he called *vanadium* (from a Scandinavian deity *Vanadis*). In the same year (*P.* 21, 49) Wöhler found that the lead ore examined in 1801 by Del Rio contained lead vanadate; and he showed that the metal which Del Rio had called erythronium, and had then supposed to be impure chromium, was really vanadium. In 1831 Berzelius supposed he had prepared vanadium by heating an oxychloride in NH_3, and also by heating the highest oxide with K (*P.* 22, 1); but in 1867 Roscoe (*T.* 1868. 1; 1869. 679; *v.* also 1870. 317) showed that one of the substances which until then had been taken to be the element V was a nitride, and that another substance, taken to be V, was an oxide of this element. Roscoe obtained pure V by heating VCl_2 to redness for many hours in dry H. Roscoe was led to doubt the accuracy of the statement of the properties and at. w. of V that had been accepted on the authority of Berzelius, because he found that several compounds of V and Pb were isomorphous, but that it was impossible to assign comparable formulæ to these compounds if the at. w. given by Berzelius for V were accepted (*v. T.* 1868. 1 *et seq.*). Berzelius gave the value 68·5 to the at. w. of V; he assigned the formulæ VO, VO_2, and VO_3 (O = 8) to the three oxides, and classed V with Cr, Mo, and W. Roscoe's researches showed that the at. w. of the metal is 51·2, that the oxides are best represented as V_2O_3, V_2O_4, and V_2O_5, that the substance thought to be V was really chiefly V_2O_2, that the compound supposed by Berzelius to be VCl_3 was $VOCl_3$, and that V must be classed with P and As.

Occurrence.—Small quantities of compounds of V are found fairly widely distributed; the element does not occur uncombined. The chief minerals that contain V compounds are *mottramite* (Cu-Pb vanadate), *descloizite* (Pb-Zn vanadate), *dechenite* (Pb-Zn-Cu vanadate), *roscoeite* (Al vanadate with K silicate), *vanadinite* (vanadate of lead with lead chloride), and some other minerals, which generally contain vanadates of Cu, Pb, Zn, or Ca. Small quantities of compounds of V are found in all *pisolitic limonites* (Böttger, *C. C.* 1873. 514), in some *pitchblendes*, *clays*, and *basalts*, and in a few other rocks. Compounds of V have also been found, in small quantities, in the slag from copper extraction works (Karsten, *P.* 52, 629; Witz a. Osmond, *Bl.* [2] 38, 49); in many specimens of pig-iron (*v.* Riley, *C. J.* 17, 21; *cf.* Hodges, *C. N.* 26, 238; Walz, *Am. Ch.* 6, 453); in some meteorites (*v.* Apjohn, *C. J.* 27, 104); in caustic soda and sodium phosphate (Schöne a. Rammelsberg, *B. B.* 1864. 681; Donath, *D. P. J.* 240, 318); and, according to Lockyer (*Pr.* 27, 279), probably in the sun.

Preparation.—1. From the refinery slag of the Taberg iron-ore. The finely-powdered slag is heated with KNO_3 and Na_2CO_3, the fused substance is digested with boiling water, and solution of a salt of Ba or Pb is added to the filtered liquid; the ppd. Ba or Pb vanadate is decomposed by boiling with a slight excess of H_2SO_4Aq, and the solution is filtered from $BaSO_4$ or $PbSO_4$; the filtrate is neutralised by NH_3Aq and concentrated, and pieces of NH_4Cl are placed in the liquid until some NH_4Cl remains undissolved; the NH_4VO_3 which is thus ppd. as a white crystalline powder is washed with conc. NH_4ClAq, and then with alcohol, and is then decomposed by heating strongly in an open vessel, whereby V_2O_5 is produced (Berzelius, *P.* 22, 1). Wöhler (*A.* 78, 125) employed a very similar process for preparing V_2O_5 from *limonite*.—2. From vanadinite. L'Hôte (*C. R.* 101, 1151) recommends to mix finely-powdered *vanadinite* (approximately $3Pb_3V_2O_8.PbCl_2$) with four times its weight of lampblack and a little oil, to heat strongly in a closed vessel, and then to heat to 300° in a stream of dry Cl, whereby $VOCl_3$ is formed, and distilled over into a cooled U-tube; other compounds of V are readily prepared from $VOCl_3$.—3. From the cobalt-ore of Mottram in Cheshire. This source of V compounds was discovered by Roscoe (*v. C. J.* [2] 6, 326). The Cheshire Keuper sandstone contains carbonates of Cu, carbonate of Pb and *galena*, *black cobalt-ochre*, iron oxides, and salts of As, Ag, Mn, and Ba. The compound of V was probably *vanadinite*. The sandstone was crushed, and the metallic compounds were dissolved by HClAq; bleaching-powder and milk of lime were added till the reaction was alkaline; and it was from the pp. thus obtained that Roscoe prepared V and its compounds. The lime pp. contained chiefly As, Cu, Fe, Pb, V, and Ca in combination with SO_4 and PO_4; it was heated in a furnace with ground coal to remove As, then roasted with a quarter its weight of Na_2CO_3

and lixiviated with water; the solution was saturated with H_2S and filtered, and H_2S was boiled off; crude oxide of V was then ppd. by NH_3Aq; the oxide was dried and heated with conc. HNO_3Aq to oxidise it to vanadic acid, which was then boiled with saturated $(NH_4)_2CO_3Aq$, and the somewhat soluble NH_4 vanadate was crystallised from water, and then strongly heated in an open vessel; the V_2O_5 thus obtained was suspended in water into which NH_3 was passed; the solution of NH_4 vanadate was filtered from silica, phosphates, &c., evaporated to dryness, and heated in an open vessel until V_2O_5 remained.

The metal vanadium is prepared by reducing VCl_2 in H (for preparation of VCl_2 *v.* VANADIUM DICHLORIDE, p. 844). The process is conducted in perfectly pure and dry H; every trace of moisture and air must be excluded. The pure and dry H is passed for 12 hours through a porcelain tube, connected (by specially arranged paraffin-joints) by a glass tube to the H apparatus; the VCl_2 is then placed in the porcelain tube (a special arrangement for doing this is described by Roscoe), and H is passed through the apparatus for 6 hours. The porcelain tube is then gradually heated to full redness, and the passage of H is continued so long as HCl is given off, after which the tube is allowed to cool for several hours in the stream of H. The process occupies from 40 to 80 hours according as from 1 to 4 g. of VCl_2 are used. The V thus obtained contains traces of H and O. Reduction proceeds more quickly at a white heat, but the product is not so pure; it generally contains c. 95 to 96 p.c. V. (For details, and figures of the apparatus, *v.* Roscoe, *T.* 1869. 679; 1870. 317; or *C. J.* [2] 8, 344; 9, 23.)

Moissan (*C. R.* 116, 1225) obtained V containing from 17·5 to 25·7 p.c. C, by heating a mixture of C and one of the oxides of V in an electric furnace, using a current of 70 volts and 1,000 ampères; with a current of 70 volts and 850 ampères reduction proceeded very slowly.

Vanadium, mixed with V_2O_3, was obtained by Roscoe (*l.c.*) by strongly heating a mixture of one of the chlorides of V with Na in an atmosphere of H, and lixiviating with water; the admixed black, powdery V_2O_3 can be removed from the heavier, grey, lustrous, metallic powder, by repeated washings with water, and a substance containing c. 91 p.c. V can be obtained.

The substance supposed by Berzelius (*P.* 22, 1) to be V, and obtained by heating V_2O_5 with K, was shown by Roscoe to consist chiefly of V_2O_2. The black powder which Uhrlaub (*P.* 103, 134) prepared by heating V oxychloride in NH_3, and which he supposed to be V, was found by Schafarik (*W. A. B.* 33, 5) to be VN_2 (*cf.* Roscoe, *l.c.*).

Properties.—A light-grey, lustrous powder; under the microscope it is seen to be composed of crystalline, silver-white particles. Does not become coherent and dense when strongly compressed. S.G. 5·5 at 15°. Not magnetic. Is not oxidised in air at the ordinary temperature, nor by moistening and then drying *in vacuo*. Has not been melted, except perhaps when reduced from the oxides by C in an electric furnace (*v.* Moissan, *C. R.* 116, 1225). When powdered V is thrown into a Bunsen flame it burns brilliantly; when strongly heated in O it forms V_2O_5; and when slowly heated in air it perhaps forms V_2O, then V_2O_3, V_2O_4, and finally V_2O_5. Burns in Cl, forming VCl_4; combines with N to form VN; also combines with S. V is insoluble in HClAq; it dissolves in hot conc. H_2SO_4 and in HNO_3Aq. V dissolves in molten NaOH, giving off H, and forming a vanadate. V acts on glass vessels in which it is heated, forming a compound with Si; it also alloys with Pt (R., *l.c.*).

The at. w. of V has been determined (1) by reducing V_2O_5 to V_2O_3 by heating in H (Berzelius, *P.* 22, 15 [1831]; Roscoe, *T.* 1868. 8); (2) by oxidising V_2O_3 to V_2O_5 by HNO_3 (B., *l.c.* [1831]); (3) by analysing $(V_2O_2)(SO_4)_2.4H_2O$ (B., *l.c.*, p. 18 [1831]); (4) by ppg. $VOCl_3$ by $AgNO_3Aq$, removing excess of Ag from the filtrate, evaporating to dryness, heating, and weighing the V_2O_5 produced (B., *l.c.* [1831]); (5) by determining the weight of Ag required to ppt. the Cl from $VOCl_3$; also by weighing the AgCl ppd.; also by filtering from AgCl, evaporating, and weighing the V_2O_5 obtained (Roscoe, *T.* 1868. 23); (6) by determining V.D.s of, and analysing, VCl_4 and $VOCl_3$ (*q. v.*). The results obtained by Berzelius (with the necessary corrections on account of the wrong formulæ used by him; *v.* Roscoe, *l.c.*) gave values for at. w. of V varying from 49·3 to 52·5; Roscoe's values from the reduction of V_2O_5 to V_2O_3 varied from 51·13 to 51·55, and from the analyses of $VOCl_3$ from 50·32 to 51·877. The S.H. of V has not been determined.

Vanadium is both metallic and non-metallic in its reactions. V_2O_4 interacts with strong acids to form divanadyl salts, $V_2O_2(SO_4)_2$, &c.; hypovanadates $V_4O_7(OM)_2$ are also derived from a hydrate of V_2O_4; V_2O_5 interacts with conc. H_2SO_4 to form $V_2O_5.3SO_3$ and $V_2O_5.2SO_3.xH_2O$; V_2O_5 also forms $V_2O_5.H_2O$ (=HVO_3) and $V_2O_5.2H_2O$ (=$H_4V_2O_7$), which react as acids, and salts of the acid H_3VO_4 are also known; V_2O_5 also combines with various acidic oxides (P_2O_5, MoO_3, &c.) and basic oxides, to form complex, salt-like compounds. The sulphides of V dissolve in alkali sulphide solutions; several thiovanadates have been isolated, *e.g.* $(NH_4)_3VS_4$; and also thio-oxyvanadates, *e.g.* Na_3VS_3O. The haloid compounds of V are generally decomposed by water to oxyhaloid compounds.

Vanadium is placed in Group V., with N, P, As, Nb, Sb, Di, Er, Ta and Bi. V is the second member of the even series family of this group, the family consisting of N, V, Nb, Ta and an unknown element with an at. w. between those of Th (=232) and U (=239). Group V does not show a marked division into families; the gradation of properties from N to Bi is fairly regular, nevertheless the families (1) N and P, (2) V, Nb and Ta, (3) As, Sb and Bi are distinctly indicated. No hydrides of members of the vanadium family have been isolated with certainty. The highest oxides, M_2O_5, are salt-forming; all of them interact with alkalis to form salts containing the elements M in the acidic radicles; V_2O_5 also forms basic salts $(VO)_xR_y$, with strong acids; normal salts have not been obtained by the reactions of M_2O_5 with acids. Oxyacids of V, viz. HVO_3 and $H_4V_2O_7$, have been isolated, but definite oxyacids of Nb and Ta are unknown. Both Nb and Ta form chlorides, corresponding with their highest oxides M_2O_5; but the highest haloid compound of V is VX_4, corresponding with V_2O_4; oxyhaloid compounds of V of the form of VX_3 exist ($VOCl_3$, $VOBr_3$) (*v.* Nitrogen group of elements, vol. iii. p. 571).

In considering the relations between vanadium and the elements of Group V., the position of V in series 4 must be taken into account: as compared with the elements that form series 3, in which series P is placed, the elements of the vanadium series are metallic (V is preceded by Ti, Sc, Ca and K, and is followed by Cr, Mn, and the iron elements); the elements of the vanadium series are nearly as metallic, and also as non-metallic, as Rb, Sr, Y, Nb, Mo, —, and the Ru metals, which elements form series 6, *i.e.* the niobium series. Hence V would be expected to be distinctly more like a metal, in its chemical relations, than P, and about equal to Nb in its metallic and non-metallic tendencies. As V is the second member of the even series family of Group V., it might be expected to resemble N, which is the first of the even series elements of this group; but it is to be remembered that the differences between the first and second even series members of the groups (*i.e.* the differences between Li and K, Be and Ca, B and Sc, C and Ti, N and V, O and Cr, F and Mn), become more marked in passing from Group I. to Group VII., and it is also to be remembered that the resemblances between the first even series members and the succeeding odd series members, become more marked as the atomic weights increase; F is more like Cl and Br than O is like S, Se, and Te; but O resembles S, Se, and Te more than N resembles P, As, Sb, &c.; and C is more like Si, Ge, Sn, &c., than B is like Al, Ga, In, &c.; but C less resembles Si, &c., than N resembles P, &c.

Reactions and Combinations.—(Roscoe, *T.* 1869. 679; 1870. 317.) 1. Heated in *air*, V burns to V_2O_5; lower oxides are first formed if the temperature is low.—2. Does not decompose *water* at 100°.—3. Heated to redness in *chlorine* burns to VCl_4; heated in *bromine* produces VBr_3; does not combine with *iodine*.—4. Heated with excess of *sulphur*, V forms V_2S_3 (*v.* Kay, *C. J.* 37, 728).—5. Heating in a stream of pure *nitrogen* produces VN.—6. V combines directly with *silicon* and also with *platinum*.—7. *Molten potash* or *soda* dissolves V, forming an alkali vanadate and giving off H.—8. V dissolves in *conc. sulphuric acid* (? forming a vanadyl salt); also in *nitric acid*, probably forming a basic nitrate; also, slowly, in *hydrofluoric acid* (? forming VF_3).

Detection and Estimation.—Small quantities of compounds of V give a colourless borax or microcosmic salt bead in the outer flame, becoming green in the reducing flame; if much V compound is present the bead is yellow in the outer flame. Solutions of V_2O_5 in acids are not ppd. by H_2S, but are reduced to solutions of V_2O_2 which are lavender-blue; if reduction is effected by Zn, Cd, or Na-amalgam the liquid becomes green, then blue, and finally lavender-blue; after reduction the solution bleaches indigo very rapidly, and soon absorbs O. Solutions of vanadates, either neutral or acidified by acetic acid, give finely-divided black pps. with tincture of galls, and the liquids appear like ink. When an acidified solution of a vanadate is shaken with an ethereal solution of H_2O_2, the latter solution becomes dark red (Werther, *J. pr.* 88, 195).

Vanadium is generally estimated by converting it into an ammonium salt, strongly heating this in air, and either weighing the V_2O_5 thus produced or heating in H and weighing the V_2O_3 that remains. For a volumetric method of estimating V *v.* Gerlach (*B.* 10, 1216).

Vanadium, acids of, *v.* Vanadium oxyacids, and salts and derivatives thereof, p. 851.

Vanadium, bromides of. Only one bromide of V has been obtained.

Vanadium tribromide VBr_3. Mol. w. not known; from analogy of PBr_3, $AsBr_3$, &c., the formula VBr_3 is probably molecular. Formed by heating V or VN to redness in vapour of Br. Also by passing Br vapour over a mixture of V_2O_3 and C kept at a red heat; $VOBr_3$ is formed, then $VOBr_2$, and then VBr_3 sublimes (Roscoe, *T.* 1870. 317). Roscoe (*l.c.*) recommends to prepare VBr_3 by placing pure VN in a porcelain boat in a tube of hard glass, driving out all air by dry CO_2, then passing vapour of Br through the tube while that part where the boat is placed is heated to redness, when brown vapours are given off and condense on the cooler parts of the tube, and finally driving out all traces of Br by a stream of dry CO_2. VBr_3 is a greyish black, opaque, amorphous, very deliquescent solid; loses Br even in a sealed tube; heated gently in air gives V_2O_3, and at a higher temperature V_2O_5. Dissolves in water, without giving off any Br, forming a brown liquid which goes green on addition of a few drops of HClAq; this reaction is said by R. to be characteristic of a salt of V_2O_3.

Vanadium, chlorides of. Three chlorides have been isolated: VCl_2, VCl_3, and VCl_4. V burns when heated in Cl, forming VCl_4, and the other chlorides are formed by reducing VCl_4 by H. The V.D. of VCl_4 has been determined, and the formula VCl_4 is molecular; the formula VCl_3 is probably molecular, from the analogy of $AsCl_3$, PCl_3, $BiCl_3$, &c.; VCl_2, AsI_2, PI_2 and $BiCl_2$ are the only haloid compounds of the form MX_2 that have been isolated in Group V.; the mol. w.s of these compounds have not been determined.

Vanadium tetrachloride VCl_4. Mol. w. 192·68. Prepared by Roscoe (*T.* 1869. 691).

Formation.—1. V or VN is heated in Cl.—2. The vapour of $VOCl_3$, mixed with excess of Cl, is passed slowly over a long layer of sugar-charcoal heated to redness.

Preparation.—VN is heated to redness in a tube of hard glass, in a current of pure, dry Cl, which must be free from air. The first few drops of distillate are rejected, as they contain traces of $VOCl_3$ formed from traces of oxide in the nitride used. The dark-red liquid that is formed is saturated with dry Cl, then heated for some hours in a current of dry CO_2 in a vessel connected with an upright condenser, and then fractionated.

Properties and Reactions.—A thick, dark, brownish-red liquid; boils at 154° under 760 mm. pressure. S.G. 1·8584 at 0°, 1·8363 at 8°, 1·8159 at 30°. V.D. 98·1 at c. 200°. Does not solidify at any temperature above −18°. Slowly decomposes to VCl_3 and Cl at ordinary temperatures, more quickly when exposed to light, and rapidly when heated. Gives off white fumes in the air. Dissolves in water, forming a blue solution, which does not bleach; this solution is oxidised by $KMnO_4Aq$ to $HClAq$ and V_2O_5Aq, $2VCl_4$ taking up O. Reacts violently with alcohol and ether, forming deep-coloured liquids. When heated with Br in a sealed tube, VCl_3 is formed. VCl_4 does not combine with Cl to form a higher chloride. H_2S reacts with VCl_4 to form VCl_3, HCl, and S (Kay, *C. J.* 38, 736).

VANADIUM TRICHLORIDE VCl_3. Mol. w. not determined, but formula is probably molecular from analogy of PCl_3, $AsCl_3$, &c. Prepared by heating VCl_4 in a retort as long as Cl is given off, and heating the residual solid to 160° in a stream of dry CO_2 (Roscoe, *T.* 1869. 691). Also by heating pure V_2S_3 in a stream of dry, air-free Cl, separating S_2Cl_2 by repeatedly distilling the liquid product, and heating the residue at 140° in dry CO_2 to remove the last traces of S_2Cl_2 (Halberstadt, *B.* 15, 1619). Lustrous, peach-blossom coloured tablets, resembling $CrCl_3$; S.G. 3·0 at 18°. Deliquesces very rapidly in air to a brown liquid, which goes green on addition of a drop or two of HClAq; this solution is oxidised by $KMnO_4Aq$, $2VCl_3$ taking up 2O, to HClAq and V_2O_5Aq. Soluble in alcohol and in ether. Heated in air forms V_2O_5. Heated in H is reduced to VCl_2 and then, gradually, to V.

VANADIUM DICHLORIDE VCl_2. Mol. w. not known. Formula possibly V_2Cl_4. Prepared by passing vapour of VCl_4, mixed with a large excess of pure, dry H, through a glass tube heated to dull redness. The distillation of VCl_4 should be slow, and the mixture of vapour of VCl_4 and H should be brought at once into the heated part of the tube. Forms apple-green, micaceous, hexagonal plates; S.G. 3·23 at 18°; very hygroscopic. Dissolves in water, forming a violet solution, which bleaches indigo and litmus, and reacts as a solution of a salt of V_2O_2. Dissolves in alcohol and in ether. The solution in water is oxidised by $KMnO_4Aq$ to HClAq and V_2O_5Aq, $2VCl_2$ taking up 3O. Heated in H, is slowly reduced to V; heating to whiteness in NH_3 produces VN (Roscoe, *l.c.*).

Vanadium, ferrocyanide of, *v.* vol. ii. p. 337.

Vanadium, fluorides of. Only one fluoride, VF_3, has been isolated; there are indications of the existence of a higher fluoride in solutions in conc. HFAq.

VANADIUM TRIFLUORIDE $VF_3.3H_2O$. Mol. w. not known; formula probably molecular, from analogy of trihalides of other elements of Group V. Prepared by evaporating a solution of V_2O_3 in HFAq at 100°, and crystallising from water containing a little HFAq. A white crystalline crust, consisting of rhombohedra. Easily soluble in water; solution reacts acid. Insoluble in conc. alcohol. Effloresces in air; loses some water at 100°, and all at 130°, with absorption of O; V_2O_5 is formed on heating to redness in air. An aqueous solution reduces Ag salts to Ag, Hg and Cu salts to mercurous and cuprous salts; alkalis or alkali carbonates ppt. $V_2O_3.xH_2O$ from VF_3Aq (E. Petersen, *J. pr.* [2] 40, 44).

Vanadofluorides. (*Fluovanadites.*) A number of compounds of the forms $VF_3.xM^{I}F$ and $VF_3.xM^{II}F_2$ were obtained by Petersen (*l.c.*) by adding various fluorides to solutions of V_2O_3 in HFAq, and crystallising. These salts are generally greenish coloured, and crystalline; most of them are soluble in water, but not in KFAq; they lose water of crystallisation from 100° to 200°. The vanadofluorides may be regarded as salts of hypothetical acids HVF_4, H_2VF_5, and H_3VF_6; they may also be formulated as double salts (*v. supra*). The following salts are described by Petersen (*l.c.*):

Ammonium vanadofluorides $NH_4VF_4.2aq$, $(NH_4)_2VF_5.aq$, and $(NH_4)_3VF_6$.

Cadmium vanadofluoride $CdVF_5.7aq$ (Piccini a. Giorgis, *G.* 22 [1] 55).

Cobalt vanadofluoride $CoVF_5.7aq$.

Nickel vanadofluoride $NiVF_5.7aq$.

Potassium vanadofluoride $K_2VF_5.aq$

Sodium vanadofluoride $Na_5V_2F_{11}.aq = 2VF_3.5NaF.aq$ (? $Na_2VF_5.aq$).

Zinc vanadofluoride $ZnVF_5.7aq$ (P. a. G., *l.c.*).

Vanadoxyfluorides. (*Fluoxyvanadates.*) These salts are generally produced by dissolving V_2O_5 in HFAq, adding metallic fluorides, and crystallising; also by dissolving V_2O_5 in solutions of metallic fluorides, and crystallising; some of them are obtained by treating solutions of V_2O_5 in metallic fluoride solutions with reducing agents, and then crystallising. The vanadoxyfluorides have been examined by Baker (*C. J.* 33, 388 [1878]), Ditte (*C. R.* 105, 1067; 106, 270 [1888]), Piccini a. Giorgis (*G.* 18, 186 [1889]; *G.* 22 [1] 55 [1892]), and Petersen (*B.* 21, 3257 [1888]; more fully in *J. pr.* [2] 40, 193, 271 [1890]). There are still considerable discrepancies between the results obtained by the different observers. For a criticism of Baker's results *v.* Petersen (*J. pr.* [2] 40, 289–92). The vanadoxyfluorides belong to two main classes: (1) those obtained by dissolving V_2O_5 in HFAq, adding a fluoride (or carbonate), and crystallising: many of these salts are also formed by dissolving V_2O_5 in solutions of fluorides, and crystallising; (2) those obtained by partially reducing solutions of V_2O_5 in HFAq, then adding fluorides, and crystallising. The first class of salts may be divided into (i.) those wherein one atom of O in V_2O_5 is substituted by 2F, and which, therefore, are represented as $xMF.yVO_2F$ (V_2O_5 gives $V_2O_4F_2 = 2VO_2F$); and (ii.) those wherein 3O in V_2O_5 is substituted by 6F, and which, therefore, are represented as $xMF.yVOF_3$ (V_2O_5 gives $V_2O_2F_6 = 2VOF_3$). Salts of the second class are regarded as compounds of MF with VOF_2, and VOF_2 is looked on as obtained by substituting 2O in V_2O_4 by 4F (V_2O_4 gives $V_2O_2F_4 = 2VOF_2$). The salts derived from V_2O_5, *i.e.* $xMF.yVO_2F$ and $xMF.yVOF_3$, are often called *fluoxyvanadates*, and those derived from V_2O_4, *i.e.* $xMF.yVOF_2$, are often called *fluoxyhypovanadates*; the former class of salts will here be called *vanadoxyfluorides*, and the latter *hypovanadoxyfluorides*.

Ammonium vanadoxyfluorides. Three salts are described by Baker (*C. J.* 33, 388 [1878]), and also by Piccini a. Giorgis (*G.* 22 [1] 55, [1892]; the formulæ given by the different experimenters do not agree.

Lamellar ammonium vanadoxyfluoride. This salt was obtained by Baker by dissolving V_2O_5 in NH_4HF_2Aq, and then adding more NH_4HF_2; it separates in small yellow, pearly, hexagonal plates. P. a. G. obtained the salt by dissolving V_2O_5 in a slight excess of HFAq, adding NH_4F in the ratio $3NH_4F:2V_2O_5$, and evaporating. B. gives the formula $6NH_4F.V_2O_5.2VOF_3.2aq$; P. a G. give the formula $3NH_4F.2VO_2F$. If both formulæ are expressed as $3NH_4F.2VO_xF$, then $x = 1\frac{3}{4}$ in Baker's formula and = 2 in the formula of P. a. G. A salt obtained by Petersen (*J. pr.* [2] 40, 193, 271 [1890]), by a similar process to those used by B. and by P. a. G., was formulated by him as $7NH_4F.4VO_2F.HF$.

Pyramidal ammonium vanadoxyfluoride. Obtained by Baker by adding NH_4HF_2 to a solution of the lamellar salt; P. a. G. prepared the salt by dissolving V_2O_5 in excess of HFAq, and exactly neutralising the hot solution by NH_3Aq. This salt crystallises in yellow, simple pyramids (Baker). The formula assigned by B. is $12NH_4F.V_2O_5.2VOF_3$, while that given by P. a. G. is $3NH_4F.VO_2F$; Petersen gives the same formula as P. a. G. If Baker's formula is expressed as $3NH_4F.VO_xF^y$, x must be put $= 1\frac{3}{4}$, and $y = 1\frac{1}{2}$.

Acicular ammonium vanadoxyfluoride. Baker obtained this salt by dissolving the pyramidal salt in warm HFAq and allowing to cool; P. a. G. prepared it by a similar reaction. This salt crystallises in pale-yellow acicular prisms; when dry it has the odour of HF; it acts on glass. The formula given by P. a. G. is $3NH_4F.2VOF_2.aq$; Baker assigned to this salt the formula $3NH_4HF_2.2VOF_3$, but his analyses were, admittedly, not very trustworthy.

Adopting the formulæ given by P. a. G. for the three ammonium vanadoxyfluorides, these salts are represented as

(1) $3NH_4F.2VO_2F = (NH_4)_3V_2O_4F_5$
(2) $3NH_4F.VO_2F = (NH_4)_3VO_2F_4$
(3) $3NH_4F.2VOF_3 = (NH_4)_3V_2O_2F_9$.

A few of the other vanadoxyfluorides seem to belong to one or other of these types; P. a. G. and also Petersen, describe a *potassium vanadoxyfluoride* $3KF.2VO_2F = K_3V_2O_4F_5$, belonging to the same form as the lamellar ammonium salt. But most of the vanadoxyfluorides described belong to forms which are not represented by the ammonium salts. The following are the principal salts:—

Ammonium salts. $9NH_4F.5VOF_3.3HF$; $7NH_4F.4VOF_3.HF$ (Petersen).

Potassium salts $2KF.VO_2F$; $2KF.VOF_3$; $3KF.2VOF_3.HF$; $4KF.VF_5.VOF_3$ (P.).

Sodium salt $3NaF.VOF_3.VO_2F.aq$ (P. a. G.).

Zinc salts. $ZnF_2.VO_2F.7aq$ (P. a. G.); $ZnF_2.ZnO.2VOF_3.14aq$ (B.).

In none of these compounds does the atomic ratio of V to O exceed 1:2. According to Ditte (*C. R.* 105, 1067; 106, 270 [1888]), many compounds of alkali fluorides with V_2O_5 are formed by heating the constituents together, digesting with water, and crystallising; the atomic ratio of V to O in these compounds, as given by Ditte, is 2:5. The formulæ assigned to the compounds may be generalised as $xV_2O_5.yMF$; M = K or Na, $x = 1, 3$, and 4, and $y = 1, 2, 4$, and 8. Ditte (*l.c.*) says that crystals of $V_2O_5.4NH_4F.4aq$ are obtained by dissolving V_2O_5 in hot conc. NH_4FAq, and that this compound is formed, along with $V_2O_5.8NH_4F.4aq$, when V_2O_5 is dissolved in cold conc. NH_4FAq; but the experiments of Baker, Piccini a. Giorgis, and Petersen, all agree in assigning to the compounds formed in these reactions formulæ wherein the atomic ratio of V to O does not exceed 1:2.

Hypovanadoxyfluorides. (*Fluoxyhypovanadates.*) These compounds are formed by partially reducing mixtures of V_2O_5 and fluorides, or carbonates, dissolved in HFAq. If sufficient F is assigned to the metal present to form the normal fluoride, then the atomic ratio of V to the remaining F in these compounds is 1:2, and that of V to O is 1:1; the formulæ are written $xMF.yVOF_2$. All the salts described by Baker and Piccini a. Giorgis, except one, belong to the form $2M^IF.VOF_2$ or $M^{II}F_2.VOF_2$; these formulæ may evidently be written M^I_2(or M^{II})VOF_4.

Ammonium hypovanadoxyfluoride $2NH_4F.VOF_2.aq$ ($= (NH_4)_2VOF_4.aq$) was prepared by Baker (*C. J.* 33, 395) by passing H_2S into a solution of V_2O_5 in HFAq, concentrating, filtering, and adding NH_4F. The same salt was prepared by Piccini a. Giorgis (*G.* 22 [1] 55) by electrolytically reducing a solution of NH_4VO_3 in HFAq, after adding NH_4F; also by reducing NH_4VO_3 in HFAq by SO_2Aq, neutralising by NH_3Aq, and adding NH_4F; and in each case dissolving the crystals that were formed (said by P. a. G. to be $3NH_4F.VOF_2$) in hot HFAq, and crystallising. Petersen (*J. pr.* [2] 40, 196) also obtained this salt. The salt crystallises in clear blue monoclinic forms; $a:b = \cdot9653:1$ (Baker, *l.c.*).

Petersen (*J. pr.* [2] 40, 197) described two other ammonium hypovanadoxyfluorides, $7NH_4F.4VOF_2.5aq$ and $3NH_4F.VOF_2$.

The other hypovanadoxyfluorides described by P. a. G. (*l.c.*) are $2KF.VOF_2$ and $MF_2.VOF_2.2aq$ where M = Cd, Co, Ni and Zn. The K salt was prepared by reducing V_2O_5 in HFAq by SO_2Aq and adding KF; the other salts by dissolving MO, or MCO_3, along with V_2O_5 in HFAq, and reducing electrolytically. According to Petersen (*l.c.* pp. 199, 200), the salts $7KF.3VOF_2$ and $8NaF.3VOF_2.2aq$ also exist.

P. a. G. (*l.c.*) remark that the tendency to form highly fluorinated compounds increases in the family V, Nb, Ta as the atomic weight increases; thus, VO_2F is not affected by a little HFAq, while Nb_2OF forms $NbOF_3$, and $TaOF_3$ is converted into TaF_5. They also point out that the three compounds, $ZnF_2.VO_2F.7aq$, $ZnF_2.VOF_2.7aq$, and $ZnF_2.VF_3.7aq$, all crystallise with the same number of molecules of water, all contain the same number of atoms, have the same crystalline form, and are geometrically isomorphous.

VANADIUM PENTAFLUORIDE VF_5. According to Petersen (*J. pr.* [2] 40, 271), this compound exists in a solution of V_2O_5 in conc. HFAq. No compound was isolated, nor is any trustworthy evidence given of the existence of VF_5 in solution.

Vanadium, haloid compounds of. When V is heated in excess of Cl the tetrachloride VCl_4 is produced; heating in Br produces the tribromide VBr_3. V does not combine with I. The haloid compounds of V belong to the forms VX_4, VX_3, and VX_2; X = Cl in each case, X = Br or F in the one case of VX_3. The formula VX_4 is molecular; the other formulæ are probably molecular. VCl_4, $BiCl_3$, AsI_3, and PI_3 are the only dihalides known of members of Group V. Attempts to prepare halides higher than VX_4 have failed. Solutions in water of the haloid compounds of V behave like solutions of the corresponding oxides in haloid acids; VCl_4Aq like a solution of V_2O_4 in HClAq, VX_3Aq like a solution of V_2O_3 in HXAq, and VCl_2Aq like a solution of V_2O_2 in HClAq. VCl_4 is decomposed by heat to VCl_3 and Cl, and heating VCl_3 with H produces VCl_2. VF_3 combines with metallic fluorides to form *vanadofluorides*, many of which belong to the form $M^I_2VF_5$ or $M^{II}VF_5$ (*v.* p. 844). Several oxychlorides and oxybromides of V have been isolated: VOX_3 and VOX_2, where X = Cl or Br; also VOCl, V_2O_2Cl, and VO_2Cl; the existence of other oxybromides also is probable. No oxyfluoride has been isolated with certainty. But many compounds exist which may be regarded as containing the oxyfluorides VO_2F, VOF_3, and VOF_2 respectively; the compounds $VO_2F.xMF$ and $VOF_3.xMF$ are obtained by dissolving V_2O_5 and fluorides in HFAq and crystallising; they are described as *vanadoxyfluorides* (p. 844); the compounds $VOF_2.xMF$ are obtained by partially reducing solutions of V_2O_5 and fluorides in HFAq, they are described as *hypovanadoxyfluorides* (p. 845).

Vanadium, iodides of. No iodide of V has been isolated. No reaction occurs when vapour of I is passed over VN heated to redness, nor do I and V_2O_3 react at any temperature (Roscoe, *C. J.* [2] 9, 28). I does not react with V_2O_5 when digested therewith for a long time in presence of water or alcohol (Guyard, *Bl.* [2] 25, 351).

Vanadium, nitrides of. V and N combine directly. Two nitrides are known.

VANADIUM MONONITRIDE VN. Mol. w. not known. Obtained by heating V in a stream of pure N; also by saturating $VOCl_3$ with dry NH_3, and heating to full whiteness in a stream of NH_3. Better prepared by heating NH_4VO_3 in the air, and then heating the residue to a full white heat in a stream of dry NH_3 (Roscoe, *C. J.* [2] 8, 344). VN may also be prepared by heating V_2O_3 to whiteness in NH_3 (R., *l.c.*). VN is a greyish-brown, metal-like powder; heated in air it is oxidised to V_2O_4 and then to V_2O_5; heated with soda-lime it gives off NH_3.

VANADIUM DINITRIDE VN_2. A black powder; exposed to air gives off NH_3 and is oxidised. Prepared by saturating $VOCl_3$ with dry NH_3, heating the solid so obtained in a glass tube as long as NH_4Cl sublimes, washing the residue with water containing a little NH_3, and drying *in vacuo* over H_2SO_4 (Roscoe, *C. J.* [2] 6, 349); examined by Uhrlaub, who did not succeed in determining its composition (*P.* 103, 134; *cf.* Schafarik, *W. A. B.* 33, 5).

Vanadium, oxides and hydrated oxides of. By gently heating V in air the oxide V_2O is possibly formed, and, on continued heating, oxidation proceeds to V_2O_2, V_2O_3, V_2O_4, and finally V_2O_5. The oxides V_2O_4, V_2O_3, and V_2O_2 are also formed by reducing V_2O_5 by heating with H or K. Several oxides intermediate between V_2O_4 and V_2O_5 seem also to exist. The oxides V_2O_2, V_2O_3, V_2O_4, and V_2O_5 are feebly basic; V_2O_4 and V_2O_5 are also acidic. The oxides of V correspond in composition with the oxides of N; corresponding oxides of Bi are known. The names generally given to the oxides of V do not, unfortunately, tally with the names given to the corresponding oxides of N; thus, V_2O_2 is generally called hypovanadous oxide, while NO is called nitric oxide; V_2O_5 is called vanadic oxide, while the name nitrogen peroxide is often quite wrongly applied to NO_2. The mol. w. of none of the oxides of V is known.

? VANADIUM MONOXIDE (? V_2O). 'When the powdered metal is . . . slowly heated in a current of air it glows brightly, with absorption of oxygen, forming in the first place a brown oxide (V_2O or V_2O_2); and on further heating this oxide again glows, and passes through the black trioxide and blue tetroxide to pentoxide' (Roscoe, *C. J.* [2] 8, 357). This statement seems to contain all that is known of an oxide lower than V_2O_2.

VANADIUM DIOXIDE V_2O_2. (*Hypovanadous oxide.*) This substance was supposed by Berzelius (*P.* 22, 1) to be V; Roscoe (*T.* 1868. 1) proved it to be an oxide with the atomic ratio V:O = 1:1. The mol. w. is not known; the formula is generally written V_2O_2 rather than VO, as the double formula is, on the whole, more in keeping with the reactions of the compound.

Formation.—1. By heating one of the higher oxides with K (Berzelius, *l.c.*).—2. By passing vapour of $VOCl_3$, mixed with much dry H, over red-hot charcoal (Schafarik, *A.* 109, 85).—3. By strongly heating V_2O_3 and V_2O_5, mixed in the ratio V_2O_3:V_2O_5, out of contact with air (Petersen, *J. pr.* [2] 40, 193).

Preparation.—A mixture of much dry H and vapour of $VOCl_3$ (*q. v.* p. 854) is passed through a hard glass tube containing powdered charcoal and kept red hot. Some solid oxychlorides are deposited on the cooler parts of the tube, while the V_2O_2 remains mixed with the C. The contents of the tube are then strongly heated in a current of dry H to remove traces of Cl compounds; and the grey metal-like V_2O_2 is separated from the C (Roscoe, *C. J.* [2] 6, 334). When Zn, Cd, or Na-amalgam is added to a solution of V_2O_5 in H_2SO_4Aq (prepared by dissolving the oxide in hot conc. acid and diluting with 50 pts. water), the liquid becomes blue, green, and finally lavender. The lavender solution absorbs O very rapidly; exposure to the air for a few seconds causes the colour to change to deep chocolate-brown. By determining the quantity of standardised $KMnO_4Aq$ decolourised by the lavender solution, Roscoe (*C. J.* [2] 6, 334) proved that this solution contained V_2O_2, probably combined with SO_3. After passing air into the lavender solution until it becomes permanently blue, the solution contains V_2O_4; if the free acid in the lavender solution is neutralised by zinc, and the liquid is then exposed to the air until permanently brown, and a little acid is then added, a green solution is formed which contains V_2O_3 (R., *l.c.*).

Properties and Reactions.—A light-grey, lustrous powder; or a lustrous, metal-like, crystalline crust, S.G. 3·64; very brittle; fuses at a very high temperature. Heated to redness in air, V_2O_2 burns to V_2O_3; heated in O, burns to V_2O_5. Insoluble in water; dissolves in dilute acids, giving a lavender solution, which bleaches strongly; from these solutions KOHAq or

NH_3Aq ppts. a brown hydrated oxide, which rapidly oxidises (Brierley, *C. J.* 49, 824). According to Petersen (*J. pr.* [2] 40, 194), V_2O_2 dissolves in HFAq, and on evaporation, solution of the residue in water, and evaporation over H_2SO_4, blue, microscopic crystals are obtained, which are, perhaps, $VOF_2.x$aq; no analyses were made. Addition of alkali fluorides to V_2O_2 in HFAq produces various compounds of the form $xVOF_2.yMF$ (*v.* HYPOVANADOXYFLUORIDES, p. 845).

HYDRATE OF VANADIUM DIOXIDE. By adding NH_3Aq to a lavender-coloured solution of V_2O_2 (? in H_2SO_4Aq), Brierley (*C. J.* 49, 824) obtained a deep-purple gelatinous pp. which he said was hydrated V_2O_2; the pp. rapidly oxidised in the air.

VANADIUM TRIOXIDE V_2O_3. (*Vanadous oxide. Vanadium sesquioxide.*) Mol. w. not known. This compound was represented by Berzelius as VO (V = 68·5, O = 8).

Formation.—1. By heating V_2O_5 to redness in H (Schafarik, *A.* 109, 85). The presence of traces of P_2O_5 prevents reduction (Roscoe, *C. J.* [2] 6, 331).—2. By heating V_2O_5 in a carbon crucible (Berzelius, *P.* 22, 1).

Preparation.—Pure V_2O_5 is heated in perfectly pure and dry H until the substance ceases to lose weight; the tube is allowed to cool completely in H, and then a stream of dry air is passed through it (Roscoe, *C. J.* [2] 6, 331). When a solution of V_2O_5 in conc. H_2SO_4 is much diluted, and then treated with Mg until the liquid is green, this solution contains V_2O_3, combined with SO_3 (*v.* VANADOUS SALTS, *infra*). A similar solution is obtained from the lavender solution of V_2O_2 in H_2SO_4Aq (prepared from V_2O_5 in H_2SO_4, *v. supra*) by neutralising free acid by zinc, exposing to the air, and adding a little acid (Roscoe, *C. J.* [2] 6, 337).

Properties and Reactions.—V_2O_3 is a black powder, resembling graphite; or, formed by reducing $VOCl_3$ by H, it is a black, lustrous, crys-alline crust. S.G. 4·72 at 16°. Does not fuse n the blowpipe flame. When warm V_2O_3 is exposed to the air it glows and oxidises to V_2O_5; nd even at the ordinary temperature it takes up , being changed after some months to V_2O_4 (R., c.). Heated in Cl gives V_2O_5 and $VOCl_3$ (R., *l.c.*). Heated in NO_2 to 300°–400° V_2O_3 is oxidised to V_2O_5 (Sabatier a. Senderens, *C. R.* 115, 236). Heating to redness in H_2S produces V_2S_3 (Kay, *C. J.* 37, 728). V_2O_3 dissolves in hot conc. H_2SO_4, forming $V_2O_3.xSO_3$ (*v.* VANADOUS SALTS, *infra*). V_2O_3 dissolves in HFAq, and $VF_3.3H_2O$ has been isolated from this solution (*v.* VANADIUM TRIFLUORIDE, p. 844).

HYDRATE OF VANADIUM TRIOXIDE. By adding KOHAq, or NH_3Aq, to an aqueous solution of $V_2O_3.4SO_3.9H_2O$ (*v. infra*) Brierley (*C. J.* 49, 824), obtained a dirty green, gelatinous pp., which oxidised rapidly in air. According to B., this pp. was hydrated V_2O_3.

VANADOUS SALTS $V_2O_3.xX$ (X = acidic oxide) or $V_2R_3^{II}$ (R^{II} = acidic radicle). Only one salt derived from an oxyacid has been certainly isolated; it has the composition $V_2O_3.4SO_3.xH_2O$, or the formula may be written $V_2H_2(SO_4)_4.yH_2O$.

Vanadous tetrasulphate, or *acid vanadous sulphate*, $V_2O_3.4SO_3.xH_2O$ or $V_2H_2(SO_4)_4.yH_2O$.

A hydrate with $x = 3$ or $y = 2$ was obtained by Gerland (*B.* 10, 2111 [1877]) by heating a solution of V_2O_4 in a large excess of conc. H_2SO_4 for a long time at 120°, and treating the blue crystalline crust thus formed (consisting chiefly of $V_2O_4.3SO_3.x$aq, *v.* HYPOVANADIC SALTS, p. 848) with boiling water, when $V_2O_3.4SO_3.3H_2O$ remained. G. supposed that reduction of V_2O_4 was effected by dust in the air.

Brierley (*C. J.* 49, 822 [1886]) prepared $V_2O_3.4SO_3.9H_2O(=V_2H_2(SO_4)_4.8H_2O)$ by electrolysing a solution of V_2O_4 in H_2SO_4. The solution was prepared by reducing V_2O_5 in conc. H_2SO_4, after dilution, by SO_2. The deep-blue solution was placed in a Pt dish which formed the negative electrode, and a porous pot containing dilute H_2SO_4Aq was arranged so that it just touched the surface of the liquid in the Pt dish; a plate of Pt immersed in the H_2SO_4Aq formed the positive electrode. The Pt dish was warmed during the process, so that electrolysis and evaporation proceeded together. Electrolysis was continued until the liquid was deep green, and a drop placed in a little water showed no trace of blue colour. Conc. H_2SO_4, equal to twice the bulk of the green liquid, was added; after 24 hours the green, sandy pp. was collected, washed with conc. alcohol, and dried over H_2SO_4 in coal-gas. The salt dissolved in water, and alkali ppd. from this solution a dirty-green gelatinous substance, said by B. to be $V_2O_3.xH_2O$. This pp. dissolved in an aqueous solution of $V_2O_3.4SO_3.9H_2O$, forming a chocolate-brown solution, giving a lustrous green solid on evaporation, which dissolved in water to form a brown solution. B. concluded that the brown solution contained a compound of V_2O_3 and SO_3 more basic than $V_2O_3.4SO_3$.

Gerland (*B.* 11, 106 [1878]) mentions the *normal vanadous sulphate* $V_2(SO_4)_3(=V_2O_3.3SO_3)$ as if he had prepared it; no details are given.

VANADIUM TETROXIDE V_2O_4. (*Hypovanadic oxide.*) Mol. w. not known. Represented by Berzelius as VO_2(V = 68·5, O = 8).

Formation.—1. By allowing V_2O_3 to absorb O from the air (*cf.* HYPOVANADO-VANADIC OXIDES, p. 851).—2. By strongly heating a mixture of 5 pts. V_2O_3 and 6 pts. V_2O_5, in absence of air.—3. By the electrolysis of molten V_2O_5 (Buff a. Wöhler, *A.* 110, 277).—4. By heating $V_2O_4Cl_2.5$aq in a stream of CO_2 (Crow, *C. J.* [2] 15, 453).

Preparation.—A solution of V_2O_4 in H_2SO_4, obtained by reducing V_2O_5 in conc. H_2SO_4 by SO_2, is ppd. by Na_2CO_3Aq, and the pp. is washed and dried by heating *in vacuo* (Berzelius, *P.* 22, 1).—2. V_2O_3 is exposed to the air for some months, until the colour has changed to blue (Roscoe, *C. J.* [2] 6, 338).—3. V_2O_5 is dissolved in hot conc. HClAq; when Cl ceases to be given off the liquid is saturated with H_2S, filtered from S, evaporated to dryness at 100° and the $V_2O_4Cl_2.x$aq thus formed is heated to redness in a stream of dry CO_2 (Crow, *l.c.* pp. 457, 458).

Properties and Reactions.—A blue, lustrous, crystalline powder; prepared by heating $V_2O_4Cl_2$ in CO_2 it forms a dark-green, amorphous powder (Crow, *l.c.*). Infusible at a high temperature. Insoluble in water. When kept in a loosely-stoppered bottle V_2O_4 gradually absorbs O, forming V_2O_5 (Crow, *l.c.*). Dissolves easily in acids, forming bright-blue liquids; the same solutions are obtained by the action of moderate reducers, such as SO_2Aq, H_2SAq, or $H_2C_2O_4Aq$, on solutions of V_2O_3 in acids, also by passing air into V_2O_2 in H_2SO_4Aq until the liquid becomes permanently blue (Roscoe, *l.c.*; *v. infra*, Hypovanadic salts). Petersen (*J. pr.* [2] 40, 194) supposed that the blue microscopic crystals he obtained by dissolving V_2O_4 in excess of HFAq and evaporating were $VOF_2.x$aq, but he did not obtain enough to make an analysis. V_2O_4 dissolves readily in alkali solutions, forming *hypovanadates*, $M_2V_4O_9$ (*q.v.* under Vanadium oxyacids, and salts and derivatives thereof, p. 853).

Hydrates of hypovanadic oxide. By adding Na_2CO_3Aq, drop by drop, to a solution of V_2O_4 in HClAq or H_2SO_4Aq, till the supernatant liquid was colourless, filtering rapidly in CO_2, and drying on a porous tile over H_2SO_4 *in vacuo*, Crow (*l.c.*) obtained the black, amorphous *heptahydrate* $V_2O_4.7$aq; and on heating this in CO_2 for some hours at 100° he obtained the *trihydrate* $V_2O_4.3$aq.

HYPOVANADIC (or *vanadyl*) SALTS $V_2O_4.xX$ (X = acidic oxide). Only a few compounds of V_2O_4 with acidic oxides have been isolated. The sulphates have been studied more than any other salts; they are most simply represented as $V_2O_4.xSO_3.yH_2O$. The compound $V_2O_4.2SO_3$ may be called the normal sulphate; the formula may be expressed as $V_2O_2.(SO_4)_2$ or $VO.SO_4$. The compound $V_2O_4.3SO_3.6H_2O$ may be called acid sulphate; the formula may be expressed as $V_2O_2.SO_4(SO_4H)_2.5H_2O$ or $(V_2O_2)H_2(SO_4)_3.5H_2O$, or $(VO.SO_4)_2.H_2SO_4.5H_2O$, or it may be written $V_2O_4.2SO_3.H_2SO_4.5H_2O$. When the formulæ of the compounds of V_2O_4 with acidic oxides are written $V_2O_4.X$ the compounds are generally called *hypovanadic salts*; when the formulæ are written $V_2O_2.xR$ (R = acidic radicle) the name *divanadyl salts* is usually given to the compounds; and when these compounds are regarded as $VO.xR$, it is customary to call them *vanadyl salts*. Hypovanadic sulphates are obtained (1) by dissolving V_2O_4 in hot conc. H_2SO_4 and boiling; (2) by dissolving V_2O_5 in conc. H_2SO_4, reducing by SO_2 or $H_2C_2O_4$, and evaporating; (3) by dissolving V_2O_5 in conc. H_2SO_4 and boiling in the air for some time. In reaction (3) $V_2O_5.xSO_3$ seems to be formed and then partially reduced, by dust or products of combustion of coal-gas, to $V_2O_4.xSO_3$; the products are mixtures of $V_2O_5.xSO_3$ and $V_2O_4.xSO_3$ (Gerland, *B.* 11, 98).

Hypovanadic disulphate, or *normal divanadyl sulphate*, $V_2O_4.2SO_3$ or $V_2O_2.(SO_4)_2$. (*Vanadyl sulphate* $VO.SO_4$.) Prepared by Gerland (*B.* 10, 2109 [1877]; supplementing *B.* 9, 869) by dissolving V_2O_4 in a large excess of conc. H_2SO_4 and heating to the boiling-point of the liquid for a long time. The salt separated as a green-blue powder; insoluble in water, cold or hot; insoluble HClAq and H_2SO_4. (G. does not say how the salt was obtained pure for analysis; no analyses are given of the salt prepared exactly as described above.) Various *hydrates* are described by G. obtained by different processes. Crow (*C. J.* [2] 15, 456 [1876]), obtained the *heptahydrate* by repeatedly treating hexahydrated trisulphate (*v. infra*) with absolute alcohol.

Hypovanadic trisulphate, or *acid divanadyl sulphate*, $V_2O_4.3SO_3.xH_2O$ or $(V_2O_2)H_2(SO_4)_3.yH_2O$ [$y = x - 1$]. (*Acid vanadyl sulphate* $(VO.SO_4)_2.H_2SO_4.yH_2O$.) Hydrates with $x = 4$ and 3 (or $y = 3$ and 2) were prepared by Gerland (*B.* 10 2, 109); and a hydrate with $x = 6$ (or $y = 5$) by Crow (*C. J.* [2] 15. 455).

By dissolving V_2O_4 in a large excess of conc. H_2SO_4, heating for a long time at c. 120°, and drying the small, blue, transparent crystals that formed on a porous tile over H_2SO_4, Gerland obtained a substance which gave analytical results approaching those required by the formula $V_2O_4.3SO_3.4H_2O$. The salt was not obtained quite free from admixed $V_2O_5.4SO_3.xH_2O$. This *tetrahydrate* was partially decomposed by cold water, giving lustrous scales which, after washing with alcohol and ether and drying over H_2SO_4, had the composition of a *trihydrate*, $V_2O_4.3SO_3.3H_2O$.

Crow obtained a *hexahydrate* $V_2O_4.3SO_3.6H_2O$, by reducing by SO_2 a solution of V_2O_5 in conc. H_2SO_4, heating at 100° for some time, drying the light-blue crystals that separated on a tile, removing acid by washing with ether, and drying by pressure between paper. The crystals deliquesced in air to a blue syrup; they were insoluble in ether, and scarcely soluble in absolute alcohol.

The formulæ of the various hydrated hypovanadic sulphates are as follows:—

Hypovanadic sulphates; or	*Divanadyl sulphates*; or	*Vanadyl sulphates.*
$V_2O_4.2SO_3$	$V_2O_2.(SO_4)_2$	$VO.SO_4$ (Gerland).
$V_2O_4.2SO_3.3H_2O$	$V_2O_2.(SO_4)_2.3H_2O$	$2(VO.SO_4).3H_2O$ (G.)
$V_2O_4.2SO_3.4H_2O$	$V_2O_2.(SO_4)_2.4H_2O$	$VO.SO_4.2H_2O$ (Crow, confirming Berzelius).
$V_2O_4.2SO_3.7H_2O$	$V_2O_2.(SO_4)_2.7H_2O$	$2(VO.SO_4).7H_2O$ (G., also C.)
$V_2O_4.2SO_3.10H_2O$	$V_2O_2.(SO_4)_2.10H_2O$	$VO.SO_4.5H_2O$ (G.)
$V_2O_4.2SO_3.13H_2O$	$V_2O_2.(SO_4)_2.13H_2O$	$2(VO.SO_4).13H_2O$ (G.)
$V_2O_4.3SO_3.3H_2O$	$(V_2O_2)H_2(SO_4)_3.2H_2O$	$2(VO.SO_4).H_2SO_4.2H_2O$ (G.)
$V_2O_4.3SO_3.4H_2O$	$(V_2O_2)H_2(SO_4)_3.3H_2O$	$2(VO.SO_4).H_2SO_4.3H_2O$ (G.)
$V_2O_4.3SO_3.6H_2O$	$(V_2O_2)H_2(SO_4)_3.5H_2O$	$2(VO.SO_4).H_2SO_4.5H_2O$ (C.)

Bevan (*C. N.* 38, 294) obtained *divanadyl dithionate* by adding BaS_2O_6Aq to $V_2O_2(SO_4)_2Aq$, filtering, and evaporating *in vacuo*: the salt was not obtained pure. By dissolving V_2O_4 in HNO_3Aq Berzelius (*P.* 22, 1) obtained a blue liquid which probably contained *hypovanadic nitrate*; but no solid could be isolated, as on evaporation to dryness decomposition occurred, with formation of V_2O_5. V_2O_4 also dissolves in H_3PO_4Aq; on evaporation at 50° blue crystals are obtained, which deliquesce to a blue syrup; these crystals are probably *hypovanadic phosphate*, but no analyses are given (B., *l.c.*). Berzelius obtained what were probably compounds of V_2O_4 with As_2O_5, B_2O_3, CrO_3, MoO_3, and a few other acidic oxides (cf. *Lehrbuch* [5th ed.] 3, 1053).

Vanadium pentoxide V_2O_5. (*Vanadic oxide. Vanadic anhydride.*) Mol. w. not known. Represented by Berzelius as VO_3 (V = 68·5, O = 8).

Formation.—1. By strongly heating any of the lower oxides in air or O.—2. By heating $NH_4.VO_3$ in air to dull redness.—3. By decomposing $VOCl_3$ by water.—4. By heating $V_2O_3.4SO_3.9aq$ to bright redness (Brierley, *C. J.* 49, 824).

Preparation.—Pure $VOCl_3$ is decomposed by water, and the ppd. V_2O_5 is washed till the washings are free from acid (HClAq is produced) and heated until dry (Schafarik, *J. pr.* 76, 142). For the preparation of V_2O_5 from *vanadinite* and other sources of V compounds, *v.* Vanadium, *Preparation* of (p. 841).

Properties.—A pale-yellow powder, with a reddish tinge. When heated to full redness out of contact with any reducing agents, V_2O_5 melts, and solidifies on cooling to a mass of yellow-red, crystalline needles, appearing ruby-red by transmitted light; should the V_2O_5 used contain V_2O_4, which is often the case when the V_2O_5 is prepared by heating $NH_4.VO_3$, the solid obtained by fusion and cooling appears violet to nearly black, and does not seem to be crystalline (Berzelius, *P.* 22, 1). As molten V_2O_5 cools nearly to its solidifying-point much heat is given out, and the mass glows until solidification is complete (B., *l.c.*). V_2O_5 is said not to be changed at a white heat, provided no trace of a reducing agent is present (B., *l.c.*); but according to Read (*C. J.* 65, 313 [1894]) molten V_2O_5 gives off O, producing V_2O_3, which on cooling in air takes up O, forming steel-blue crystals of V_2O_4. The crystals of V_2O_5 are rhombic (*v.* Nordenskjold, *P.* 112, 160). S.G. (crystalline) 3·5 at 20° (Schafarik, *J. pr.* 76, 142). V_2O_5 is odourless and tasteless; it reddens moist litmus paper; 1,000 pts. boiling water dissolve scarcely 1 pt. V_2O_5 (B., *l.c.*). With molten alkalis or alkali carbonates V_2O_5 produces *vanadates* (*q.v.* p. 851). V_2O_5 dissolves in conc. H_2SO_4, HClAq, HNO_3Aq, or HFAq (*cf.* Vanadic salts, p. 850).

According to Ditte (*C. R.* 101, 698), V_2O_5 exists in three forms: (1) *red*, obtained by heating $NH_4.VO_3$ in a closed crucible, treating with HNO_3 and repeatedly heating to redness; (2) *yellow*, obtained by heating $NH_4.VO_3$ to 440° in a stream of air; and (3) *crystalline*, obtained by treating the yellow form with HNO_3, and then fusing. D. says that the red form is somewhat soluble in water, 1,000 c.c. dissolving 8 g. at 20°; that the yellow form is very slightly soluble, and the crystalline form is insoluble, in water. He also says that the red form absorbs water from the air, producing hydrates with $2H_2O$ and $5H_2O$; and that addition of NHCl, KCl (and other salts) to an aqueous solution of the red variety causes ppn. of a hydrate of the yellow form of V_2O_5, which hydrate, when dry, is a dark-red powder having the composition $V_2O_5.2H_2O$ (= $H_4V_2O_7$) and is almost insoluble in water. (No analyses are given by D.)

Reactions.—1. When *heated* and kept molten, V_2O_3 is formed, and this absorbs O as it cools in air and forms V_2O_4 (Read, *C. J.* 65, 313 [1894]). 2. Heated to redness in *hydrogen* till it ceases to lose weight, V_2O_5 is reduced to V_2O_3 (Schafarik, *A.* 109, 85); traces of P_2O_5 prevent the reduction (Roscoe, *C. J.* [2] 6, 331).—3. Heating with *potassium* produces V_2O_3 (Berzelius, *P.* 22, 1).—4. V_2O_3 is produced by heating V_2O_5 in a *carbon* crucible (B., *l.c.*). For action of Mg, Zn, &c. on solutions of V_2O_5, *v.* Vanadic salts, (p. 850).—5. When mixed with *carbon and heated in chlorine*, V_2O_5 yields $VOCl_3$ (Roscoe, *C. J.* [2] 6, 342).—6. Electrolysis of molten V_2O_5 produces V_2O_4 (Buff a. Wöhler, *A.* 110, 277).—7. According to Ditte (*C. R.* 103, 55), *fusion with potassium cyanide* produces V_2O_3 (N, K_2O, and CO_2 being also formed). Carnot (*C. R.* 104, 1803, 1850; 105, 119) says that a *boiling solution of potassium cyanide* produces KVO_3 (CO_2 and N being given off); and that by dropping V_2O_5 into excess of boiling KCNAq there is formed $K_2V_4O_9$ (with evolution of N and CO_2). No analyses are given either by D. or C.—8. Ditte (*C. R.* 103, 55) asserts that the products of the interaction of V_2O_5 and *potassium iodide or bromide* are $K_2V_4O_9$, KVO_3, and I or Br. The reactions are said to occur between V_2O_5 and molten KI or KBr; and KIAq is said to react in the same way as the molten salt.—9. When V_2O_5 is heated with molten *boron trioxide*, a pale-yellow glass is formed, which is said by Guyard (*Bl.* [2] 40, 354) to be a vanadic borate; no analyses, composition, or methods of purification are given.—10. V_2O_5 dissolves in *hot conc. sulphuric acid*, forming $V_2O_5.xSO_3$, generally along with more or less $V_2O_4.xSO_3$ (*v.* Vanadic salts, p. 850).—11. V_2O_5 dissolves in *conc. hydrochloric acid*; Cl is given off on heating; after the passage of H_2S followed by evaporation at 100° the oxychloride $VO_2Cl.xaq$ is obtained (Crow, *C. J.* 30, 457; *cf.* Vanadium dioxymonochloride, p. 854).—12. By dissolving V_2O_5 in *conc. hydrochloric acid in presence of platinic chloride*, Brauner (*M.* 3, 58) obtained large tablets having the composition $2(VOCl_2.PtCl_4).21aq$.—13. An oxyiodide $2VOI_2.9aq$ is obtained, according to Ditte (*C. R.* 102, 1310), by adding excess of *hydriodic acid* to a warm aqueous solution of red V_2O_5, removing free I by shaking with silver powder, filtering, and evaporating *in vacuo*. (No analyses are given.)—14. V_2O_5 dissolves in *hydrofluoric acid*, forming a pale-yellow solution, the colour of which becomes deeper on dilution (Piccini a. Giorgis, *G.* 22 [1] 55). Petersen (*J. pr.* [2] 40, 271) supposed that a solution in conc. HFAq contained VF_5; but he did not separate this compound, nor does he give any direct evidence in favour of its existence beyond the preparation from the solution of V_2O_5 in HFAq of a compound which may be represented as $2KF.VF_5.VOF_3$, and other compounds of the forms $xMF.yVOF_3$ and $xMF.yVO_2F$. By adding metallic fluorides to solutions of V_2O_5 in HFAq, and crystallising, vanadoxyfluorides are formed; these compounds are of the forms $xMF.yVOF_3$ and $xMF.yVO_2F$ (*v.* Vanadoxyfluorides, p. 844).—15. Vanadoxyfluorides are also formed by dissolving V_2O_5 in *alkali fluoride solutions*, and crystallising (*cf. infra, Combinations*, No. 5).—16. If a *solution of V_2O_5 in hydrofluoric acid is partially reduced*, and then evaporated with metallic fluorides, *hypovanadoxyfluorides* (*q. v.* p. 845) are formed; these salts are of the form $xMF.yVOF_2$.—17. By boiling V_2O_5 with *hydrogen peroxide* solution, a black liquid was obtained that deposited a black-brown crust of indefinite composition (Cammerer, *Chem. Zeit.* 19, 957).—18. By fusion with *alkali* or *alkali carbonates* vanadates are formed (*v.* Vanadates, p. 851).

Combinations.—1. With *water*, but not directly, to form $V_2O_5.H_2O$ and $V_2O_5.2H_2O$ (*v. Metavanadic acid* and *Pyrovanadic acid*, under Vanadium oxyacids, and salts and derivatives thereof, p. 851).—2. With various *acidic oxides*: (1) With SO_3 to form $V_2O_5.xSO_3$, formed by dissolving V_2O_5 in hot conc. H_2SO_4; (2) with As_2O_5 to form $V_2O_5.xAs_2O_5$; (3) with P_2O_5 to form $V_2O_5.xP_2O_5$; (4) with I_2O_5 to form $V_2O_5.xI_2O_5$; (5) with MoO_3 to form $V_2O_5.xMoO_3$; (6) with WO_3 to form $V_2O_5.xWO_3$; (7) with P_2O_5 and SiO_2 to form $V_2O_5.xP_2O_5.ySiO_2$. Most of these compounds combine with the stronger bases M_2O and MO to form salt-like compounds. The compounds of V_2O_5 with SO_3 are described as *vanadic sulphates* under Vanadic salts (*infra*); the compounds with other acidic oxides are described respectively as *arseno-vanadic acids and salts*, *iodo-vanadic acids*, *molybdo-vanadic acids and salts*, *phospho-vanadic acids and salts*, *phospho-silico-vanadic acid*, and *tungsto-vanadic acids and salts*, under Vanadium oxyacids, and salts and derivatives thereof (*v.* pp. 853–4).—3. With *vanadium tetroxide* to form oxides intermediate between V_2O_4 and V_2O_5 (*v.* Hypovanado-vanadic oxides, p. 851).—4. With *vanadium trioxide* to form V_2O_4; produced by heating equivalent weights of the two oxides out of contact with air (Berzelius, *P.* 22, 1; Petersen, *J. pr.* [2] 40, 193).—5. With *alkali fluorides*. According to Ditte (*C. R.* 105, 1067; 106, 270), several compounds of the form $xV_2O_5.yMF$ are formed by fusing V_2O_5 with alkali fluorides, extracting with water, and crystallising; D. gives formulæ where $x=1$, 3 and 4, $y=1$, 2, 4 and 8, and $M=K$ and Na; but he does not give analyses of the salts (*v.* Vanadoxyfluorides, p. 844).

Hydrates of vanadic oxide. The hydrates $V_2O_5.H_2O=HVO_3$ and $V_2O_5.2H_2O=H_4V_2O_7$ have been isolated; these compounds are acids (*v.* Vanadic acids, p. 851). Ditte (*C. R.* 101, 698) asserts, without giving analyses, that a pentahydrate $V_2O_5.5H_2O$ is formed by absorption of water from the air by the red form of V_2O_5 (*v.* Vanadium pentoxide, *Properties*, p. 849).

VANADIC SALTS $V_2O_5.xX$ ($X=$ acidic oxide). A few compounds of this form have been isolated. The sulphates have been better studied than the other salts. Two sulphates, $V_2O_5.2SO_3.xH_2O$ and $V_2O_5.3SO_3.xH_2O$, have been isolated. If x is taken to be 2 in the first salt and 3 in the second, then the formulæ may be written as $(VO_2)_2SO_4.H_2SO_4.H_2O$ and $(VO_2)_2SO_4.2H_2SO_4.H_2O$ respectively: [$(VO_2)_2SO_4.H_2SO_4.H_2O=V_2O_5.2SO_3.2H_2O$; $(VO_2)_2SO_4.2H_2SO_4.H_2O=V_2O_5.3SO_3.3H_2O$]. If the salts are anhydrous, as seems most probable from the analyses, then the formulæ may be written $(VO_2)_2SO_4.SO_3$ and $(VO_2)_2SO_4.2SO_3$ respectively. Neither of the salts can be regarded as the normal salt. The sulphates are obtained by dissolving V_2O_5 in hot conc. H_2SO_4.

Vanadic disulphate $V_2O_5.2SO_3(?\,xH_2O)$. **Prepared by Berzelius (*P.* 22, 39); examined also by Fritsche (*J. pr.* 53, 93), Gerland (*B.* 11,** 98), and Münzig (*C. C.* 1889 (ii.) 908). The salt seems to be without water of crystallisation; F. (*l.c.*) says it crystallises with H_2O. V_2O_5 is dissolved in hot conc. H_2SO_4, and the solution is boiled for a considerable time, when small crystals separate, some of which are brown and some ruby-red, lustrous, and transparent. The crystals are heated in a bath of molten lead until SO_3 ceases to be given off (G., *l.c.*). According to Münzig (*l.c.*), the orange-coloured crystalline powder that separates when V_2O_5 is added to boiling conc. H_2SO_4 until the acid is saturated is $V_2O_5.2SO_3$. By keeping a solution of V_2O_5 in a large excess of conc. H_2SO_4 at 130°–150° for a long time, Gerland (*l.c.*) obtained a hard, opaque, sealing-wax red, crystalline crust composed of V_2O_5 and SO_3 in approximately the ratio $V_2O_5:2SO_3$.

$V_2O_5.2SO_3$ [$=(VO_2)_2SO_4.SO_3$] is described by G. (*l.c.*) as a clear red, crystalline, deliquescent solid; addition of a drop or two of water ppts. $V_2O_5.xH_2O$.

Vanadic trisulphate $V_2O_3.3SO_3(?\,xH_2O)$. This salt seems to have been obtained by Berzelius (*l.c.*). Ditte (*C. R.* 102, 757) gave x the value 3; Gerland's analyses (*l.c.*) were inconclusive, the percentage of water found varying from ·8 to 7·3. G. (*l.c.*) prepared this salt by long-continued boiling of a solution of V_2O_5 in a large excess of conc. H_2SO_4; small crystals separated, some of them brown and some ruby-red and transparent (probably regular octahedra). When the boiling was not continued for so long a time, G. noticed that fine, golden-yellow, lustrous needles separated. The composition of the crystals in each case was very nearly that required by the formula $V_2O_5.3SO_3$. More or less $V_2O_4.2SO_3$ was always formed; G. found that addition of a little $HClO_4$ prevented the formation of much $V_2O_4.2SO_3$.

$V_2O_5.3SO_3$ is very deliquescent; soluble in cold water or alcohol; a slight rise of temperature suffices to ppt. $V_2O_5.xH_2O$. By adding to a solution of this salt in cold water the proper quantity of K_2SO_4, G. (*l.c.*) obtained small, amber-yellow crystals, which, after a few washings with cold water, pressure between paper, and drying over H_2SO_4, had the composition of the *double salt* $V_2O_5.2SO_3.K_2O.6aq$. The same crystals were obtained by using the disulphate $V_2O_5.2SO_3$. Replacement of K_2SO_4 by $(NH_4)_2SO_4$ produced the *double salt* $V_2O_5.2SO_3.(NH_4)_2O.4aq$. No double salts were obtained by using Na_2SO_4 or $MgSO_4$, but the trisulphate ($V_2O_5.3SO_3$) crystallised unchanged.

Gerland (*B.* 11, 102) found that when a solution of V_2O_5 in hot. conc. H_2SO_4 was largely diluted and dialysed, H_2SO_4Aq passed rapidly through the dialyser, along with small quantities of V compounds, until the liquid in the dialyser contained V_2O_5 and SO_3 in the ratio $V_2O_5.3SO_3$, after which SO_3Aq passed very slowly through, and the composition of the substance in the dialyser gradually approached $V_2O_5.2SO_3$. By dialysing a diluted solution of V_2O_5 in cold conc. H_2SO_4, the conditions being the same as in the experiment with the hot acid, G. found that SO_3Aq passed through the dialyser regularly, and that, after a time, the ratio of V_2O_5 to SO_3 in the dialyser was 1:1·32. G. supposed these results to mean that a solution of V_2O_5 in cold

H_2SO_4 contains loose, easily decomposed compounds of V_2O_5 and H_2SO_4, but that a solution of V_2O_5 in hot H_2SO_4 contains $V_2O_5.3SO_3$, which gradually loses SO_3 until $V_2O_5.2SO_3$ is formed.

Solutions of V_2O_5 in conc. H_2SO_4 may be reduced to sulphates of lower oxides (Roscoe, *C. J.* [2] 6, 334; Rammelsberg, *B. B.* 1880. 787):—Zn, Cd, or Na-amalgam causes reduction to lavender solutions of $V_2O_2.xSO_3$; Mg effects reduction to green solutions of $V_2O_3.xSO_3$; and H_2S, SO_2, or oxalic acid reduces only to blue solutions of $V_2O_4.xSO_3$.

By fusing V_2O_5 with B_2O_3 (Guyard, *Bl.* [2] 25, 354) obtained a green glass, which he took to be a *vanadic borate*; no analyses or descriptions are given.

The compounds of V_2O_5 with As_2O_5, I_2O_5, P_2O_5, MoO_3, and WO_3 respectively—or some of these compounds—may perhaps be regarded as vanadic arsenates, iodates, &c.; *v.* ARSENO-VANADIC ACIDS AND SALTS, IODO-VANADIC ACIDS, &c., p. 853.

HYPOVANADO-VANADIC OXIDES. Several oxides seem to exist intermediate between V_2O_4 and V_2O_5. Roscoe noticed that V_2O_3 gradually absorbed O and H_2O from the air, forming a greenish solid; Brierley (*C. J.* 49, 30) found that a pale grass-green substance was formed after some months, having the composition $V_2O_4.2V_2O_5.8aq = V_3O_7.4aq$. By dissolving this solid in dilute H_2SO_4Aq, and neutralising by KHOAq, B. obtained $2V_2O_4.4V_2O_5.5K_2O.aq$. By gently heating the compound $2V_2O_4.3V_2O_5.3(NH_4)_2O.6aq$ (*v.* HYPOVANADO-VANADATES, p. 853), B. (*l.c.*) obtained a dark-green solid that absorbed water from the air, and then had the composition $3(V_2O_4.V_2O_5).8aq = 3V_4O_9.8aq$ (*cf.* Ditte, *C. R.* 101, 151; also Manasse, *A.* 240, 23).

Compounds of SO_3 with oxides intermediate between V_2O_4 and V_2O_5 are formed by the reducing action of zinc on solutions of V_2O_5 in H_2SO_4 (*v.* Rammelsberg, *B. B.* 1880. 787).

Vanadium oxyacids, and salts and derivatives thereof. Two oxyacids have been isolated, HVO_3 and $H_4V_2O_7$, corresponding with HPO_3 and $H_4P_2O_7$; salts of these, also salts of the tribasic acid H_3VO_4, and several more complex salts, are known. Salts derived from the hypothetical hypovanadic acid $V_4O_7(OH)_2$ ($= 2V_2O_4.H_2O$) have also been prepared; and several compounds are known which are most simply regarded as $xV_2O_4.yV_2O_5.zMO$, and which may be called hypovanado-vanadates. V_2O_5 also combines with several acidic and basic oxides simultaneously to form compounds of the general form $xV_2O_5.yX{:}xMO$; these compounds are generally described as arseno-vanadates, phospho-vanadates, &c.

VANADIC ACIDS. Two vanadic acids, HVO_3 and $H_4V_2O_7$, have been isolated; salts of the third acid, H_3VO_4, are known, but the acid itself has not certainly been prepared.

Metavanadic acid HVO_3. (*Monobasic vanadic acid. Monohydrate of vanadic oxide* $V_2O_5.H_2O$.) Gerland (*B.* 9, 872 [1876]) prepared this acid by adding an excess of NH_4ClAq to cold $CuSO_4Aq$, then adding NH_4VO_3Aq till a permanent pp. formed, heating to 75°, washing the lustrous yellow scales that slowly separated with dilute H_2SO_4Aq and SO_2Aq (to remove V_2O_4), then washing with water, and drying at 100° until the smell of NH_3 ceased. Manasse (*A.* 240, 52) obtained HVO_3 by decomposing conc. solutions of the Ca, Mg, or Sr salt by a little HNO_3Aq, and washing the pp. with dilute HNO_3Aq, and then with hot water. Metavanadic acid forms golden-yellow crystalline scales; it is unchanged in air; dissolves very slightly in water; insoluble in absolute alcohol; soluble in NH_3Aq, KOHAq, or NaOHAq. By adding NH_4VO_3Aq to $CuSO_4Aq$, filtering from the pp. that formed, and dialysing for several days, Gerland (*l.c.* p. 874) obtained a solution in the dialyser of vanadic acid, which remained clear when heated, and on continued evaporation gave a pp. of red amorphous V_2O_5. Metavanadic acid forms a series of salts (*v.* METAVANADATES, *infra*).

This compound is used as a colour in place of gold bronze, under the name of *vanadium bronze*. According to Guyard (*Bl.* [2] 25, 350), the substance commonly known as vanadium bronze is really an ammonium vanadate.

Pyrovanadic acid $H_4V_2O_7$. (*Tetrabasic vanadic acid. Dihydrate of vanadic oxide* $V_2O_5.2H_2O$.) This acid is obtained by decomposing a fairly conc. solution of an alkali vanadate of the form $M_2V_4O_{11}$ or $M_2V_6O_{16}$ (*v.* TETRAVANADATES and HEXAVANADATES, p. 852) by HNO_3Aq, washing with cold water, and drying in the air (von Hauer, *J. pr.* 80, 324). According to Ditte (*C. R.* 101, 698), the red form of V_2O_5 (*v.* p. 849) absorbs H_2O from the air, forming $V_2O_5.2H_2O$, and also $V_2O_5.5H_2O$. Pyrovanadic acid is described as a brown, amorphous powder, resembling FeO_3H_3; dried over H_2SO_4, it is said to lose half its water. Very slightly soluble in water; the solution is clear yellow; it reddens litmus. $H_4V_2O_7$ is insol. in absolute alcohol; it dissolves readily in NH_3Aq. For salts of this acid *v.* PYROVANADATES (p. 852).

VANADATES. The greater number of the vanadates belong to the series (1) MVO_3, (2) $M_4V_2O_7$, (3) M_3VO_4, (4) $M_2V_4O_{11}$, or (5) $M_2V_6O_{16}$. Series (1), (2), and (3) may be called normal salts; the formulæ may be written as (1) $M_2O.V_2O_5$, (2) $2M_2O.V_2O_5$, and (3) $3M_2O.V_2O_5$. Series (4) and (5) may be called acid salts; the formulæ may be written as (4) $M_2O.2V_2O_5$, and (5) $M_2O.3V_2O_5$. Acid salts are also known intermediate between series (1) and (4); the chief of these are (6) $3M_2O.4V_2O_5 = M_6V_8O_{23}$ ($M_2O{:}V_2O_5 = 1{:}1\frac{1}{3}$), (7) $3M_2O.5V_2O_5 = M_6V_{10}O_{28}$ ($M_2O{:}V_2O_5 = 1{:}1\frac{2}{3}$), and (8) $2M_2O.3V_2O_5 = M_4V_6O_{17}$ ($M_2O{:}V_2O_5 = 1{:}1\frac{1}{2}$). A few salts of the form $4M_2O.V_2O_5 = M_8V_2O_9$ ($M_2O{:}V_2O_5 = 1{:}\frac{1}{4}$) may be called basic salts. Some salts, especially those of Sr and Tl, belong to more complex forms.

Roscoe (*C. J.* [2] 9, 28) has shown that the alkali orthovanadates, M_3VO_4 or $3M_2O.V_2O_5$, are easily decomposed in aqueous solution at the ordinary temperature to pyrovanadates, $M_4V_2O_7$, and MOHAq; but that orthovanadates are formed, rather than meta- or pyro-vanadates, by fusing V_2O_5 with alkali carbonates; further, that aqueous solutions of alkali pyrovanadates are readily decomposed by CO_2 to alkali carbonates and metavanadates.

METAVANADATES M^IVO_3 or $M_2O.V_2O_5$.

Ammonium metavanadate NH_4VO_3. Obtained by dissolving $V_2O_5.xH_2O$ in excess of NH_3Aq, warming, and allowing to evaporate

Forms a white, crystalline crust. Dissolves slowly in cold water, quickly in boiling water. Decomposed by heat, giving V_2O_5 when air is present. According to Berzelius (*P.* 22, 1), when a solution of $V_2O_5.xH_2O$ in excess of NH_3Aq is allowed to evaporate without having been heated, NH_4VO_3 separates in lemon-yellow crystals (*v.* B., *l.c.*; Roscoe, *C. J.* [2] 6, 322; Ditte, *C. R.* 102, 918; Norblad, *B.* 8, 126; Wagner, *D. P. J.* 223, 633; Böttger, *C. C.* 1873 514).

Barium metavanadate $Ba(VO_3)_2.aq$. A yellowish-white pp.; obtained, along with red crystals, by ppg. NH_4VO_3Aq by $BaCl_2Aq$ (Manasse, *A.* 240, 23). Sl. sol. in water. Loses H_2O when heated to c. 200° (Berzelius; Norblad, *l.c.*).

Potassium metavanadate $KVO_3.x$aq. Formed by dissolving V_2O_5 in KOHAq in the ratio V_2O_5:KOH. Various hydrates have been obtained as white crystalline solids, melting to a clear yellow liquid, which solidifies to white, lustrous KVO_3 (*v.* Berzelius, *l.c.*; Ditte, *C. R.* 104, 902, 1061, 1168).

Sodium metavanadate $NaVO_3$. Obtained by Roscoe (*C. J.* [2] 9, 31) by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5:2Na_2CO_3$, dissolving in water, crystallising $Na_4V_2O_7.18$aq, and passing CO_2 into an aqueous solution of this salt, when $NaVO_3$ crystallised out and Na_2CO_3 remained in solution. Small yellowish-white crystals, probably monoclinic prisms, melting readily and solidifying to a yellow crystalline mass (*cf.* Norblad, *l.c.*). Hydrates with 2, 4, and 5 H_2O have been obtained (*cf.* Ditte, *l.c.*).

The other metavanadates that have been prepared are $Cd(VO_3)_2$ (Ditte, *C. R.* 104, 1705); $Ca(VO_3)_2.4$aq (von Hauer, *J. pr.* 69, 385; 80, 324; Manasse, *A.* 240, 23; *cf.* Roscoe, *C. J.* [2] 9, 32); $Co(VO_3)_2.3$aq (D., *l.c.*; Radau, *A.* 251, 114), forms *double salts* with KVO_3 (R., *l.c.*); $Pb(VO_3)_2$ (R., *l.c.*; D., *l.c.*); $LiVO_3.2$aq (Ditte, *C. R.* 104, 1168); $Mg(VO_3)_2.6$aq (D., *l.c.*; Manasse, *l.c.*); $Mn(VO_3)_2.4$aq (Radau, *l.c.*); $AgVO_3.4NH_3.2$aq (D., *l.c.*); $Sr(VO_3)_2.4$aq (Norblad, *l.c.*; Manasse, *l.c.*); $Zn(VO_3)_2.2$aq (D., *l.c.*).

ORTHOVANADATES $M^I_3VO_4$ or $3M_2O.V_2O_5$.

Potassium orthovanadate K_3VO_4. Obtained by fusing V_2O_5 with K_2CO_3; decomposed by water, giving KOHAq and $K_4V_2O_7$ (Rammelsberg, *B. B.* 1883. 3).

Sodium orthovanadate $Na_3VO_4.xH_2O$. Roscoe (*C. J.* [2] 9, 29) obtained the salt with $16H_2O$ by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5:3Na_2CO_3$, allowing to cool, dissolving in as little cold water as possible, quickly adding excess of conc. alcohol, allowing to stand for some hours, washing the crystals that formed with small quantities of alcohol, and drying on a porous plate over H_2SO_4 *in vacuo* (*cf.* Czudnowicz, *P.* 120, 34; Rammelsberg, *B. B.* 1883. 3). Baker (*C. J.* 47, 353) obtained $Na_3VO_4.xH_2O$ with $x=8(?)$, 10, and 12; he also obtained the *double salt* $Na_3VO_4.NaF.19H_2O$. The crystalline forms are given by B., and the various hydrates of Na_3VO_4 are shown to be isomorphous with corresponding arsenates and phosphates. Na_3VO_4Aq changes to $Na_4V_2O_7Aq$ and NaOHAq; the change occurs slowly at ordinary temperatures, and rapidly at higher temperatures (R., *l.c.*).

The other orthovanadates that have been prepared are $Ca_3(VO_4)_2.CaCl_2$ (Hautefeuille, *C. R.* 103, 600; 104, 501); $Pb_3(VO_4)_2$ and $3Pb_3(VO_4)_2.PbCl_2$ (R., *l.c.*); Ag_3VO_4 (R., *l.c.*); Tl_3VO_4 (Carnelley, *C. J.* 26, 323).

PYROVANADATES $M^I_4V_2O_7$ or $2M_2O.V_2O_5$.

Barium pyrovanadate $Ba_2V_2O_7$. Obtained, as a white amorphous powder, by adding $BaCl_2Aq$ to freshly-prepared Na_3VO_4Aq, washing, and drying at 100°. The salt is slightly soluble in water (Roscoe, *C. J.* [2] 9, 33).

Potassium pyrovanadate $K_4V_2O_7$. Hard, deliquescent monoclinic prisms, formed by adding KOHAq to KVO_3Aq, rapidly evaporating to a syrup, and placing over H_2SO_4 (Norblad, *B.* 8, 126).

Sodium pyrovanadate $Na_4V_2O_7.16H_2O$. Formed by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5:2Na_2CO_3$, dissolving, and crystallising; also by exposing Na_3VO_4Aq to air free from CO_2 until addition of alcohol ppts. silky scales ($Na_4V_2O_7$) (Roscoe, *l.c.*, p. 31). White six-sided tables; e. sol. water, insol. alcohol. $Na_4V_2O_7Aq$ is decomposed by CO_2 to Na_2CO_3Aq and $NaVO_3Aq$ (R., *l.c.*).

The other pyrovanadates that have been prepared are $2Ca_2V_2O_7.5$aq (Roscoe, *l.c.*; *cf.* Ditte, *C. R.* 104, 1705); $Cu_2V_2O_7.3$aq (von Hauer, *l.c.*); $Pb_2V_2O_7$ (Ditte, *l.c.*); $2Pb_2V_2O_7.PbO$ (Roscoe, *l.c.*); $Li_4V_2O_7.6$aq (von H., *l.c.*); $Mn_2V_2O_7$ (Ditte, *l.c.*); $Ag_4V_2O_7$ (Roscoe, *l.c.*; Ditte, *l.c.*); $Tl_4V_2O_7$ (Carnelley, *C. J.* 26, 323); $Zn_2V_2O_7$ (D., *l.c.*).

TETRAVANADATES $M_2^IV_4O_{11}$ or $M_2O.2V_2O_5$ (also called *divanadates*).

Ammonium tetravanadate $(NH_4)_2V_4O_{11}.x$aq; $x=3$ or 4. Formed by adding a little acetic acid to boiling NH_4VO_3Aq and evaporating *in vacuo*; also by saturating NH_3Aq with V_2O_5 in a closed, warmed flask, and allowing to evaporate; red prismatic crystals with a golden-yellow sheen (Berzelius, *P.* 22, 1; Rammelsberg, *B. B.* 1883. 3; von Hauer, *l.c.*; Ditte, *C. R.* 102, 918).

Potassium tetravanadate $K_2V_4O_{11}.x$aq; $x=3$, 4, 7, and 10. Obtained by saturating K_2CO_3Aq at 80° with excess of V_2O_5 and allowing to cool; also by adding acetic acid to V_2O_5 in KOHAq, concentrating at 80°, and letting cool (Ditte, *C. R.* 104, 902, 1061, 1168; *cf.* Norblad, *B.* 8, 126). Orange-coloured tablets (*v.* also Gibbons, *C. N.* 30, 267).

The other tetravanadates are $CaV_4O_{11}.9$aq (Manasse, *A.* 240, 23); PbV_4O_{11} (Ditte, *l.c.*); $Li_2V_4O_{11}.9$aq (Norblad, *l.c.*); $MgV_4O_{11}.9$aq. (B., *l.c.*; von Hauer, *l.c.*); $NiV_4O_{11}.3$aq (Radau, *A.* 251, 114); $Na_2V_4O_{11}.9$aq (Berzelius, *P.* 22, 1; von Hauer, *l.c.*; Norblad, *l.c.*); $SrV_4O_{11}.9$aq (B., *l.c.*; von H., *l.c.*).

HEXAVANADATES $M_2^IV_6O_{16}.xH_2O$ or $M_2O.3V_2O_5.xH_2O$ (also called *trivanadates*). These salts have been described by Norblad (*B.* 8, 126) and Ditte (*C. R.* 104, 902, 1061, 1168). The chief are those where $M_2=(NH_4)_2$, Cd, Ca, K_2 and Na_2.

The principal vanadates belonging to other series than those already mentioned are the following:—(1) $3M_2O.4V_2O_5$ $(=M_3^{II}V_8O_{23})$, M = Ca and Sr (*v.* Manasse, *l.c.*); (2) $3MO.5V_2O_5$ $(=M^{II}_3V_{10}O_{28})$, M = Ba, Mg, K_2 (*v.* Manasse, *l.c.*; Radau, *A.* 251, 114); (3) $2MO.3V_2O_5$ $(=M^{II}_2V_6O_{17})$, M = $(NH_4)_2$, Ba, Li_2, Mg, K_2, Na_2 (*v.* Ditte, *l.c.*; also *C. R.* 96, 1048; Manasse, *l.c.*; Norblad, *l.c.*); (4) $4M_2O.V_2O_5(=M^I{}_8V_2O_9)$, $M=Li$ and Na (*v.* Ditte, *l.c.*).

Several other vanadates not belonging to any of these series have also been described; for Ca and Sr salts (and double salts), *v.* Manasse (*l.c.*); and for Tl salts *v.* Carnelley (*C. J.* 26, 323).

HYPOVANADATES. Salts of hypothetical hypovanadic acid $V_4O_7(OH)_2$ $(=2V_2O_4.H_2O)$. These salts belong to the form $M^I{}_2V_4O_9.xH_2O$ $(=M_2O.2V_2O_4.xH_2O)$. The formation of the NH_4 and K salts was described by Berzelius; a series of salts was prepared and examined by Crow (*C. J.* [2] 15, 458). The alkali salts are obtained by treating fairly conc. VO_2ClAq (*v.* HYDRATED VANADIUM DIOXYMONOCHLORIDE, p. 854) with excess of caustic alkalis, allowing the pps. to settle in closed vessels, washing with alkali solution, then with dilute alcohol containing a little acetic acid, and finally with alcohol alone, and drying between paper. The salts of Pb and Ag are obtained by ppn. from a solution of the K salt. The salts form brown to black crystalline powders; the alkali salts dissolve in water. Crow prepared salts with $M_2=(NH_4)_2$, Ba, Pb, K_2, Ag_2, and Na_2.

HYPOVANADO-VANADATES. Salts of the form $nV_2O_4.mV_2O_5.pM_2O.xH_2O$. Alkali salts of this series were obtained by Brierley (*C. J.* 49, 32) by reducing V_2O_5Aq by SO_2, adding V_2O_5 in alkali, then a slight excess of alkali, and then acetic acid; pouring into alkali acetate solution, washing the pps. with alcohol, and drying over $CaCl_2$. The salts crystallise in greenish-black, or black, prisms. The following were prepared: (1) $2V_2O_4.V_2O_5.2Na_2O.13H_2O$; (2) $2V_2O_4.V_2O_5.2K_2O.6H_2O$; (3) $2V_2O_4.2V_2O_5.(NH_4)_2O.14H_2O$; these salts are soluble in water: (4) $2V_2O_4.4V_2O_5.5K_2O.H_2O$; (5) $2V_2O_4.4V_2O_5.3(NH_4)_2O.6H_2O$; these are insoluble in water.

COMPLEX VANADIC ACIDS AND SALTS. Vanadic oxide V_2O_5 combines with several anhydrides, such as As_2O_5, I_2O_5, P_2O_5, &c., and many of the compounds thus produced combine with basic oxides. The compounds of V_2O_5 with certain anhydrides are generally regarded as acidic; and the compounds formed of V_2O_5, anhydrides, and bases are usually classed as salt-like substances. It is quite likely that many of the compounds of V_2O_5 with anhydrides, such as As_2O_5, P_2O_5, &c., would be better classed as salts, just as the compounds of V_2O_5 with SO_3 are classed as salts.

Arseno-vanadic acids and salts. By boiling V_2O_5 with excess of H_3AsO_4Aq, and concentrating the solution, Fernandez (*B.* 17, 1632) obtained lustrous, golden-yellow crystals of $V_2O_5.As_2O_5.11aq$ (*cf.* Friedheim a. Schmitz-Dumont, *B.* 23, 2600). Gibbs (*P. Am. A.* 21, 50) obtained $xV_2O_5.yAs_2O_5.zaq$ (x and y probably either 5 and 8, or 7 and 6), by decomposing a mixture of Na vanadate and arsenate by HNO_3Aq. For various compounds of the form $mV_2O_5.nAs_2O_5.pMO$, where m and n are 1 and 1, 2 and 3, 1 and 2, 2 and 1, &c., and p varies from 1 to 5, *v.* F. a. S.-D. (*l.c.*).

Iodo-vanadic acids. Ditte (*C. R.* 102, 757) says that compounds of V_2O_5 and I_2O_5 are formed by heating V_2O_5 with conc. HIO_3Aq; he gives formulæ, but no analyses.

Molybdo-vanadic acids and salts. For descriptions of numerous compounds of the forms $xV_2O_5.yMoO_3.zaq$, $xV_2O_5.yMoO_3.pMO.zaq$, and also $xV_2O_5.yMoO_3.mP_2O_5.pMO.zaq$, *v.* Gibbs (*P. Am. A.* 18, 232).

Phospho-vanadic acids and salts. Various compounds of V_2O_5, P_2O_5, and H_2O are described by Gibbs (*P. Am. A.* 21, 50); Ditte (*C. R.* 102, 757) also assigned formulæ to substances obtained by heating V_2O_5 with conc. H_3PO_4. Friedheim (*B.* 23, 1530) obtained $V_2O_5.P_2O_5.2H_2O$ by dissolving V_2O_5 in syrupy H_3PO_4.

For descriptions of a great many compounds of the form $xV_2O_5.yP_2O_5.nMO.zaq$, *v.* Gibbs (*l.c.*); and *cf.* Friedheim (*l.c.*).

F. divides the compounds formed by reacting with V_2O_5 on alkali phosphates into two classes, which he calls *luteo-* and *purpureo- compounds.*

Luteo- compounds are formed by (1) the interactions of phosphoric and vanadic acids in solution; (2) the interactions of solutions of phosphates and vanadates in presence of small quantities of acids; (3) the interactions of solutions of phosphates and vanadic acid; (4) the interactions of vanadates and phosphoric acid, by heating solutions nearly to boiling and evaporating. These compounds are yellow, granular, and indistinctly crystalline; the alkali compounds are very slightly soluble in water, solution being accompanied by decomposition. The following luteo- compounds are described by F.:

$V_2O_5.P_2O_5.2H_2O.9aq$,
$V_2O_5.P_2O_5.(NH_4)_2O.H_2O.2aq$,
$2V_2O_5.P_2O_5.(NH_4)_2O.7aq$,
$V_2O_5.P_2O_5.K_2O.H_2O.2aq$, and
$2V_2O_5.P_2O_5.K_2O.7aq$.

Purpureo- compounds are formed by dissolving vanadic acid in conc. solutions of alkali phosphates, and by adding phosphoric acid to conc. solutions of alkali vanadates; in each case the solutions should be strongly heated. The purpureo- compounds described by F. belong to the form $12V_2O_5.P_2O_5.7M_2O.26aq$; they are dark-red crystalline substances, sol. in water.

F. regards the luteo- compound of the form $V_2O_5.P_2O_5.2H_2O.9aq$ as acid phosphate of the radicle VO_2, thus $(VO_2)H_2PO_4.9aq$; he compares this with the acid orthophosphates MH_2PO_4. The compounds of the form $V_2O_5.P_2O_5.M_2O.H_2O.xaq$ are looked on as double acid phosphates of alkali metal and VO_2, thus $NH_4(VO_2)HPO_4$. The luteo- compounds $2V_2O_5.P_2O_5.M_2O.xaq$ are formulated by F. as double compounds of alkali metavanadates and $(VO_2)H_2PO_4$; thus $2V_2O_5.P_2O_5.K_2O.2H_2O.5aq = 2(KVO_3.(VO_2)H_2PO_4.2\frac{1}{2}aq)$. The purpureo- compounds which belong to the form $12V_2O_5.P_2O_5.7M_2O.xaq$ are looked on by F. as double compounds of acid vanadates and acid phosphates; this view of their constitution is expressed by the statement

$$12V_2O_5.P_2O_5.7M_2O.xH_2O = P_2O_5.2M_2O.H_2O + 12V_2O_5.5M_2O + (x-1)H_2O.$$

These views of F. are considerably modified in a later paper (*Zeit. f. anorg. Chemie*, 5, 437), where the purpureo- compounds are looked on as divanadates with some V_2O_5 isomorphously replaced by P_2O_5. According to F., many of the substances described by Gibbs and by Ditte do not exist.

Berzelius (*P.* 22, 1) described a compound of V_2O_5, P_2O_5, and SiO_2, with H_2O, which may be named *phospho-silico-vanadic acid.*

TUNGSTO-VANADIC ACIDS AND SALTS. The compounds of V_2O_5 with WO_3 and bases that have been described are very numerous, and the formulæ given are generally extremely complex (*v.* Gibbs, *P. Am. A.* 18, 232; Rosenheim, *A.* 251, 197, 234; and especially Friedheim, *B.* 17, 1505; 23, 1505; 24, 1173).

Vanadium, oxybromides of. Two compounds of V with O and Br have been isolated; $VOBr_2$ and $VOBr_3$, corresponding with two of the five oxychlorides. According to Schafarik (*W. A. B.* 33, 14; 47 [11] 251), other oxybromides also exist.

VANADIUM OXYDIBROMIDE $VOBr_2$. (*Vanadyl dibromide.*) A brown, deliquescent powder. Prepared by heating $VOBr_3$ (*v. infra*); decomposition to $VOBr_2$ and Br occurs slowly at temperatures below 180°, and suddenly at 180°. Heated in air forms V_2O_5; dissolves in water, forming a blue solution (Roscoe, *C. J.* [2] 9, 26). Ditte (*C. R.* 102, 1310) says that a compound $VOBr_2.4H_2O$ is formed, as dark-green, deliquescent crystals, by treating red V_2O_5 with HBr. D. writes the formula $V_2O_3Br_2.2HBr.7H_2O$.

VANADIUM OXYTRIBROMIDE $VOBr_3$. (*Vanadyl tribromide.*) Prepared by passing vapour of pure Br over V_2O_3 heated to redness, condensing the yellowish-white vapours that are formed, removing excess of Br from the red liquid by heating to 40°–50° at c. 100 mm. pressure in a current of perfectly dry air, and then distilling *in vacuo* (Roscoe, *C. J.* [2] 9, 24). $VOBr_3$ is a red, very hygroscopic liquid that boils at 130°–136° at 100 mm. pressure; S.G. 2·9673 at 0°, 2·9325 at 14·5°; decomposes slowly at the ordinary temperature, and suddenly at 180°, to $VOBr_2$ and Br (R., *l.c.*).

Vanadium, oxychlorides of. Five compounds of V with O and Cl have been isolated: VOCl, $VOCl_2$, $VOCl_3$, V_2O_2Cl, and $VO_2Cl.x$aq.

VANADIUM OXYMONOCHLORIDE VOCl. (*Vanadyl monochloride.*) Obtained by the regulated reduction of $VOCl_3$ by H. The mixed vapours are passed through a red-hot tube; VOCl is deposited near the end whereat the vapours enter the tube. A brown, light, flocculent powder; insol. in water; easily dissolved by HNO_3Aq (Roscoe, *C. J.* [2] 6, 347).

VANADIUM OXYDICHLORIDE $VOCl_2$. (*Vanadyl dichloride.*) Prepared by heating a slight excess of $VOCl_3$ with zinc for some days in a sealed tube, at 400°, cutting off the part of the tube on which the sublimate of $VOCl_2$ has formed (V_2O_4 and $ZnCl_2$ are the other products), quickly placing it in a wider tube, and removing $VOCl_3$ by heating in a stream of dry CO_2 at 130°. Also obtained by passing vapour of $VOCl_3$ and H through a red-hot tube; $VOCl_2$ is deposited near the end of the tube whereat the gases enter, and V_2O_2Cl at the further end of the tube (Roscoe, *l.c.*, p. 348). Lustrous, grass-green, deliquescent tablets; S.G. 2·88 at 13°; slowly decomposed by water; soluble in dilute HNO_3Aq. A compound with $PtCl_4$, having the composition $2(VOCl_2.PtCl_4).21$aq, is said by Brauner (*M.* 3, 58) to be formed by dissolving V_2O_5 in conc. HClAq in presence of $PtCl_4$Aq.

VANADIUM OXYTRICHLORIDE $VOCl_3$. (*Vanadyl trichloride.*) Mol. w. 173·27.

Formation.—1. By heating V_2O_3 gently in a stream of Cl (Berzelius, *P.* 22, 1).—2. By heating a mixture of V_2O_5 and C in Cl.

Preparation.—A mixture of V_2O_5 and sugar-charcoal is heated to redness in a stream of dry H, and allowed to cool in that gas; a stream of dry Cl is then passed over the mixture, which is heated to redness, and the product is condensed; the liquid thus obtained is heated for some hours in a flask with an inverted condenser, in a current of dry CO_2, and then rectified over Na (Roscoe, *C. J.* [2] 6, 342).

Properties and Reactions.—A clear, mobile, lemon-yellow liquid (Berzelius, *l.c.*; Roscoe, *l.c.*; Schafarik, *A.* 109, 85). S.G. 1·836 at 17·5°, 1·828 at 24° (R., *l.c.*); 1·86534 at $\frac{0^\circ}{0^\circ}$, 1·63073 at b.p. (Thorpe, *C. J.* 37, 348). B.P. 127·19° (T., *l.c.*). S.V. 106·25. Does not solidify above −15° (R., *l.c.*). V.D. 88·38 at 186° (R., *l.c.*; *cf.* T., *C. N.* 24, 827; Schafarik, *l.c.*). Gives off thick, yellowish-red fumes in the air. Dissolves in a little water, forming a thick, red liquid; dissolves in much water, forming a clear yellow liquid; dissolves in absolute alcohol with a red colour, but the solution soon becomes blue, owing to reduction. Heated to 60°–70° in a closed tube with ether forms needles of the composition $VOCl_3.Et_2O$ (Bedson, *C. J.* 29, 309).

DIVANADIUM DIOXYMONOCHLORIDE V_2O_2Cl. (*Divanadyl monochloride.*) Yellow-bronze, microscopic crystals, resembling *mosaic gold*; formed by passing $VOCl_3$ and H through a red-hot tube. The crystals are deposited on the part of the tube farthest from the end whereat the gases enter (Roscoe, *C. J.* [2] 6, 348). Insoluble in water; soluble in HNO_3Aq. This compound was thought by Schafarik (*A.* 109, 85) to be V.

HYDRATED VANADIUM DIOXYMONOCHLORIDE $VO_2Cl.x$aq. (*Hypovanadic chloride* $V_2O_4Cl_2.x$aq.) Formed, as a brown, deliquescent solid, by passing H_2S into a solution of V_2O_5 in hot HClAq, filtering from S, and evaporating (Crow, *C. J.* 30, 457). Heated in a stream of dry CO_2 gives off HCl and H_2O, and leaves V_2O_4. C. (*l.c.*) gives the hydration as $V_2O_4Cl_2.5$aq.

Vanadium, oxyfluorides of. No compound of V with O and F has been isolated with certainty. V_2O_2 dissolves in excess of HFAq; on evaporation, solution in water, and evaporation over H_2SO_4, Petersen (*J. pr.* [2] 40, 194) obtained blue, microscopic crystals which he supposed might be $VOF_2.x$aq, inasmuch as a solution of these crystals in HFAq treated with fluorides yielded salts of the form xMF.yVOF$_2$ (*v.* HYPOVANADOXYFLUORIDES, p. 845). P. did not obtain enough of the blue crystals for analysis.

Vanadium, oxyiodides of. According to Ditte (*C. R.* 102, 1310), an oxyiodide $2VOI_2.9H_2O$ is formed, as a black, deliquescent mass, by adding excess of HIAq to a warm solution of red V_2O_5, removing free I by shaking with finely-divided Ag, filtering, and evaporating *in vacuo*. The compound is said to react with NH_3Aq, giving $(NH_4)_2V_4O_9$. D. writes the formula as $V_2O_2I_2.2HI.8H_2O$; but no analyses are given.

No reaction occurs when I is heated with V_2O_3 (Roscoe, *C. J.* [2] 9, 28); nor when V_2O_5 is digested with water, or alcohol, and I (Guyard, *Bl.* [2] 25, 351). V_2O_5 and I_2O_5 probably combine (*v.* Ditte, *C. R.* 102, 757, 1019).

Vanadium, oxysulphides of. None of these compounds has been certainly isolated. Oxysulphides may perhaps be formed by decomposing alkali thiovanadates in solution by dilute acids (*v.* Kay, *C. J.* 37, 728).

Vanadium, salts of. Compounds of the oxides V_2O_3, V_2O_4, and V_2O_5 with acidic oxides have been isolated; the formulæ of one or two of the compounds may be written as derived from oxyacids by replacing H by V, but it is simpler, and more in keeping with the facts that are known, to represent all the compounds by the general formula $V_2O_x.yX$, where X is an acidic oxide. The best-studied compounds of V_2O_4 with acidic oxides may be represented as salts of the radicle V_2O_2 (divanadyl), or of the radicle VO (vanadyl); and the compounds of V_2O_5 with acidic oxides as acid salts of the radicle VO_2. The sulphates have been better studied than the other salts; the following table presents the compositions of the sulphates.

I. *Vanadous sulphates* (*v.* p. 847):
$V_2O_3.4SO_3.x\text{aq} = V_2H_2(SO_4)_4.y\text{aq}$ $(y = x - 1)$;
??$V_2O_3.3SO_3 = V_2(SO_4)_3$.

II. *Hypovanadic sulphates* (*v.* p. 848):
$V_2O_4.2SO_4 = V_2O_2.(SO_4)_2 = (VO)SO_4$;
$V_2O_4.3SO_3.x\text{aq} = V_2O_2.H_2(SO_4)_3.y\text{aq}$ $(y = x - 1)$
$= (VO.SO_4)_2.H_2SO_4.y\text{aq}$.

III. *Vanadic sulphates* (*v.* p. 850):
$V_2O_5.2SO_3 = (VO_2)_2SO_4.SO_3$; or if the salt contains $x$aq, then $V_2O_5.2SO_3.x\text{aq} =$
$(VO_2)_2SO_4.H_2SO_4.y\text{aq}$ $(y = x - 1)$;
$V_2O_5.3SO_3 = (VO_2)_2SO_4.2SO_3$; or if the salt contains $x$aq, then
$V_2O_5.3SO_3.x\text{aq} = (VO_2)_2SO_4.2H_2SO_4.yH_2O$
$(y = x - 2)$.

Alkalis probably ppt. $V_2O_3.x\text{aq}$ from solutions of vanadous sulphates (*v.* p. 847); from solutions of hypovanadic sulphates alkalis ppt. $V_2O_4.x\text{aq}$ (*v.* p. 848).

V_2O_2 dissolves in oxyacids, forming lavender solutions which probably contain $V_2O_2.xX$, where X is an acidic oxide (*v.* p. 846).

Various salts of V_2O_3, V_2O_4, and V_2O_5 besides the sulphates probably exist, but they have not been thoroughly examined (*v.* Hypovanadic salts, p. 848; Vanadic salts, p. 850; Arseno-vanadic acids and salts, p. 853; Iodo-vanadic acids, p. 853; Molybdo-vanadic acids and salts, p. 853; Phospho-vanadic acids and salts, p. 853; and Tungsto-vanadic acids and salts, p. 854).

Vanadium, silicide of. Roscoe (*C. J.* [2] 8, 358) says that V acts on glass or porcelain vessels when strongly heated therein, forming a compound with Si; tubes in which V chlorides are reduced by heating in H get coated with a grey lustrous mirror of this compound. No details or analyses are given.

Vanadium, silicofluoride of. By boiling V_2O_3 with H_2SiF_6Aq and alcohol, Guyard (*Bl.* [2] 40, 352) obtained a greyish, uncrystallisable mass which he took to be a silicofluoride of V; no analyses or details of preparation are given.

Vanadium, sulphides of. Berzelius (*P.* 22, 1) described two compounds of V and S, one obtained by ppg. a solution of an alkali thiovanadate by dilute acid, and the other by heating V_2O_3 in H_2S. B. gave the formulæ VS_2 and VS_3 to the compounds he described. The sulphides of V were re-examined by Kay in 1880 (*C. J.* 37, 728), who found that the pp. obtained by adding dilute HClAq or H_2SO_4Aq to a solution of sodium vanadate saturated with H_2S, or to solution of V_2O_5 in an alkali hydrosulphide, contained O, but probably had not a definite composition; and that the product of heating V_2O_3 in H_2S is the trisulphide V_2S_3; Kay prepared three sulphides, V_2S_2, V_2S_3 and V_2S_5, corresponding to three of the four oxides; the sulphides dissolve in solutions of alkali sulphides, probably forming *thiovanadates* (*q. v. infra*).

Vanadium disulphide V_2S_2. (*Hypovanadous sulphide.*) Prepared by heating V_2S_3 to full redness, for a long time, in H quite free from O. Forms black lustrous plates, or a brownish-black powder; S.G. 4·2 to 4·4. Absorbs O very quickly when heated in air, giving V_2O_3, V_2O_4, and then V_2O_5, with evolution of SO_2. Not acted on by boiling HClAq, dilute or conc., nor by boiling dilute H_2SO_4Aq, or cold conc. H_2SO_4. Dissolves in hot conc. H_2SO_4; dissolves in HNO_3Aq. Slowly acted on by NaOHAq or KOHAq, hot or cold; dissolves in $(NH_4)_2S$Aq or KHSAq, forming purple to reddish-brown solutions (Kay, *l.c.* p. 735).

Vanadium trisulphide V_2S_3. (*Vanadous sulphide.*) Formed by strongly heating V_2O_3 in a stream of H_2S (Berzelius, *l.c.*; Kay, *l.c.* p. 736); also by heating any chloride of V or $VOCl_3$, to redness in H_2S (K., *l.c.*); and by strongly heating V_2O_5 in a stream of vapour of CS_2 so long as any reaction occurs (K., *l.c.*). Forms dark, lustrous plates, or a black amorphous powder; S.G. 3·7 to 4·0. Oxidised by heating in air, finally to V_2O_5, giving off SO_2. Scarcely acted on by dilute HClAq or H_2SO_4Aq, hot or cold, nor by conc. HClAq; readily oxidised by HNO_3Aq. Soluble in $(NH_4)_2S$Aq or KHSAq, forming purple-red to golden-red solutions; also somewhat soluble in KOHAq, NaOHAq or NH_4OHAq (Kay, *l.c.*).

Vanadium pentasulphide V_2S_5. (*Vanadic sulphide.*) Prepared by mixing V_2S_3 with ⅔ its weight of pure powdered S, heating to fusion (c. 400°) in a narrow tube quite filled with CO_2 and sealed, cooling, and dissolving out excess of S with CS_2. A black powder; S.G. 3·0. Heated in a gas that does not react with it, V_2S_5 gives off S and leaves V_2S_3; heated in air gives off SO_2, forming V_2O_3 and finally V_2O_5. Behaves towards acids similarly to V_2S_3. Dissolves in hot NaOHAq; also in $(NH_4)_2S$Aq or KHSAq, forming yellow to red solutions (Kay, *l.c.* p. 738).

Vanadium thio-acids, and salts thereof. No compound of V with H and S has been isolated, but some thiovanadates, and also some oxythiovanadates, have been prepared by Krüss a. Ohnmais (*B.* 23, 2547).

Ammonium thio-orthovanadate $(NH_4)_3VS_4$. Obtained, in purple crystals, resembling $KMnO_4$, S.G. 1·62, by passing H_2S into a solution of NH_4VO_3 in NH_3Aq S.G. ·898; the solution is saturated in the cold, and is kept cold while H_2S is passed in. A brown pp. is formed, and this dissolves after passing in more H_2S to a dark-violet liquid, from which the salt crystallises after some time.

Sodium monoxy-thio-orthovanadate $Na_3VOS_3.5\text{aq}$. Obtained by saturating 80 c.c

NaOHAq S.G. 1·122, with H_2S, adding a solution of 3 g. $Na_4V_2O_7$ in 6 c.c. water, cooling the liquid by ice, and passing in H_2S for 4 hours. The salt was also obtained without water of crystallisation by Krüss (*Zeit. f. anorg. Chemie*, 3, 264) by fusing a mixture of V_2O_5, Na_2CO_3, and S, until excess of S was removed. Small crystals, that melt at the ordinary temperature to a red, oily liquid (K. a. O., *l.c.*).

Sodium trioxy-thio-orthovanadate Na_3VO_3S. 10aq. Obtained by heating $Na_4V_2O_7Aq$ to boiling, adding freshly prepared NaSHAq, cooling by ice, and adding alcohol. A red oil, that solidifies to a crystalline mass which melts at 18° (K. a. O., *l.c.*).

Ammonium monoxy-thio-pyrovanadate $(NH_4)_4V_2OS_6$. Formed by passing H_2S into a cooled solution of NH_4VO_3 in NH_3Aq S.G. greater than ·898, and allowing the liquid to stand for some months, when crystals separate having S.G. 1·715 (K. a. O., *l.c.*).

Potassium monoxy-thio-pyrovanadate $K_4V_2OS_6$. 3aq. Obtained by passing H_2S into KVO_3 in KOHAq S.G. 1·472, air being excluded and the liquid cooled by ice. Crystals resemble $KMnO_4$; S.G. 2·144; loses all water slowly at 150°. By evaporating the mother-liquor from this salt *in vacuo*, large crystals of the salt $2K_4V_2OS_6$. 3aq are obtained (K. a. O., *l.c.*).

M. M. P. M.

VANADOXYFLUORIDES and *Hypovanadoxyfluorides*; *v.* pp. 844–5.

VANADYL COMPOUNDS; compounds of the radicle VO: *v.* Vanadium oxybromides (p. 854), Vanadium oxychlorides (p. 854), and Hypovanadic salts (p. 848).

VANILLIC ACID *v. Methyl derivative* of Protocatechuic acid.

VANILLIN *v. Methyl derivative* of Protocatechuic aldehyde.

VANILLO-DIACETONAMINE *v.* Acetonamine.

VAPOUR DENSITIES. The term 'vapour density' is now generally employed to signify the specific gravity of a gas referred to hydrogen as unity. For descriptions of the principles of the methods used in determining vapour densities, *v.* Densities, relative, vol. ii. p. 374; and for an account of the application of vapour densities to finding molecular weights, *v.* Atomic and molecular weights, vol. i. p. 340.

VEGETABLE PROTEÏDS *v.* Proteïds.

VERATRALBINE *v.* Jervine.

VERATRIC ACID *v. Di-methyl derivative* of Protocatechuic acid.

Homo-veratric acid *v.* Di-oxy-phenyl-acetic acid.

VERATROLE *v. Di-methyl ether* of Pyrocatechin.

VERATRUM ALKALOIDS.

Veratrine $C_{32}H_{49}NO_9$. *Cevadine.* [205°]. S. ·12 at 15° Occurs in the seeds of *Veratrum Sabadilla* (Meissner, *N. J. T.* 5, 3; Pelletier a. Caventou, *A. Ch.* [2] 14, 69; Couerbe, *A. Ch.* [2] 52, 352; Merck, *A.* 95, 200; *Ar. Ph.* 231, 135; Delondre, *J. Ph.* [3] 27, 417; Weigelin, *C. C.* 1872, 229; Schmidt, *Ar. Ph.* [3] 10, 511; *B.* 9, 1115; *A.* 185, 224). Occurs also in the root of *Sarracenia purpurea* (St. Martin, *Z.* [2] 2, 442; Hétet, *C. R.* 88, 185). Prepared by extracting the seeds with boiling alcohol containing a little tartaric acid, concentrating the extract, adding water, filtering from resin, adding Na_2CO_3, and shaking with ether. The ethereal solution is shaken with dilute tartaric acid solution, and the acid solution mixed with Na_2CO_3 and extracted with ether. The ethereal extract is mixed with ligroïn and allowed to evaporate spontaneously, when a viscid mass first separates, followed by crystals which are recrystallised from alcohol (Wright a. Luff, *C. J.* 33, 338). If commercial veratrine [144°] be dissolved in alcohol at 70°, water added till turbidity ensues, and the solution evaporated at 50° to 60°, crystalline veratrine separates first, then a resinous mixture of veratrine and veratridine, while the mother-liquor contains veratridine and veratroïn veratrate (Rosetti, *Ar. Ph.* [3] 21, 81).

Properties.—Needles (from alcohol), sol. ether, insol. water. Inactive to light. Very poisonous, a small quantity producing vomiting and purging. Introduced into the nose it produces sneezing. Alkaline to test papers. Conc. H_2SO_4 forms a yellow colour changing to crimson, 1 pt. colouring 3,000 pts. H_2SO_4 (Vasmer, *Ar. Ph.* 2, 74). Conc. HClAq forms a violet solution on warming. HNO_3 forms a red solution, becoming yellow. Veratrine mixed with sugar (3 pts.) is coloured by H_2SO_4 dark green and finally deep blue (Weppen, *Fr.* 13, 454). A solution of ammonium selenite (1 g.) in H_2SO_4 (20 c.c.) gives a yellow colour at 30°; in 3 hours a red pp. is formed, the liquid remaining yellow (Da Silva, *C. R.* 112, 1267). On heating with alcoholic potash or baryta it yields angelic acid and cevine (W. a. L.; Rosetti; Stransky, *M.* 11, 482). ICl forms a yellow flocculent pp., sol. hot HClAq (Dittmar, *B.* 18, 1612). Conc. HClAq yields tiglic acid. Veratrine yields tiglic acid and (β)-methyl-pyridine on distillation. On distilling veratrine with lime the products are (β)-methyl-pyridine and its hexahydride and isobutyric acid (Ahrens, *B.* 23, 2705). Veratrine is not affected by boiling dilute H_2SO_4.

Salts.—B'HCl. Amorphous.—$B'_2H_2PtCl_6$: amorphous.—$B'HAuCl_4$. Yellow needles (from alcohol).—$B'HAuCl_4$ 2aq (Rosetti, *J.* 1883, 1351).—$B'HHgCl_3$. Crystalline pp., v. sol. alcohol.—$B'_2H_2SO_4$ (dried at 100°).—$B'HI_3$. Reddish-brown amorphous solid (Bauer, *J.* 1874, 861).

Benzoyl derivative $C_{32}H_{48}BzNO_9$. [170°–180°]. Brown crystals (containing 1½ aq) (from ether).—$B'HAuCl_4$.

Dibromide $C_{32}H_{49}Br_2NO_9$. Formed by allowing the tetrabromide to stand in contact with dilute KOHAq. Light-yellow amorphous solid.

Tetrabromide $C_{32}H_{49}Br_4NO_9$. Formed by shaking veratrine with bromine-water. Yellow amorphous powder, insol. water, v. sol. alcohol and ether (Ahrens, *B.* 23, 2701).

Cevine $C_{27}H_{43}NO_8$ (W. a. L.); $C_{27}H_{44}NO_8$ (Rosetti). *Cevedine.* [145°] (W. a. L.); [182°–185°] (R.). Formed by boiling veratrine with alcoholic NaOH (W. a. L.). Yellow resin, v. sol. alcohol, sl. sol. ether. Its aqueous solution becomes turbid on warming. Does not attack the mucous membrane, gives a crimson colour with H_2SO_4, and a brown colour with cane-sugar and H_2SO_4. Its salts are amorphous.—$B'HHgI_3$ (dried at 100°). Precipitate.

Veratridine $C_{37}H_{53}NO_{11}$ (W. a. L.); $C_{32}H_{49}NO_9$ (Rosetti). *Veratrine.* [180° cor.] (W. a. L.); [150°-155°] (R.). S. 3 at 15°. If the viscid mass which separates before veratrine when a solution of the crude base in alcohol-ligroïn is evaporated be shaken with ether, cevadilline remains undissolved, while veratridine dissolves in the ether (Wright a. Luff). Amorphous resin, sl. sol. ether. Decomposed by alcoholic potash into veratric acid and verine $C_{28}H_{45}NO_8$ [c. 95°] (W. a. L.) or veratroïn $C_{55}H_{92}N_2O_{16}$ [143°-148°] (R.), an amorphous base, sol. ether. Veratridine dissolves in boiling water, being converted into veratroïn veratrate $C_{55}H_{92}N_2O_{16}C_9H_{10}O_4$ 2aq (Rosetti), which melts, when anhydrous, at 165°-170°. H_2SO_4 forms a yellow solution which turns crimson.—Salts.—$B'HAuCl_4$. Amorphous.—$B'H_2SO_4$ 10aq, crystalline.

Cevadilline $C_{34}H_{53}NO_8$. Obtained as above (W. a. L.). Amorphous, sl. sol. ether, m. sol. benzene. Decomposed by alcoholic potash.

Salts.—$B'HAuCl_4$.—$B'HHgI_3$. Gelatinous. Cevadilline is perhaps identical with the sabadilline $C_{41}H_{66}N_2O_{13}$ of Wiegelin (*C. C.* 1872, 229), to which Hesse (*A.* 192, 186) assigns the formula $C_{21}H_{35}NO_7$; while sabatrine $C_{51}H_{86}N_2O_{17}$ (W.) or $C_{26}H_{45}NO_9$ (H.) was probably a mixture of decomposition-products (Wright a. Luff).

Veratrum album. The alkaloids in the root of this plant, and in that of *V. viride*, are described under JERVINE.

VERATRUMIC ACID is VERATRIC ACID.

VERINE *v.* VERATRUM ALKALOIDS.

VERNIN $C_{16}H_{20}N_8O_8$ 3aq. Occurs in young vetch plants (*Vicia sativa*), in young red clover (*Trifolium pratense*), in pumpkin seeds, in ergot, and in the blossom of *Corylus avellana* and *Pinus sylvestris* (E. Schulze, *J. pr.* [2] 32, 447; *H.* 10, 80, 326). Separated from asparagin by crystallisation from hot water. Minute silky prisms, v. sol. hot water, insol. alcohol. Its aqueous solution is neutral, gives no pp. with $Pb(OAc)_2$, but is ppd. by $AgNO_3$, by picric acid, and by phosphotungstic acid in presence of HCl. Boiling hydrochloric acid forms guanine.—$Ag_2C_{16}H_{18}N_8O_8$. Gelatinous pp.

VERNONIN $C_{10}H_{24}O_7$. Occurs in the root of *Vernonia nigritiana*, used on the west coast of Africa as a febrifuge (Heckel a. Schlagdenhauffen, *C. R.* 106, 1446). White powder, sl. sol. ether and chloroform, sol. alcohol. Conc. H_2SO_4 gives a brown colour, changing to purple. Cardiac poison, 80 pts. being required to produce the effect of 1 pt. of digitalin. Decomposed by boiling dilute HCl into glucose and a resin $C_4H_{10}O_2$.

VICIN $C_{28}H_{51}N_{11}O_{21}$. S. 1 at 23°. Occurs in the seeds of *Vicia sativa*, *V. Faba*, and *V. Faba minor* (Ritthausen, *J. pr.* [2] 2, 333; 24, 202; 29, 359). Obtained by extracting the seeds with cold dilute H_2SO_4 (1:50), neutralising with lime, filtering from $CaSO_4$, evaporating to dryness and crystallising from 85 p.c. alcohol. The yield is ·25 p.c.

Properties.—Tufts of small needles, nearly insol. alcohol. Loses $2H_2O$ at 160°. Sol. alkalis and alkaline earths, reppd. on neutralisation. Not affected by boiling baryta-water. Sol. dilute HCl and H_2SO_4, but after boiling the solution gives a deep-blue colour with $FeCl_3$ and NH_3, and a violet pp. with baryta. Boiling KOHAq (S.G. 1·1) also forms divicin. When evaporated with HNO_3 (S.G. 1·2) the residue is edged with deep violet. Potash-fusion forms KCy.

Salts.—$B'_4 4H_2SO_4$.—$B'_4 11HCl$. Slender needles.

Divicin $C_{21}H_{50}N_{20}O_{16}$. By boiling vicin with water (5 pts.) containing H_2SO_4 (1 pt.) at 0° there is formed crystalline $(C_{32}H_{28}N_{20}O_8)2\frac{1}{2}SO_4$, which yields divicin on treatment with exactly the calculated quantity of KOHAq. Flat prisms (from water). Reduces $AgNO_3$ at once. Not ppd. by baryta. A little $FeCl_3$ followed by NH_3 gives a splendid blue colour.—$B'8HNO_3$. Whetstone-shaped crystals, got by adding HNO_3 to a solution of divicin.

Convicin $C_{20}H_{28}N_6O_{11}$ 2aq. Obtained from powdered vetch seeds by extracting with alcohol, allowing vicin to crystallise from the extract, ppg. the mother-liquor with $HgCl_2$ and potash, decomposing the pp. with aqueous H_2S, and evaporating. The mixture of vicin and convicin so obtained is treated with dilute H_2SO_4, which dissolves the vicin only. Thin plates (from water), often resembling leucine. Hardly sol. cold water, sl. sol. alcohol. Not decomposed by boiling KOHAq (S.G. 1·1). Potash-fusion gives off NH_3, but forms no KCy. Insol. cold dilute HCl and H_2SO_4. Its aqueous solution gives a flocculent pp. with $Hg(NO_3)_2$.

VINACONIC ACID *v.* TRI-METHYLENE DI-CARBOXYLIC ACID.

VINCETOXIN $C_{10}H_{12}O_6$. [59°]. $[\alpha]_D = -50°$. Extracted by milk of lime from powdered asclepias root (Tanret, *C. R.* 100, 277; *Bl.* [2] 43, 620). Occurs in two forms, one soluble and one insoluble in water. Both forms are lævorotatory, amorphous, sl. alcohol, insol. ether. Boiling dilute HCl yields an amorphous, inactive sugar, which does not ferment with yeast.

VINYL ALCOHOL $CH_2:CH.OH$. This substance might be expected to be identical with aldehyde $CH_3.CHO$, but Poleck a. Thümmel (*B.* 22, 2863) suppose it to be present in ether that has been exposed to air and sunlight, and that its presence is indicated by the formation of a pp. $C_2H_3OHgOHg_2Cl_2$ when a solution of mercury oxychloride in Na_2CO_3Aq is added to commercial ether. This pp. is white, and is converted by boiling potash into explosive greenish-black 'acetylene mercury' $C_2H_2O_4Hg_4$, and by adding nitric acid to its alkaline solution into $C_2HHg_2OCl_2$, which is not explosive. H_2S passed into water containing the compound $C_2H_3O_2Hg_3Cl_2$ yields (γ)-tri-thio-acetic aldehyde [76°].

VINYL-DIACETONAMINE *v.* ACETONAMINES.

VINYL-AMINE $CH_2:CH.NH_2$. Formed by the action of moist Ag_2O or of KOHAq on bromo-ethylamine hydrobromide at 48° (Gabriel, *B.* 21, 1049, 2665). Known only in aqueous solution. Volatile with steam. Decomposes in aqueous solution even in the cold. SO_2 converts it into taurine.

Salts.—$^{\times}B'HCl$. Poisonous. Its aqueous solution is decomposed by heat.—$B'_2H_2PtCl_6$. Crystals, v. sol. water.—$B'_2 2BiI_3$. Minute scarlet hexagonal leaves.—$B'HAuCl_4$. Golden crystals.—$B'C_6H_3N_3O_7$. [142°]. Slender yellow needles.

Reference.—DI-IODOVINYLAMINE.

VINYL BROMIDE *v.* BROMO-ETHYLENE.

Vinyl tribromide *v.* TRI-BROMO-ETHANE.

VINYL CHLORIDE *v.* CHLORO-ETHYLENE.

VINYL ETHANE *v.* BUTYLENE.

VINYL-ETHYL-CARBINOL *v.* PENTENYL ALCOHOL.

VINYL-ETHYLENE *v.* BUTINENE.

VINYL ETHYL OXIDE $CH_2:CH.OEt$. (35·5° i.V.). S.G. $\frac{14\cdot5}{17\cdot5}$ ·7625. Formed by heating chloro-acetal $CH_2Cl.CH(OEt)_2$ with sodium at 140° (Wislicenus, *A.* 192, 106). Liquid, smelling like ether mixed with allyl compounds. Combines with Cl and Br, forming di-chloro- and di-bromo- di-ethyl oxide. A small quantity (1 g.) of iodine converts large quantities of the oxide (200 g.) into a viscid liquid. Dilute (1:4) H_2SO_4 forms aldehyde and $EtHSO_4$.

Reference.—CHLORO-VINYL-ETHYL OXIDE.

VINYL-ETHYL-PYRIDINE $C_5H_3NEt.CH:CH_2$. (98°–102° at 21 mm.). Formed by heating $C_5H_3NEt.CH_2.CH_2OH$ with conc. HCl at 170° (Prausnitz, *B.* 25, 2394). Oil, v. sol. ether.—$B'_2H_2Hg_5Cl_{12}$. Needles, sl. sol. hot water.

VINYL IODIDE *v.* IODO-ETHYLENE.

VINYL-MALONIC ACID *v.* TRIMETHYLENE DICARBOXYLIC ACID.

VINYL OXIDE $(C_2H_3)_2O$. (39°). Formed by the action of dry Ag_2O on vinyl sulphide (Semmler, *A.* 241, 90).

Reference.—HEXA-CHLORO-DI-VINYL OXIDE.

***o*-VINYL-PHENOL** $CH_2:CH.C_6H_4.OH$.

Methyl ether $CH_2:CH.C_6H_4.OMe$. *o-Vinyl-anisole.* (c. 198°). S.G. $\frac{15}{15}$ 1·0095, $\frac{30}{30}$ 1·0005. Formed from either of the methyl derivatives of *o*-oxy-phenyl-acrylic acid by successive treatment with HI and Na_2CO_3Aq (Perkin, *C. J.* 33, 211; 39, 429). Oil. Polymerises readily (at 150°), forming a glassy mass, which, however, on distillation, regenerates the original oil. It smells like high-boiling coal-tar naphtha. It forms a colourless compound with bromine. Forms a red solid with H_2SO_4.

***p*-Vinyl-phenol.** *Methyl ether* $CH_2:CH.C_6H_4OMe$. [3°]. (205°). S.G. $\frac{15}{15}$ 1·0029; $\frac{30}{30}$ ·9956. Formed by distilling methoxy-phenyl-acrylic acid (*q. v.*) and from the same acid by successive treatment with conc. HI (S.G. 1·94) and Na_2CO_3.

Reference.—BROMO- and NITRO- VINYL-PHENOL.

VINYL-PIPERIDINE $C_5H_{10}(C_2H_3)N$ (?). (147°). Formed by dehydration of oxy-ethyl-piperidine [32°] (Ladenburg, *B.* 22, 2587). Liquid, smelling like tropidine and coniine, v. sol. water.

Reference.—BROMO-VINYL-PIPERIDINE.

***p*-VINYL-ISOPROPYL-BENZENE** $C_{11}H_{14}$ *i.e.* $C_6H_4Pr.CH:CH_2$. (204°). S.G. $\frac{15}{4}$ ·8902. Formed by distilling cumyl-acrylic acid at 210° or by boiling α-bromo-β-cumyl-propionic acid with Na_2CO_3Aq (Perkin, *C. J.* 1877, ii. 660). Oil, smelling like cuminic aldehyde. Partially polymerises on boiling, and also on keeping, forming a glassy mass, reconverted into the original hydrocarbon by heat. Yields $C_{11}H_{14}Br_2$ [71°].

α-VINYL-PYRIDINE C_7H_7N *i.e.*

$$N\left\langle\begin{matrix}C(C_2H_3):CH\\CH\text{———}CH\end{matrix}\right\rangle CH$$

(159°). S.G. ^{0} ·9985. Formed by passing a mixture of pyridine and ethylene through a red-hot tube (Ladenburg, *B.* 20, 1643). Formed also by distilling oxy-ethyl-pyridine under high pressure or in presence of KOH (Ladenburg, *B.* 22, 2585), and by the action of NaOHAq on β-bromo-β-pyridyl-propionic acid (Einhorn, *A.* 265, 229). Liquid smelling like conyrine, m. sol. water, v. sol. alcohol. Decomposed by distillation under atmospheric pressure, but boils at 81° under 29 mm. Oxidised by $KMnO_4$ to picolinic acid, and reduced in alcoholic solution by Na to ethyl-pyridine.—**Salts:** $B'_2H_2PtCl_6$. [174°]. Crystals, m. sol. water.—$B'HAuCl_4$. [144°]. Yellow needles.

Tetra-vinyl-pyridine $C_5H(C_2H_3)_4N$. (277°). S.G. ^{0} 1·0515. Formed in the preparation of γ-ethyl-pyridine by heating pyridine ethylo-iodide in sealed tubes at 320° (Karan, *B.* 25, 2776). Sl. sol. water.—$B'_2H_2PtCl_6$. [175°].—$B'HAuCl_4$. [148°].—$B'HHgCl_3$. [146°]. Needles.

VINYL-QUINOLINE *v.* QUINOLYL-ETHYLENE.

VINYL SULPHIDE C_4H_6S *i.e.* $S(CH:CH_2)_2$. (101°). S.G. ·913. Constitutes the chief part of the essential oil of *Allium ursinum* (Semmler, *A.* 241, 90). Liquid, smelling like allyl sulphide.

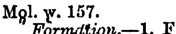
Reactions.—1. Dry Ag_2O forms vinyl oxide.—2. Moist Ag_2O gives aldehyde.—3. Alcoholic $HgCl_2$ forms crystals of $C_8H_{12}Cl_4Hg_2S_2$, which, when heated with potassium sulphocyanide, yields vinyl sulphocyanide.—4. $PtCl_4$ added to its alcoholic solution ppts. $(C_2H_3)_6Cl_8Pt_2S_3$, which is decomposed by ammonium sulphide into vinyl chloride and dark-brown $(C_2H_3)_2PtS_3$.—5. $AgNO_3$ forms $(C_2H_3)_2SAgNO_3$.—6. Br gives $(C_2H_3Br_2)_2SBr_2$ [195°].—7. *Oxidising agents* yield CO_2, oxalic acid, and H_2SO_4 only.

VINYL-TOLUIDINE so called is DI-*p*-TOLYL-DI-ETHYLENE-DIAMINE.

VIOLAQUERCITRIN *v.* this vol. p. 373.

VIOLANTIN $C_8H_6N_6O_9$ 4aq. Formed by mixing hot conc. solutions of nitroso- and nitro-barbituric acids (violuric and dilituric acids). Formed also by warming hydurilic acid with dilute HNO_3 (Baeyer, *A.* 127, 223). Yellowish-white, crystalline powder, decomposed by water into its two component acids, but may be re-crystallised from HOAc or 50 p.c. alcohol. It is also split up into its components by salts of the stronger acids.

VIOLURIC ACID $C_4H_3N_3O_4$ *i.e.*



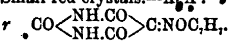
$$C_2O_2\left\langle\begin{matrix}NH\\NH\end{matrix}\right\rangle C:NOH.$$

Nitroso-barbituric acid. Mol. w. 157.

Formation.—1. From hydurilic acid by the action of nitric acid (S.G. 1·2) or nitrous acid (Baeyer, *A.* 127, 200).—2. By heating dilituric (nitro-barbituric) acid with glycerin.—3. By warming ferrous diliturate with KCy.—4. By boiling an aqueous solution of alloxantin with hydroxylamine hydrochloride (Pellizzari, *G.* 17, 258).—5. By adding hydroxylamine to an aqueous solution of alloxan (Ceresole, *B.* 16, 1133).—6. By adding KNO_2 to barbituric acid (Baeyer, *A.* 130, 140).

Properties.—Trimetric crystals (containing aq); $a:b:c$ = ·83:1:1·92. M. sol. cold water, sl. sol. alcohol. Its aqueous solution is ppd. by alcohol. $FeSO_4$ gives a deep indigo-blue colour. HNO_3 forms nitro-barbituric acid. Br forms di-bromo-barbituric acid and nitrous fumes. Reducing agents form uranil (amido-barbituric acid). Conc. HClAq forms hydroxylamine on heating.

Salts.—NH_4A'. Dark-blue prisms.—$KA'2aq$. Deep-blue crystals, v. sol. water, forming a blue solution; turned red by excess of KOH. A solution of the K salt in conc. HClAq deposits $(KA')_2(HCl)_3$ 6aq in colourless efflorescent prisms.—$BaA'_2 4aq$. Red dimetric tables, nearly insol. cold water.—MgA'_2 6aq. Purple-red crystals.—PbA'_2 4aq. Small red crystals.—AgA'.



Benzyl ether $CO<\begin{smallmatrix}NH.CO\\NH.CO\end{smallmatrix}>C:NOC_7H_7$. [226°]. Formed by the action of benzyl chloride on silver violurate (Conrad a. Guthzeit, *B.* 15, 2849). Silvery scales, sol. hot water and alcohol.

VIRIDIC ACID *v.* Caffetannic acid.

VIRIDINE $C_{12}H_{19}N$. (251°). S.G. 1·024. A homologue of pyridine occurring in coal-tar (Thenius, *C. C.* 1862, 53). Yellowish oil, with slight greenish fluorescence, sl. sol. water, v. sol. alcohol and ether.—$B'_2H_2PtCl_6$. Greenish brown, insol. water, alcohol, and ether. The mercuric chloride double salt melts at 85° and crystallises from water.

Isomeride $C_{12}H_{19}N$. (230°-235°). Obtained, with other bases, by heating methyl-ethyl-acroleïn with alcoholic ammonia (Hoppe-Seyler, *M.* 9, 651).—$B'HAuCl_4$. [93°].—$B'_2H_2PtCl_6$. [135°].

VISCIN $C_{10}H_{24}O_4$ (?). The glutinous constituent of the stalk, leaves, and berries of the mistletoe (*Viscum album*). Extracted from the bark by kneading with water, washing the sticky mass with 90 p.c. alcohol, and extracting the viscin with cold ether. The residue consists of viscaoutchin and woody-fibre (Reinsch, *C. C.* 1861, 145). Colourless, tasteless, semi-fluid mass, S.G. 1·0, decomposed by distillation, yielding oily viscene (226°) S.G. ·85, which forms a crystalline Na salt with conc. NaOHAq. Viscaoutchin is very glutinous. Its S.G. is ·978, and it is insol. alcohol and ether, sol. oil of turpentine.

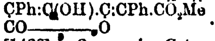
VISCOSE is Dextrane (*q. v.*).

VITELLIN *v.* Proteïds.

VITELLOSE *v.* Proteïds.

VOLUMES, SPECIFIC; *v.* Specific volumes, p. 498.

VULPIC ACID $C_{19}H_{14}O_5$ *i.e.*



$$\begin{array}{l} \text{ÇPh:C(OH).Ç:CPh.CO}_2\text{Me} \\ \text{CO}\text{————}\text{O} \end{array}$$

Methyl pulvate. [148°]. Occurs in *Cetraria vulpina*, a lichen growing in Norway, and used there, mixed with nux vomica, as poison for wolves (Bebert, *A.* 2, 342; Strecker a. Möller, *A.* 113, 56; Spiegel, *B.* 13, 1629; 14, 1686; *A.* 219, 15). The lichen contains 2½ to 4 p.c. of the acid, which may be extracted by warm milk of lime. Vulpic acid is also formed by dissolving pulvic anhydride in a solution of KOH in MeOH. It appears to occur in the lichen *Parmelia parietina* (Berzelius; Stein, *J.* 1864, 553).

Properties.—Yellow plates or needles, sol. alcohol and ether, v. e. sol. chloroform, nearly insol. boiling water. Decomposed above 200° into MeOH and pulvic anhydride. Boiling milk of lime converts it into pulvic acid. Boiling KOHAq forms di-benzyl-glycollic acid and CO_2.

Salts.—NH_4A'. Yellow crystals, sol. water.—$BaA'_2 2aq$. Yellow needles (from water).—$BaA'_2 7aq$.—$KA'aq$. Light-yellow needles, sl. sol. water.—AgA'. Pp. Blackens at 190°.

Acetyl derivative $C_{19}H_{13}AcO_4$. [156°]. Colourless needles, insol. NaOHAq.

Methyl ether v. Di-methyl ether of Pulvic acid.

Isovulpic acid $C_{18}H_{11}MeO_5$. [124°]. Formed, in small quantity, together with pulvic anhydride, by heating vulpic acid at 200° (Spiegel). Thin golden plates (from alcohol). Forms orange solutions in alkalis.

W

WACKENRODER'S SOLUTION. The soluion obtained by passing H_2S for a long time into nearly saturated SO_2Aq. The solution conains $H_2S_3O_6$, much $H_2S_4O_6$, $H_2S_5O_6$, and probably $H_2S_6O_6$, along with H_2SO_4, dissolved colloidal S, and a little S in suspension; *v.* Thionic acids, p. 698.

WALDIVIN $C_{18}H_{24}O_{10}$. [230°]. S.G. 1·46. S. ·17 at 15°; 3 at 100°. S. (alcohol) ·53. Extracted by dilute alcohol from the powdered fruit of *Simaba waldivia* (Tanret, *Bl.* [2] 35, 104; *C. R.* 91, 886). Hexagonal prisms (containing 5aq), v. sol. chloroform, insol. ether. Neutral to litmus. Inactive to light. Tastes bitter.

WATER. H_2O. (*Hydrogen monoxide.*) Mol. w. 17·96. (For physical data *v. Properties.*)

Occurrence.—Pure water is never found in nature. The properties of different specimens of naturally occurring waters depend on the impurities they contain, and these impurities are derived from the substances with which the water has come into contact; hence it is customary to classify natural waters in accordance with their origin, as *rain-water*, *surface-water*, *well-water*, *mineral spring-water*, and *sea-water*. The composition of the substances found in these waters, and the properties of the waters themselves—that is, of the various more or less dilute aqueous solutions—are discussed in pp. 939-960 of vol. iv. of the Dictionary of Applied Chemistry. Solid water, more or less pure, is found as ice and snow. Water vapour is a constant constituent of the atmosphere. A great many minerals, and also many organic substances, contain water combined with other compounds.

Historical.—In 1781 Cavendish showed experimentally that water was the only product of burning H and O mixed in certain proportions, and that almost the whole of the H and O disappeared. The account of the experiments made by Cavendish was published in 1784 (*T.* 1784. 116).

‘When a mixture of inflammable and dephlogisticated air [*i.e.* in modern language, hydrogen and oxygen] is exploded in such proportions that the burnt air is not much phlogisticated, the condensed liquor contains a little acid, which is always of the nitrous kind . . .; but if the proportions be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but seems pure water, without any addition whatever; and as, when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into pure water' (*l.c.* p. 133).

Translated into modern language, this statement would be taken as asserting that water is formed by exploding a mixture of H and O in proper proportions. It is, however, worthy of note that Cavendish did not himself interpret his experimental results as we interpret them to-day. He regarded 'dephlogisticated air' [oxygen] as 'nothing but dephlogisticated water, or water deprived of its phlogiston.' He said: 'We must allow . . . that inflammable air [hydrogen] is either pure phlogiston . . . or else water united to phlogiston' (*l.c.* pp. 137, 140).

The formation of water by burning H and O was thought of by Cavendish as the restoration of phlogiston to water that had been deprived of this principle. 'Water,' he said, 'consists of dephlogisticated air united to phlogiston.' Cavendish evidently thought of H and O as what we might now call *forms of water*; one of these was water with too little phlogiston, and the other was water with too much phlogiston; the explosion restored the phlogistic balance, and the properties of water were apparent. When Lavoisier had interpreted Cavendish's results, Cavendish spoke of Lavoisier's explanation as an hypothesis: 'According to this hypothesis we must suppose that water consists of inflammable air united to dephlogisticated air' (*l.c.* p. 150). Cavendish established the fact that water is the product of burning a mixture of H and O in the ratio (approximately) of 2 vols. H to 1 vol. O; but he stated this fact in language that no longer carries a definite meaning with it. Lavoisier added to the experimental basis whereon the fact rested, and he expressed the fact in language that still is clear, definite, and descriptive.

Formation.—1. By the direct union of H and O by igniting a mixture of these elements. 2. By deoxidising metallic oxides, and many other compounds that contain O, by heating with H.—3. By the decomposition of many compounds containing H and O, by heat, or by reactions with other substances.

According to Freyer a. V. Meyer (*B.* 25, 622), a mixture of H and O in the ratio 2H:O does not explode when slowly passed through a glass tube at 606°, and the temperature of ignition of the wet, gaseous mixture is between 650° and 730°. Askenasy a. V. Meyer (*A.* 269, 49) found that when pure, dry electrolytic gas was passed at a moderate rate through a glass tube heated to 518°, only c. ·7 to 1·7 mgms. of water were produced in ten hours; and that a little more water, but still only a very small quantity in proportion to the total quantity of H and O, was formed at 606°. Experiments made to determine the relation between the quantity of water formed and the time of the experiment showed that no constant relation could be arrived at, even when every precaution was taken to insure equality of conditions; the irregular action of the surfaces of the vessels was probably the cause of the irregularities in the results.

Davy (*T.* 1817) found that electrolytic gas did not explode when the pressure was so reduced that the gas was rarefied to $\frac{1}{16}$ of its ordinary density. Thomas (*C. J.* 35, 215) found that the gas exploded at 168 mm. pressure. L. Meyer a. Seubert (*C. J.* 45, 586) found that the sparks from a Ruhmkorff coil caused the combination of c. $\frac{3}{4}$ of a quantity of electrolytic gas at c. 70 mm. pressure, and that the remainder combined when the pressure was increased until it became the same as before the first explosion; this result is in keeping with Bunsen's determinations of the quantity of oxygen needed to prevent the explosion of 2H+O (*v.* M. a. S., *l.c.* p. 588). Dixon (*T.* 1884. 634) noticed that electrolytic gas did not explode at a pressure under 70 mm., but that explosion occurred under 75 mm. pressure (*cf.* D., *l.c.* p. 642).

According to the experiments of Dixon (*l.c.*), 'the union of oxygen and hydrogen is not affected by the presence or absence of water'; dry electrolytic gas exploded by the spark at a pressure between 70 mm. and 75 mm., and the wet gas exploded at the same pressure.

The velocity of explosion of electrolytic gas was found by Berthelot and Vieille (*C. R.* 95, 151) to be 2,810 metres per second (*cf.* EXPLOSION, vol. ii. p. 530).

Preparation.—Stas (*Chem. Proport.* 110) prepared pure water as follows. When large quantities were required, spring-water was *very slowly* distilled through a long copper tube, bent into zigzag form, completely filled with pure copper turnings that had been oxidised by strongly heating in O, the copper tube being surrounded by alumina and sand, and heated to full redness; the distillate was then distilled in an apparatus of platinum.

The second method recommended by Stas, especially when comparatively small quantities of pure water are required, is based upon destroying the organic matter in distilled water by the action of K manganate and permanganate. The process is described by Stas as follows:—

> I prepared potassium manganate by reacting on manganese oxide with caustic potash and potassium chlorate. I shook up the powdered product with water, just sufficient to dissolve the manganate that had been formed, and allowed the mixture to settle in a closed vessel. I then added 4 or 5 p.c. of the clear, dark-green solution to the spring water which was to be distilled, and allowed the components of this mixture to react for 24 hours. I then poured into the distillation vessel one or two litres of the conc. solution of potassium manganate that had been mixed with an equal volume of conc. caustic potash solution; this solution of potash was sufficiently conc. to make the salt so stable that its dilute solution could be heated for a long time without decomposition. I then filled the distillation vessel to c. $\frac{1}{10}$ with the water which had been in contact with the potassium manganate, and distilled in the ordinary way. When boiling began I moderated the heat, in order to prevent the liquid, which frothed much for some minutes, from passing over. When the frothing has stopped, the water may be boiled rapidly without the least inconvenience. When $\frac{1}{10}$ of the water has distilled over, that which then distils is completely free from organic substances, and also from mineral substances, if the upper part of the distillation vessel is furnished with diaphragms to hold back the extremely small drops that are always carried forward when a liquid is boiled vigorously.

Stas says that water thus prepared is perfectly free from organic matter. When he wished to obtain water absolutely free from any form of solid matter, Stas re-distilled the water that had been purified as described above, using as condenser a long tube of platinum soldered with gold. It is advisable to distil the water just before it is to be used.

On one occasion Stas used rain-water instead of well-water, and he found distinct quantities of ammonia in the distilled water thus prepared. To remove this he recommends to re-distil with $\frac{1}{1000}$ part of $NaHSO_4$ or $KHSO_4$.

Composition of water.—The gravimetric composition of water was determined by Berzelius a. Dulong (*A. Ch.* [2] 15, 86) and by Dumas (*A. Ch.* [3] 8, 189) by passing pure H over a weighed quantity of red-hot CuO, and weighing the water produced and the copper which remained. The results gave the ratio H:O = 1:8 (B. a. D.) and 1:7·98 (D.). An extended series of measurements by the same method, with many precautions, by Dittmar a. Henderson (*C. N.* 67, 127, 139, 151, 164 [1893]) gave the ratio H:O = 1:7·9327.

Several measurements have been made of the proportion by volume in which H and O combine to form water. Gay-Lussac in 1805, and Humboldt in 1805 (*A. Ch.* 53, 239), found the volumetric ratio of H:O to be 2:1. Morley, in 1891 (*Am. S.* [3] 41, 220, 276), determined the ratio of H:O to be 2·00023:1 by directly measuring the volumes of the gases. In 1892 Leduc (*C. R.* 116, 1248) found the ratio H:O = 2·0037:1, from determinations of the relative densities of H, O, and electrolytic gas. In 1893 Scott (*T.* 184, 543) completed a most carefully performed series of syntheses of water by sparking mixtures of H and O, and determined the most probable value of the volumetric ratio H:O to be 2·00245:1.

Properties.—Water is a clear, transparent, almost colourless, tasteless, odourless liquid. A column of water appears slightly blue when looked at lengthwise. Bunsen (*A.* 72, 44) pointed out that the slight blue colour of water may be observed by looking at a shining white object through a column of water 2 metres long, contained in a tube blackened inside. V. Meyer (*B.* 15, 297) recommends to join five wide, thin-walled glass tubes, c. 40 mm. internal diameter, and each c. 1½ metres long, by wide caoutchouc tubing, and thus to form a tube c. 7½ metres long; to lay the tube perfectly horizontal, and to close the end by smooth glass plates held in position by metallic clasps; then to cover the tube with black cloth. On looking through the tube the field of view appears quite colourless, but on now filling the tube with pure water (by means of brass tubes passing through the metallic clasps) a deep-blue colour is seen on looking through the column of water.

The *boiling-point* of water is 100° under the pressure of 760 mm. Zeuner (*Grundzüge der mechanischen Wärmetheorie*, Tab. 10 [1877]) gives the following table, showing the increase of boiling-point with increase of pressure:—

Pressure in atmos.	Boiling-point. °	Pressure in atmos.	Boiling-point. °
1	100	8	170·81
2	120·6	9	175·77
3	133·91	10	180·31
4	144	11	184·50
5	152·22	12	188·41
6	159·22	13	192·08
7	165·34	14	195·53

An elaborate table is given by Broch (*Trav. et Mém. du Bureau internat. des Poids et Mes.* 1, 46 [1881]) based on Regnault's determinations; the table gives the b.p. of water for each ·1 mm. from 680 to 800 mm. pressure. (The table is given in Landolt a. Börnstein's *Physikalisch-Chemische Tabellen* [Berlin, 1883], pp. 47–49.)

The *melting-point* of ice is slightly lowered by pressure. J. Thomson (*T. E.* 16) calculated that the m.p. would be lowered by *n* ·0075° for an increase of *n* atmospheres; W. Thomson (*P. M.* [3] 37, 123) confirmed this calculation by determining the m.p. of ice at 8·1 and 16·8 atmos. Mousson (*A. Ch.* [3] 56, 252) kept water liquid at −5° by greatly increasing pressure, and he found that at c. 13,000 atmos. pressure ice melted at −18°.

The *specific gravity* of water is greater at 4° than at any other temperature. Exner gives the temperature of maximum density as 3·945° (older determinations are tabulated by Exner, *W. A. B.* 68 (ii.), 463 [1873]). The following table, showing the density and volume of water from 0° to 100°, is given by Volkmann (*W.* 14, 260 [1881]); it is based on the determinations of Hagen, Matthiessen, Pierre, Kopp, and Jolly:

Temp. °	Density (*in vacuo*) i.e. wt. of 1 c.c. water in grams.	Volume of 1 gram water in c.c.
0	·999878	1·000122
1	·999933	1·000067
2	·999972	1·000028
3	·999993	1·000007
4	1·000000	1·000000
5	·999992	1·000008
6	·999969	1·000031
7	·999933	1·000067
8	·999882	1·000118
9	·999819	1·000181
10	·999739	1·000261
11	·999650	1·000350
12	·999544	1·000456
13	·999430	1·000570
14	·999297	1·000703
15	·999154	1·000847
16	·999004	1·000997
17	·998839	1·001162
18	·998663	1·001339
19	·998475	1·001527
20	·998272	1·001731
21	·998065	1·001939
22	·997849	1·002156
23	·997623	1·002383
24	·997386	1·002621
25	·997140	1·002868
30	·99577	1·00425
35	·99417	1·00586
40	·99236	1·00770
45	·99035	1·00974
50	·98817	1·01197
55	·98584	1·01436
60	·98334	1·01694
65	·98071	1·01967
70	·97789	1·02261
75	·97493	1·02572
80	·97190	1·02891
85	·96876	1·03225
90	·96549	1·03574
95	·96208	1·03941
100	·95856	1·04323

Rossetti (*P. Ergänsbd.* 5, 268 [1871]) gives he densities and volumes of water for each legree from −10° to 100°, referred both to water t 0° and to water at 4° as unity. The S.G. of ce is c. ·916 at 0° (water at 0° = 1); according o recent determinations by Zakrzevski (*W.* 47, 155 [1895]) the value is ·916660.

The *expansion* of water for various intervals f temperature has been measured by various bservers; putting $V_t = V_0\ (1 + at + bt^2 + ct^3)$, the ollowing values are given by Kopp (*P.* 72, 1 1847]; *cf.* Pierre, *P.* 86, 451; Weidner, *P.* 123, 300; Matthiessen, *P. M.* [4] 31, 149; Rossetti, *P. Ergänzbd.* 5, 258; Hirn, *A. Ch.* [4] 10, 32):

Temp.	*a*	*b*	*c*
0° to 25°	−·000061045	·0000077183	−·00000003734
25° to 50°	−·000065415	·0000077587	−·000000035408
50° to 75°	−·00005916	·0000031849	·0000000072848
75° to 100°	−·00008645	·0000031892	·0000000024487

For the expansion of water above 100° *v.* Mendeléeff (*A.* 119, 1).

As water freezes it expands by c. $\frac{1}{11}$ of its volume; one volume of water at 0° becoming 1·09082 volumes of ice at 0°. It expands when heated at temperatures below 0°; Zakrzevski (*W.* 47, 155) gives the co-efficient of expansion ·000077 (*v.* also Brunner, *P.* 64, 116; Struve, *P.* 66, 298; Marchand, *J. pr.* 35, 254).

The *compressibility* of water is small. Röntgen a. Schneider (*W.* 33, 644) give the absolute compressibility at 17·95° as ·0000462 per atmosphere of pressure (*v.* also Ramsay a. Young, *T.* 1892; and *cf.* Grassi, *A. Ch.* [3] 31, 437; and Rankine, *P. M.* [4] 1, 548; also Amaury a. Descamps, *C. R.* 68, 1564; and Cailletet, *C. R.* 75, 77).

A table showing the volume of 1 kilo. of *saturated water vapour* and the weight (in kilos.) of 1 c. metre of the vapour, at temperatures from 0° to 200°, is given by Zeuner (*v.* Landolt a. Börnstein's *Physikalisch-chemische Tabellen* [Berlin, 1883], p. 53; *cf.* Dieterici, *W.* 38, 1). According to Dieterici (*l.c.*) water vapour saturated at 0° behaves like a perfect gas.

The *vapour pressure* of water varies from 1·0288 mm. at −19° to 20926·4 mm. at 230°; for complete tables calculated from Regnault's determinations *v.* Landolt a. Börnstein's *Physikalisch-chemische Tabellen* [Berlin, 1883] pp. 40–46 (the vapour pressure is given for each 1° from −19° to 101°, and for each 1° from 101° to 230°). Ramsay a. Young (*T.* 1892) give a table of the vapour pressures of water up to 270°. In connection with the vapour pressures of water and ice, *v.* R. a. Y. (*T.* 1884. 470). For an expression representing the vapour pressure of water at any temperature up to 325°, *v.* Antoine (*C. R.* 113, 328).

The *spec. heat* of water increases as temperature rises; the quantity of heat required to raise 1 g. of water from $t°$ to $t° + 1$ is taken as unity in determinations of the spec. heats of other substances. The following table presents the data for S.H. of water at intervals of 10° from 0° to 230° (the memoirs by the different observers are: Regnault, *Acad.* 21, 729 [1847]; Jamin a. Amaury, *C. R.* 70, 661 [1870]; Bosscha, *P. Jubelbd.* 549 [1874]; von Münchhausen, *W.* 1,

t° (air therm.)	Regnault	Jamin a. Amaury	Bosscha	v. Münchhausen	Henrichsen	Baumgartner
0°	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
10	1·0005	1·0111	1·0022	1·0043	1·0036	1·0031
20	1·0012	1·0225	1·0044	1·0085	1·0079	1·0061
30	1·0020	1·0341	1·0066	1·0128	1·0131	1·0092
40	1·0030	1·0459	1·0088	1·0170	1·0191	1·0123
50	1·0042	1·0580	1·0110	1·0213	1·0259	1·0154
60	1·0056	1·0703	1·0132	1·0255	1·0335	1·0184
70	1·0072	1·0829	1·0154	1·0298	1·0419	1·0215
80	1·0090	1·0957	1·0176	1·0340	1·0511	1·0246
90	1·0109	1·1087	1·0198	1·0383	1·0612	1·0276
100	1·0130	1·1220	1·0220	1·0425	1·0720	1·0307
110	1·0155	1·1355	1·0242	1·0468	1·0837	1·0338
120	1·0177	1·1493	1·0264	1·0510	1·0961	1·0368
130	1·0204	1·1632	1·0286	1·0553	1·1094	1·0399
140	1·0232	1·1775	1·0308	1·0595	1·1235	1·0430
150	1·0262	1·1920	1·0330	1·0638	1·1384	1·0461
160	1·0294	1·2067	1·0352	1·0680	1·1540	1·0491
170	1·0328	1·2217	1·0374	1·0723	1·1706	1·0522
180	1·0364	1·2369	1·0396	1·0765	1·1879	1·0553
190	1·0401	1·2523	1·0418	1·0808	1·2060	1·0583
200	1·0440	1·2680	1·0440	1·0850	1·2249	1·0614
210	1·0481	1·2839	1·0462	1·0893	1·2447	1·0645
220	1·0524	1·3001	1·0484	1·0935	1·2652	1·0675
230	1·0568	1·3165	1·0506	1·0978	1·2866	1·0706

592; 10, 284 [1877 and 1880]; Henrichsen, *W.* 8, 83 [1879]; Baumgartner, *W.* 8, 648 [1879]).

The following values for S.H. of water, from 0° to 35°, are given by Bartoli a. Stracciati (*A. Ch.* [6] 29, 285); the values in the column 'calculated' were obtained by using the formula:

$$\begin{aligned} \text{S.H.} = \; & 1{\cdot}006630 \\ & - {\cdot}000593962t \\ & + {\cdot}0000043838650t^2 \\ & + {\cdot}00000004255520t^3 \\ & - {\cdot}000000002819t^4 \end{aligned}$$

The unit is the quantity of heat given out by 1 gram water at 15° in cooling to 14°.

t°	S.H. calcd.	S.H. observed.
0°	1·006630	1·00664
1	1·006041	1·00601
2	1·005463	1·00513
3	1·004898	1·00489
4	1·004350	1·00435
5	1·003820	1·00383
6	1·003307	1·00331
7	1·002824	1·00283
8	1·002362	1·00233
9	1·001927	1·00190
10	1·001522	1·00149
11	1·001146	1·00111
12	1·00080	1·00078
13	1·000496	1·00048
14	1·000224	1·00023
15	0·999990	1·00000
16	0·999795	0·99983
17	0·999642	0·99968
18	0·999530	0·99959
19	0·999462	0·99951
20	0·999439	0·99947
21	0·999463	0·99950
22	0·999533	0·99955
23	0·999652	0·99964
24	0·999821	0·99983
25	1·000040	1·00005
26	1·000311	1·00031
27	1·000633	1·00064
28	1·000967	1·00098
29	1·001438	1·00143
30	1·001921	1·00187
31	1·002459	1·00241
32	1·003054	—
33	1·003668	—
34	1·004408	—
35	1·005170	—

The S.H. of ice is considerably less than that of water; Regnault's determinations gave ·474 between −75° and 0°; the determinations of Person a. Desains gave ·504 between −20° and 0°; Ramsay a. Young (*T.* 1884. 475) give the value ·5 as the mean of various experiments. S.H. of water gas at 100° is given by Strecker (*W.* 17, 85) as ·37 referred to an equal weight of water = 1, and 1·36 referred to an equal volume of air = 1; the ratio $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ given by S. is 1·4, Jaeger (*W.* 36, 165 [1889] gave the value 1·33 to this ratio, and Cohen (*W.* 37, 628 [1889]) gave the value 1·287 for the temperature interval 144° to 300°.

The *heat of vaporisation* of water—*i.e.* the quantity of heat required to convert 1 g. of water at 100° into steam at 100°—is 535·77 gram-units, according to Favre a. Silbermann (*A. Ch* [3] 37, 461). The following values are given for the heat required to convert 1 g. of water at t° completely into water vapour; 606·5 when $t=0°$, 637 when $t=100°$, 676·6 when $t=230°$ (Regnault, *Acad.* 21, 635); Dieterici (*W.* 38, 1) gives 596·8 when $t=0°$; Regnault (*l.c.*) gives the formula $\lambda = A + Bt$ for the total heat of vaporisation of water at different temperatures, and gives the values $A = 606{\cdot}5$, $B = {\cdot}305$.

According to Sakhrai (*C. J.* 61, 495 [1892]), 'the temperature of the steam escaping from a boiling salt solution is exactly the same as that of the solution.'

The *heat of fusion* of ice, *i.e.* the quantity of heat required to convert 1 g. of ice at t° into 1 g. of water at t° is given as follows by different observers (the values are in gram-units of heat):—79·24 and 79·06 when $t°=0$ (Regnault, *A. Ch.* [3] 8, 19); 79·25 when $t=0°$, 74·2 when $t=-10°$, 80·22 when t varies from −2° to −21° (Person, *A. Ch.* [3] 21, 295; 30, 73); 77·85 at −2·8°, 76·75 at −4·295°, 76·11 at −6·28°, 76·0 at −6·6° (Pettersson, *J. pr.* [2] 24, 129).

The *thermal conductivity* of water, from 10° to 18°, was determined by Winkelmann (*P.* 153, 481) to be ·154; Bottomley (*Pr.* 31, 300) obtained nearly the same value; this figure means that heat sufficient to raise ·154 mgm. water from 0° to 1° passes per second through a layer of water 1 mm. thick and 1 sq. mm. area, when the difference between the temperatures of the two surfaces of the layer is maintained at 1°. For *electrical conductivity* of water *v. Reactions*, No. 2.

The *refractive indices* of water at different temperatures, and for different lights of determinate wave-lengths, have been measured by many observers. The following values have been found for $\mu_{H\alpha}$: 1·33120 at 19·9°, 1·33091 at 23·7°, 1·33050 at 26° (Brühl, *B.* 24, 644). For detailed tabulation of the results obtained by Fraünhofer, van der Willingen, Baille, Damien, Landolt, Wüllner, and Rühlmann, *v.* Landolt a. Börnstein's *Physikalisch-Chemische Tabellen* [Berlin, 1883] 205; *cf.* also Perkin (*C. J.* 61, 293), who gives values for μ for the lines A C D and F, at 15° and 83·7°.

Observations have been made on the *absorption spectrum* of water and water-gas, but the matter has not been thoroughly investigated (*v.* Vogel, *P.* 156, 326; Jansen, *B. A.* 1866. 11).

Water crystallises, as ice, in rhombohedral forms; snow is generally found crystallised in six-sided stars derived from six-sided prisms.

Molecular weight of liquid water. Several observations have been made which tend to show that the molecular weight of liquid water is greater than 18. Paterno (*B.* 21, 3180), from measurements of the lowering of the freezing-point of water dissolved in acetic acid, concluded that the mol. w. might be 18, or might perhaps be 36. From the depression of the freezing-point of paratoluidine by water dissolved therein, Eykman (*Z. P. C.* 4, 510) concluded that the mol. w. of liquid water is probably 36, and this conclusion was strengthened by Walker's experiments on the connection between heats of fusion and solubility (*Z. P. C.* 5, 194). From measurements of the surface tension of water Ramsay and Shields (*C. J.* 63, 1089 [1893]) conclude that the mol. w. of liquid water is probably 72 at the ordinary temperature.

Reactions.—1. In 1847 Grove (*T.* 1847. 1) showed that water was decomposed into H and O by *heat.* Grove formed a little ball on the end of a Pt wire, by fusing the Pt, heated the globule of Pt to whiteness by an electric current, and plunged it into a little air-free water, nearly boiling, in a small basin, with a test tube full of air-free water arranged to collect any gas that might come off. Deville (*C. R.* 56, 195, 322 [1863]) found that H and O were given off in considerable quantities when molten Pt was plunged under water. D. noticed no decomposition when steam was passed through a Pt tube heated to bright redness, but by passing a current of an indifferent gas, such as CO_2, through the hot tube, and thus sweeping away the products of decomposition, H and O were obtained.—2. Water is scarcely decomposed by an *electric current.* Kohlrausch found the electrical conductivity of the purest water he could obtain by distillation *in vacuo* to be $2{\cdot}5 \times 10^{-6}$ in C.G.S. units, or c. 72 billionths of the conductivity of Hg (*P. M.* [5] 18, 542). By calculations based on this result, Ostwald concluded that in a litre of pure water the weight of water dissociated into H and OH ions, expressed in gram-molecules, is $\cdot 6 \times 10^{-6}$ (*Z. P. C.* 11, 521). By other methods of calculation, based on other data, Ostwald arrived at the value ·2 to $\cdot 9 \times 10^{-6}$ for what has been called the *dissociation constant* of water (*Z. P. C.* 11, 521); Wijs, by calculations based on the hydrolysis of methyl acetate, obtained the values $\cdot 1 \times 10^{-7}$ (*Z. P. C.* 11, 492), and $\cdot 14 \times 10^{-6}$ (*ibid.* 12, 514); Arrhenius obtained the value $\cdot 1125 \times 10^{-6}$ (*ibid.* 11, 827); and Bredig, the value $\cdot 6 \times 10^{-6}$ (*ibid.* 11, 829). Later experiments on the conductivity of water by Kohlrausch a. Heydweiller (*Z. P. C.* 14, 316 [1894]) with water that had been distilled *in vacuo* ten years ago, had then stood in a vessel filled with water, and been again distilled *in vacuo*, gave the following results:—conductivity (Hg = 1) ·014 at 0°, ·04 at 18°, ·058 at 25°, ·089 at 34°, ·176; all these to be multiplied by 10^{-10}. K. a. H. say that 1 mm. of this water at 0° had a resistance = that of 40 million kilometres of Cu wire of the same area. K. a. H. calculate that in 1 litre of the purest water at 18° there is ·00008 mgm. H as free ions, and ·000105 mgm. at 25°.—3. *Steam* is decomposed by *electric sparks*; for conditions and details of results *v.* Thomson (*Pr.* 53, 90).

The reactions of water are so many that an approximate classification of them into groups is all that can be attempted here.—4. Many *metals* react with water, at temperatures varying from the ordinary to a full red heat, forming oxides or hydroxides and giving off H. The following metals decompose cold water: Ba, Cs, Ca, (Ce ?), (La ?), Li, K, Rb, Na, Sr. Al, Fe, Pb, Mg, (? Mn), Mo, Ti react at c. 100°; and most of the other metals at temperatures from c. 100° to a full red heat.—5. Many *non-metals* react, generally slowly, with water, forming acids and giving off O. F rapidly decomposes water at the ordinary temperature; Cl reacts slowly at the ordinary temperature, and somewhat more rapidly at a red heat; Br reacts more slowly than Cl; I has probably a very slight (? any) action. S and P react slowly at 100°; Se is said not to decompose water at 160°. Carbon gives off H at a red heat. *Boron* acts like a metal, giving off H at a red heat.—6. Many *haloid compounds* react with water, giving oxyhaloid compounds or oxides, and haloid acids.—7. Some *metallic sulphides* react with steam to form oxides and H_2S. 8. A few of the *lower oxides* decompose water; *e.g.* $CrO.xH_2O$ at the ordinary temperature, and CO at c. 600°.—9. Water reacts with many *oxides* to form hydroxides which are either basic or acidic; in some cases hydrates are formed. Hydrates of various *salts* are also produced by combining the salts with water (*v.* Hydrates, vol. ii. p. 703; *cf.* Hydroxides, vol. ii. p. 733).—10. Water *dissolves* very many compounds of the most different properties (*v.* Solutions, vol. iv. p. 484).

Small quantities of water often bring about chemical changes that do not occur when the substances are perfectly dry; for instance, a mixture of dry CO and O is not exploded by sparks, but a trace of water suffices to start the change (*v.* Baker, *C. J.* 65, 611 [1894]).

The acidic and basic characters of water are so nearly balanced that the compound cannot be classed among either acids or basic bodies. The chemical relations of water to the compounds formed by reactions between it and other substances are determined chiefly by the chemical characters of the substances that react with it; thus the relations of HOH to $M_x(OH)_y$, formed by the interaction of water and metals, are those of an acid to its salts, whereas the relations of HOH to HX, formed by the interactions of water and non-metals, are those of a basic hydroxide to salts derived therefrom. The relations between both classes of derivatives of water and the parent compound are sometimes expressed by saying that the compounds belong to the *water type* (*v.* Types, vol. iv. p. 811). M. M. P. M.

WAX. A term applied to various natural solids more or less resembling bees'-wax. They are compound ethers, but differ from fats in yielding monovalent alcohols and not glycerin on saponification. They melt below 100°, are insol. water, sl. sol. or insol. alcohol, and sol. ether. They are not volatile.

Bees'-wax. [64°]. S.G. ·965. Consists of a portion (about 5 p.c.) soluble in alcohol (cerin) and a portion insoluble in alcohol (myricin). Myricin is myricyl palmitate (Brodie, *A.* 67, 180; 71, 144). Cerin is chiefly composed of cerotic acid; but it contains small quantities of melissic acid $C_{30}H_{60}O_2$ [90°], and an acid melting at 73° (Schalfejeff, *B.* 9, 278, 1688; Nafzger, *A.* 224, 246). There is also present one or more acids whose lead salts dissolve in ether and whose Ba salts dissolve in alcohol, and which therefore probably belong to the oleïc series. Myricin may be saponified by alcoholic potash, and the myricyl alcohol separated from potassium palmitate by extraction with ligroïn. Crude myricin yields CCl_4 and C_2Cl_6 when heated with I and excess of $SbCl_5$ at 400° (Hartmann, *B.* 24, 1022). Bees'-wax contains two hydrocarbons, one of which [60°] (c. 275° at 11 mm.) is probably *n*-heptaicosane $C_{27}H_{56}$, and the other [68°] (c. 360° at 11 mm.) *n*-hentriacontane $C_{31}H_{64}$ (Schwalb, *A.* 235, 106). According to Schwalb, the myricyl alcohol of bees'-wax has the formula $C_{31}H_{64}O$ [85°], and is converted by heating with soda-lime into an acid $C_{31}H_{62}O_2$ [89°], which forms a methyl ether [71°] and an ethyl ether [70°]. Among the products of saponification of bees'-wax, ceryl alcohol $C_{27}H_{56}O$ or $C_{26}H_{54}O$, and an alcohol $C_{25}H_{52}O$ or $C_{24}H_{50}O$ occur. The last-mentioned alcohol when heated with soda-lime gives an acid $C_{25}H_{50}O_2$ or $C_{24}H_{48}O_2$ [75·5°].

Carnaüba wax *v.* vol. i. p. 710.

Chinese wax, which is produced by an insect, is almost entirely composed of ceryl cerotate $(C_{27}H_{55})C_{27}H_{53}O_2$ (Brodie, *A.* 67, 199).

Cork wax *v.* Cerin.

Pine wax *v.* Ceropic acid.

Sugar-cane wax *v.* Cerosin.

Japan wax. [42°–55°]. Obtained in the East from *Rhus succedanea.* It appears to be really a fat, since palmitin is its chief component. It also contains the ether of a fatty acid of higher melting-point than stearic acid (Sthamer, *A.* 43, 343; Buri, *Ar. Ph.* [3] 14, 403).

Wax of Ficus gummiflua of Java contains an alcohol $C_{15}H_{30}O$ [73°], v. sol. ether, and a small quantity (5 p.c.) of isoceryl alcohol $C_{27}H_{56}O$, sl. sol. ether (Kessel, *B.* 11, 2112).

Myrtle wax. [49°]. Got by boiling the berries of *Myrica cerifera* of North America with water (Moore, *J.* 1862, 506). Consists of palmitic and some lauric acid and (20 p.c. of) palmitin.

Opium wax. Contains ceryl cerotate and ceryl palmitate (Hesse, *B.* 3, 637).

Tobacco wax. Contains $C_{70}H_{140}O_2$ [63°], insol. cold alcohol, sol. ether and a small quantity of $C_{60}H_{120}O_2$ [64·5°], sl. sol. cold ether (Kissling, *B.* 16, 2433).

Coca leaf wax (Hesse, *A.* 271, 214). The wax from Trujillo coca is palmityl-(β)-amyrin $C_{46}H_{80}O_2$ [75°] $[\alpha]_D = 54·5°$. On saponification it yields palmitic acid and (β)-amyrin $C_{30}H_{50}O$ [196°] $[\alpha]_D = 94·2°$, which yields an acetyl derivative [236°] and a benzoyl derivative [228°]. The wax from the broad-leaved coca of Peru and Bolivia melts at 70°; contains palmityl-(β)-amyrin and a ketone, (β)-cerotinone $C_{53}H_{106}O$ [66°], m. sol. alcohol, ether, and ligroïn. The wax from Java coca contains the same substances, and also some ceryl cerotate and ethers of myristic acid and of oxycerotic acid $C_{27}H_{54}O_3$ [82°], which is v. e. sol. hot alcohol and ligroïn, v. sl. sol. ether, and is converted by Ac_2O at 100° into cerotolic acid $C_{27}H_{52}O_2$ [70°].

WHEY-PROTEÏD *v.* Milk.

WINE OIL. *Light oil of wine.* An oil obtained in the preparation of ether by distilling alcohol with H_2SO_4. The ether is shaken with milk of lime and fractionally distilled, the successive fractions being ether, alcohol, and wet alcohol. Light oil of wine (·25 to ·5 p.c. of the alcohol etherified) rises to the surface when the last fraction (90°–120°) is allowed to stand. When dried over $CaCl_2$ it has S.G. $\frac{17·5}{}$ ·903. It contains $C_{10}H_{20}$ (157°), $EtOC_5H_{11}$ (112°), $Et.CO.C_5H_{11}$ (154°), and $CH_3.CO.C_6H_{13}$ (164°) (Hartwig, *J. pr.* [2] 23, 449).

Heavy oil of wine, which passes over when the temperature is raised after the preparation of ether, consists of Et_2SO_4 mixed with olefines (Claesson, *J. pr.* [2] 19, 259; Serullas, *A. Ch.* [2] 39, 152).

WINTERGREEN OIL contains methyl *o*-oxybenzoate.

WINTERENE $C_{15}H_{24}$. (260°–265°.) S.G. ·934. $[\alpha]_j$ 11·2° at 16°. A dextrorotatory sesquiterpene obtained by distilling winterbark (from *Drymis Winter-Forster*) with water (Arata a. Canzoneri, *G.* 18, 527). Coloured green by Br in $CHCl_3$.

WOOD *v.* Lignone.

WOOD GUM *v.* Xylan.

WOOD NAPHTHA *v.* Methyl alcohol.

√ **WOOD OIL.** *Gurjun Balsam.* Flows from incisions in the stem of *Dipterocarpus costatus.* It contains an essential oil, which gives a splendid violet colour when its solution in CS_2 (20 pts.) is treated with a drop of a cold mixture of HNO_3 and H_2SO_4. The same reaction is exhibited by the balsam itself, and also, in a more transient manner, by cod-liver oil and copaïba balsam (Flückiger, *Ph.* [3] 7, 2). The essential oil consists chiefly of a terpene (255°) (Werner, *J.* 1862, 461), which composes 65 p.c. of the balsam (Guibourt, *J.* 1876, 907). The resin contains a neutral substance, $C_{28}H_{46}O_2$, which crystallises from light petroleum in triclinic prisms [126°–130°]; it dissolves in conc. H_2SO_4, and is reppd. from the resulting reddish solution by adding water. It is not affected by potash-fusion (Flückiger, *Ar. Ph.* [3] 12, 58). A substance $C_{20}H_{30}O_2$ [129°] is described by Brix (*M.* 2, 516) as ppd. by adding water to an alcoholic extract of wood oil. It is neutral and insol. alkalis, and yields a diacetyl derivative [75°]. It is perhaps identical with the compound $C_{28}H_{46}O_2$. Wood oil also contains gurjunic acid $C_{22}H_{34}O_4$ [220°], which crystallises from alcohol, distils with decomposition at 260°, and forms Ag_2A''.

WOOD SPIRIT *v.* Methyl alcohol.

WORMSEED OIL. *Oleum Cinæ.* Obtained by steam-distillation from wormseed, the flower-buds of *Artemisia Vahliana, A. Sieberi,* and *A. inculta* (Trommsdorff, *Tr. N. J.* 3, 312; Völckel, *A.* 38, 110; 87, 312; Hirzel, *J.* 1854, 591; 1855, 655; Kraut a. Wahlforss, *A.* 128, 293; Faust a. Homeyer, *B.* 7, 1429; Hell a. Ritter, *B.* 17, 2609; Wallach a. Brass, *A.* 225, 291). It consists chiefly of cineol $C_{10}H_{18}O$. Wormseed (*A. Gallica*) also contains betaïne and choline (Jahns, *B.* 26, 1493).

WRIGHTINE $C_{11}H_{18}N$. [122°]. Occurs in the juice of *Wrightia antidysenterica* (Stenhouse, *Ph.* [2] 5, 493; Warnecke, *B.* 19, 60). Needles with bitter taste, sl. sol. water, v. sol. alcohol and ether. Cond. H_2SO_4 at 100° gives a dark-green colour, turned dark blue by adding water. Wrightine is probably identical with conessine (*q.v.*).

X

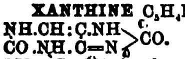
XANTHALINE $C_{37}H_{36}N_2O_9$. [206°]. Occurs in opium (T. a. H. Smith, *Ph.* [3] 23, 793). White crystalline powder, insol. water and alkalis, sl. sol. hot alcohol, m. sol. benzene, v. e. sol. chloroform. Weak base, forming yellow salts from which it is ppd. by hot water. Conc. H_2SO_4 forms a deep-orange solution, from which water ppts. the sulphate as yellow needles. Hot HNO_3 does not decompose it. Zinc and H_2SO_4 reduce it to hydroxanthaline $C_{37}H_{38}N_2O_9$, which forms white crystals [137°], nearly insol. water, v. sol. alcohol and benzene, and forms easily soluble crystalline salts. Hydroxanthaline is coloured deep-violet by H_2SO_4 (even free from HNO_3), the colour being destroyed by water, but reproduced by H_2SO_4.—$B'H_2Cl_2 4aq$: yellow needles. Gives off all its acid at 150°.

XANTHAMIDE *v. Ethyl ether* of (β)-THIOCARBAMIC ACID.

XANTHATES. The salts RS.CS.OEt where R is a metal; *v.* ETHYL DITHIOCARBONATE.

XANTHIC ACID *v.* ETHYL DITHIOCARBONATE.

XANTHINE $C_5H_4N_4O_2$ *i.e.*



$\left.\begin{array}{l}\mathrm{NH.CH{:}C.NH}\\ \mathrm{CO.NH.C{=}N}\end{array}\right\rangle\mathrm{CO}$. *Xanthic oxide.* Mol. w. 152. S. ·007 in the cold; ·08 at 100°. Occasionally found in urinary calculi (Marcet, *Essay on Calculi*, London, 1819; Liebig a. Wöhler, *A.* 26, 340; Lebon, *C. R.* 73, 47) and in urinary deposits (Bence Jones, *C. J.* 15, 78). Occurs in small quantity in the urine of man, in the pancreas, spleen, and liver of oxen, in the thymus gland of the calf, in muscle of mammalia and fishes (Scherer, *A.* 107, 314; 112, 257; Städeler, *A.* 111, 28; 116, 102; Dürr, *A.* 134, 45; Kossel, *H.* 6, 422), in some kinds of guano (Unger a. Phipson, *C. N.* 6, 16), and in yeast (Schindler, *H.* 13, 432). Occurs also in lupin seeds (Salomon, *J.* 1881, 1012; Schulze a. Barbieri, *J. pr.* [2] 27, 358), in pumpkin-seeds (E. Schulze, *J. pr.* [2] 32, 457), and in tea (Baginsky, *H.* 8, 396).

Formation.—1. By the action of nitrous acid on guanine (Strecker, *A.* 108, 141; 118, 151; 131, 121; Balke, *J. pr.* [2] 47, 542).—2. In small quantity by heating a mixture of HOAc and aqueous HCy (Gautier, *Bl.* [2] 42, 141).

Preparation.—1. Separates as a crystalline powder when $NaNO_2$ (8 g.) is added slowly to a solution of guanine (10 g.) in H_2SO_4 (20 g.) and water (150 g.) at 75° (Fischer, *A.* 215, 309).—2. The aqueous extract of sprouting lupin seeds is evaporated, the residue treated with alcohol, and the alcoholic filtrate evaporated. The residue is dissolved in water, and $AgNO_3$ and NH_3 added. The gelatinous pp. is dissolved in hot HNO_3 (S.G. 1·1), which yields on cooling a crystalline compound of hypoxanthine and silver nitrate, and on adding NH_3 to the filtrate silver-xanthine is ppd. (S. a. B.).—3. Urine is ppd. with baryta-water; the filtrate is evaporated to a small bulk and boiled with cupric acetate. The pp. is dissolved in warm nitric acid and ppd. with $AgNO_3$; the pp. is crystallised from hot diluted HNO_3, treated with ammoniacal $AgNO_3$, decomposed by H_2S, and the solution evaporated.—4. A solution containing xanthine is treated with Fehling's solution and hydroxylamine hydrochloride, and the ppd. copper compound decomposed by H_2S. The xanthine may be further purified by preparing its lead salt and decomposing this with H_2S (Balke, *J. pr.* [2] 47, 552).

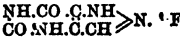
Properties.—Small scales (by evaporation) or powder composed of minute globules, nearly insol. cold water, insol. alcohol and ether. V. e. sol. KOHAq and reppd. by CO_2 and other acids. Weak base. Does not form an acetate. A cold saturated aqueous solution of xanthine gives white pps. with $HgCl_2$ and $AgNO_3$, and a yellowish-green, flocculent pp. with hot cupric acetate. An ammoniacal solution of xanthine is ppd. by $HgCl_2$, $ZnCl_2$, $CdCl_2$, and $AgNO_3$. Xanthine reduces ammoniacal cupric chloride (Drechsel, *B.* 25, 2454). Xanthine evaporated with nitric acid leaves a yellow residue turned orange by KOH (but not by NH_3), the colour becoming violet-red on warming. Solid xanthine added to a mixture of bleaching-powder and NaOHAq on a watch-glass forms a dark-green spot, changing to brown and finally disappearing. Xanthine warmed with chlorine-water and a trace of HNO_3 as long as gases escape, and then evaporated to dryness, yields a residue which is coloured rose-red by gaseous NH_3 (Weidel, *A.* 158, 365; Kossel, *H.* 6, 426).

Reactions.—1. Decomposed above 150°, giving off HCy, NH_3, cyanogen, and CO_2.—2. $KClO_3$ and HClAq at 60° form urea and alloxan.—3. Conc. HClAq at 230° forms glycocoll, formic acid, NH_3, and CO_2 (E. Schmidt, *A.* 217, 311).—4. NaOH (2 mols.) and $Pb(OAc)_2$ form a lead salt which, if dried and heated with MeI at 130°, yields theobromine (Fischer).—5. Slowly attacked by pure HNO_3, the gas evolved consisting of nitrogen (1 vol.), CO_2 (4 vols.), and N_2O (11 vols.) (Franchimont, *R. T. C.* 6, 223).

Salts.—$B'HCl$. Nodular groups of silky needles.—$B'H_2SO_4$ aq. Scales, decomposed by water.—$B'BaH_2O_2$. Sl. sol. water.—$B'_2Cu_3O_2$. Formed by the action of Fehling's solution and hydroxylamine hydrochloride (Balke).—$B'Ag_2O$. Yellowish-white flocculent pp., got by adding $AgNO_3$ to an ammoniacal solution of xanthine. Blackens on boiling.—$NaC_5H_3N_4O_2$ aq. Minute needles.

Bromo-xanthine $C_5H_3BrN_4O_2$. Formed by heating xanthine with bromine at 100°, and also by the action of nitrous acid on bromoguanine (Fischer a. Reese, *A.* 221, 343). Crystalline powder, sol. conc. HClAq and H_2SO_4, but reppd. by water; sl. sol. hot water and hot alcohol; sol. alkalis.

Isoxanthine $C_5H_4N_4O_2$ *i.e.*



$\left.\begin{array}{l}\mathrm{NH.CO.C.NH}\\ \mathrm{CO.NH.C.CH}\end{array}\right\rangle\mathrm{N}$. Formed by reducing diazo-isonitroso-methyl-uracil $C_5H_5N_3O_3$ with $SnCl_2$ and HClAq (Behrend, *A.* 245, 223). Needles (containing ½aq); sl. sol. hot water. Dissolves in Ac_2O without change. On evaporation with HNO_3 it leaves a residue coloured orange by

KOHAq. Yields $C_5H_3BrN_4O_2$ aq, crystallising from water in six-sided tables.

Pseudo-xanthine $C_5H_4N_4O_2$. A product of the action of H_2SO_4 (2 pts.) on uric acid (1 pt.) at 120° (Schultzen a. Filehne, *B.* 1, 150). Formed also by the action of nitrous acid on adenine (Kossel, *H.* 10, 258). Powder, sl. sol. water, HClAq, and NH_3Aq, v. sol. KOHAq. Its aqueous solution is acid in reaction, and on evaporation with HNO_3 leaves a lemon-yellow residue, which is turned orange on warming with KOHAq.

The name **pseudo-xanthine** is also given by Gautier (*Bl.* [2] 48, 19) to a substance $C_4H_5N_5O$ occurring in muscular tissue. This is a yellow powder, which forms a very soluble hydrochloride. Its aqueous solution is ppd. by $HgCl_2$, $AgNO_3$, and ammoniacal $Pb(OAc)_2$, but not by $Pb(OAc)_2$. This pseudo-xanthine also gives an orange colour when the residue, after evaporation with HNO_3, is treated with potash.

Paraxanthine $C_7H_8N_4O_2$. [c. 284°]. Occurs in human urine (Salomon, *B.* 16, 195; 18, 3406; *H.* 13, 187; Thudichum, *H.* 11, 415; Kossel, *H.* 13, 302). Silky needles or monoclinic tables, insol. alcohol and ether, sl. sol. cold water, v. sol. hot water. Sol. NH_3Aq and HClAq. Poisonous, acting like caffeïne and theobromine. $AgNO_3$ added to its solution in HNO_3 or NH_3Aq gives a gelatinous or flocculent pp. Picric acid forms a yellow crystalline pp. when added to its solution in HClAq. Gives a red colour (like xanthine) when the residue after evaporation with chlorine-water is exposed to gaseous NH_3. Does not give an orange colour when KOHAq is added to the residue after evaporation with HNO_3. Conc. NaOHAq forms a crystalline salt. KOHAq does the same. A solution of paraxanthine is ppd. by $Cu(OAc)_2$, phosphotungstic acid, $HgCl_2$, and ammoniacal lead subacetate, but not by mercuric nitrate.

Heteroxanthine $C_6H_6N_4O_2$. Occurs in urine of men and dogs (Salomon, *B.* 18, 3407; *H.* 11, 412). Amorphous powder, v. sl. sol. cold water, sol. NH_3Aq, insol. alcohol and ether. Its solution in HClAq is not ppd. by picric acid. $AgNO_3$, $HgCl_2$, $Cu(OAc)_2$, and ammoniacal lead subacetate give pps. When evaporated with chlorine-water and HNO_3 it leaves a residue which is coloured red by gaseous NH_3, the colour changing to blue on addition of NaOHAq. NaOHAq forms a salt crystallising in tables, v. sol. water, sl. sol. NaOHAq. The hydrochloride forms sparingly soluble crystalline aggregates, which lose HCl on treatment with water.

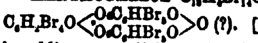
Hypoxanthine *v.* vol. ii. p. 745.

XANTHININE $C_4H_5N_3O_2$. S. ·0025 in the cold; ·025 at 100°. Formed by heating ammonium thionurate at 200° (Finck, *A.* 132, 298). Got also by heating pseudo-uric acid with H_2SO_4 at 150° (Grimaux, *Bl.* [2] 31, 535). White powder, nearly insol. water, sol. NH_3Aq, forming a solution with blue fluorescence. Its solution gives a white pp. with $HgCl_2$ and a yellow pp. with $AgNO_3$. Not attacked by HNO_3. Sol. KOHAq and reppd. by CO_2. Sol. conc. H_2SO_4, forming a laminar sulphate, decomposed by water with separation of xanthinine.—$B'Ag_2O$. Bulky yellow pp., got by pouring an ammoniacal solution of xanthinine into excess of aqueous $AgNO_3$.

XANTHOCHELIDONIC ACID *v.* CHELIDONIC ACID.

XANTHOCREATININE *v.* CREATININE and LEUCOMAÏNES.

XANTHOGALLOL $C_{18}H_4Br_{14}O_6$ *i.e.*



$C_6H_2Br_4O\!\left\langle\begin{array}{l}O\cdot C_6HBr_3O\\O\cdot C_6HBr_3O\end{array}\right\rangle\!O$ (?). [122°]. Formed by adding pyrogallol (1 pt.) to bromine (10 pts.), leaving the mixture to stand for two hours, and then shaking with water and heating (Stenhouse a. Groves, *C. J.* 28, 1; *A.* 177, 191; 179, 237; Theurer, *A.* 245, 334). Tri-bromo-pyrogallol is an intermediate body in its preparation. Yellow laminæ (from CS_2 and ligroïn), v. sol. ether and CS_2, m. sol. ligroïn. Decomposed by boiling with water or alcohol. Very stable towards oxidising agents, even crystallising unaltered from conc. HNO_3. Not reduced by sodium-amalgam or by zinc and dilute H_2SO_4. Aniline in HOAc yields an anilide [205°], to which Theurer assigns the impossible formula $C_{18}H_4Br_{11}(NHPh)_4O_6$. *p*-Toluidine forms a corresponding *p*-toluide. Reacts with phenyl-hydrazine acetate.

Reactions.—1. NaOHAq forms hexa-bromo-benzene dihydride $C_6H_2Br_6$ [139°], sl. sol. alcohol, which crystallises in prisms, while the mother-liquor contains a sodium salt of an acid $C_5H_4Br_2O_3$ [124°], which forms BaA″, crystallising from dilute alcohol in large white plates (Theurer). By the action of dilute NaOHAq on xanthogallol, Hantzsch a. Schniter (*B.* 20, 2033) obtained $C_{18}H_4Br_{11}(OH)_3O_6$, which yields $Ba_3(C_{18}H_4Br_{11}O_9)_2$ and crystalline $C_{18}H_4Br_{11}Ac_3O_6$.—2. Na_2CO_3Aq converts xanthogallol in the cold into $C_{18}H_7Br_{11}O_9$, crystallising from benzene in needles [72°] and prisms [131°], yielding the crystalline derivatives $C_{18}H_7Br_{11}O_6 3NPhH_2$ and $C_{18}H_7Br_{11}O_6 3NH_2.C_6H_4Me$.—3. HBr passed into a cooled solution of xanthogallol in MeOH forms $C_{18}H_4Br_{11}O_3(OMe)_6$, crystallising from MeOH in prisms [113°], and converted by boiling dilute NaOHAq into an acid $C_6H_2Br_4O_2(OMe)_2$ [105°], and by MeOH and hydrochloric acid into $C_6HBr_4Cl(OMe)_4$ [77°]. The brominated acid $C_6H_2Br_4O_2(OMe)_2$ reacts with aniline, forming crystalline $C_6H_2Br_4O_2(OMe)_2NH_2Ph$. Conc. H_2SO_4 converts $C_6H_2Br_4O_2(OMe)_2$ into $C_6H_2Br_4O_3$ [65°].—4. Hydrochloric acid gas passed into a cooled solution of xanthogallol in MeOH forms $C_{18}H_4Br_{11}Cl_3O_3(OMe)_6$ [86°], which is insol. water, v. sol. alcohol, does not react with aniline, and is decomposed by dilute alkalis.—5. HCl passed into an alcoholic solution of xanthogallol forms $C_{18}H_4Br_{11}Cl_3O_3(OEt)_6$, crystallising from alcohol in colourless prisms [75°], converted by NaOHAq into a product [92°]. $C_{18}H_4Br_{11}Cl_3O_6$ [104°] is a bye-product in the action of alcohol and HCl on xanthogallol. It forms large yellow crystals, v. sol. alcohol.

XANTHOGENIC ACID *v.* ETHYL DITHIOCARBONATE.

XANTHOMETHYLIC ACID *v.* METHYL THIOCARBONATES.

XANTHONE is DIPHENYLENE KETONE OXIDE.

XANTHOPURPURIN is *m*-DI-OXY-ANTHRAQUINONE.

XANTHOQUINIC ACID *v.* OXY-QUINOLINE CARBOXYLIC ACID.

XANTHORHAMNIN $C_{48}H_{66}O_{29}$ (?). Obtained from Persian berries (the fruit of *Rhamnus infectoria*) by extracting with three times their weight of 85 p.c. alcohol; the yield being 12 p.c. (Liebermann a. Hörmann, *B.* 11, 952, 1618; *A.* 196, 307; *cf.* Kane, *P. M.* [3] 23, 3; Gellatly, *N. E. P. J.* 7, 252; *C. N.* 3, 196; Hlasiwetz, *A.* 111, 108; Bolley, *A.* 115, 55; *U. J.* 13, 328; Stein, *Z.* [2] 5, 183, 568; Behrend, *B.* 11, 1353). Yellow needles (containing 2aq), v. sol. water and alcohol, insol. ether. Has little tinctorial power. Reduces Fehling's solution and ammoniacal $AgNO_3$, forming a mirror. $FeCl_3$ gives a dark-brown pp. Ppd. by ammoniacal lead acetate. Boiling dilute H_2SO_4 splits it up into rhamnetin (2 mols.) and isodulcite (4 mols.).

Salts.—$C_{48}H_{62}K_4O_{29}$. Yellow powder, v. e. sol. water.—Pb_2A^{iv}. Yellow pp.

Acetyl derivatives $C_{48}H_{54}Ac_{12}O_{29}$ (Schützenberger, *Z.* [2] 4, 668).—$C_{48}H_{49}Ac_{17}O_{29}$. Powder, v. e. sol. alcohol (Liebermann a. Bergami, *B.* 20, 2245).

XANTHOROCCELIN *v.* PICRO-ROCCELIN.

XANTHORRHŒA RESIN is ACAROID RESIN.

XANTHOXYLIN $C_{10}H_{12}O_4$. [80°]. Occurs, together with xanthoxylene $C_{10}H_{16}$ (162°) in the essential oil from japan-pepper (*Xanthoxylon piperitum*) (Stenhouse, *Ph.* [2] 13, 423; 17, 19; *A.* 104, 237). Silky monoclinic crystals, insol. water, v. sol. alcohol and ether. Its alcoholic solution is not ppd. by $AgNO_3$ or lead acetate, even on addition of NH_3Aq.

XENYLAMINE *v. p*-AMIDO-DIPHENYL.

XENYLENE-DIAMINE *v. p-p*-DI-AMIDO-DIPHENYL.

XERONIC ACID *v.* DI-ETHYL-MALEÏC ACID.

XYLAN $C_6H_{10}O_5$. *Tree gum. Wood gum.* S. 2 at 100°. $[\alpha]_D = -69{\cdot}6°$ (Tollens); $-84°$ (Thomsen). Obtained from the bark of trees (T. Thomsen, *J. pr.* [2] 19, 146; Poumarède a. Figuier, *A.* 64, 388). Obtained, to the extent of 1·73 p.c., by extracting jute with dilute (5 p.c.) NaOHAq; and got also by extracting beech-wood or pine-wood sawdust with 5 p.c. NaOHAq (Tollens, *A.* 254, 307, 320, 324, 326; *Bl.* [3] 1, 1102; Winterstein, *H.* 17, 381). Obtained also by extracting wheat-straw, first with 2 p.c. NH_3Aq, and then with 5 p.c. NaOHAq (Tollens, *A.* 260, 291). The alkaline extract is ppd. with alcohol and HCl.

Properties.—Porous mass, insol. cold, sol. hot, water; sol. NaOHAq. The hot aqueous solution becomes opalescent on cooling. Insol. alcohol, but the aqueous solution is not ppd. by alcohol unless an acid or the salt of an alkali is added. Insol. NH_3Aq, lime- and baryta-water. Its aqueous solution is lævorotatory. Gives furfuraldehyde when distilled with H_2SO_4 or HCl, and xylose when boiled with dilute H_2SO_4. Gives no colour with iodine. HNO_3 oxidises xylan to saccharic acid, but gives no mucic acid.

***o*-XYLENE** C_8H_{10} *i.e.* $C_6H_4Me_2$ [1:2]. *Di-methyl-benzene.* Mol. w. 106. [−28°] (Colson, *A. Ch.* [6] 6, 128). (142°). S.G. $\frac{0}{0}$ ·8932 (Pinette, *A.* 243, 50); ^{21} ·876 (Gladstone, *C. J.* 59, 290). μ_A 1·4928, μ_H 1·5328. C.E. (0°–10°) ·00098. S.V. 139·9 (Schiff); 137·6 (Pinette). H.C. 1,084,274 [$C,O_2 = 94{,}000$; $H_2,O = 69{,}000$] (Stohmann, *J. pr.* [2] 35, 41). M.M. 13·31 (Schönrock, *Z. P. C.* 11, 758. *Critical temperature*: 358° (Altschul, *Z. P. C.* 11, 590). Occurs in coal-tar. The S.G. of crude xylene varies between ·857 and ·866; it contains 70 to 87 p.c. *m*-xylene, 3 to 10 p.c. *p*-xylene, 2 to 15 p.c. *o*-xylene, and 3 to 10 p.c. fatty hydrocarbons (Levinstein, *B.* 17, 444; *cf.* Fittig, *A.* 148, 10). If 100 c.c. of the mixture are boiled for 45 minutes with 40 c.c. of HNO_3 (S.G. 1·42) diluted with 60 c.c. of water, the *p*- and *o*-xylene are oxidised, leaving the *m*-xylene and fatty hydrocarbons. If the residual hydrocarbons, after washing with NaOHAq followed by steam distillation, be shaken for 30 minutes with 1½ volumes of H_2SO_4, the *m*-xylene will be sulphonated and dissolved, while the fatty hydrocarbons remain. If 100 c.c. of crude xylene be shaken with 120 c.c. of H_2SO_4, the *o*- and *m*-xylene dissolve, leaving the *p*-xylene and fatty hydrocarbons. On crystallising the sodium salts of the dissolved sulphonic acids, sodium *o*-xylene sulphonate separates first, and may be converted into *o*-xylene by heating in a sealed tube with HClAq at 190° (Jacobsen, *B.* 10, 1009), or by heating with diluted sulphuric acid. Nölting, Witt, and Forel (*B.* 18, 2668) found 25 p.c. of *p*-xylene in commercial xylene. According to Nölting and Palmer (*B.* 24, 1955), crude xylene may contain 10 p.c. of ethyl-benzene. When a mixture of *o*-xylene and ethyl-benzene is treated with Br (20 pts.) and I, tetra-bromo-xylene is formed, together with a less highly brominated ethyl-benzene (Crafts, *C. R.* 114, 1110).

Formation.—1. By distilling its carboxylic acids with lime.—2. From *o*-bromo-toluene, MeI, and Na (Jannasch a. Hübner, *A.* 170, 117; Reymann, *Bl.* [2] 26, 532).—3. By heating cantharidin with P_2S_5 (Piccard, *B.* 12, 580).—4. By passing MeI through a mixture of toluene and $AlCl_3$ at 85° (Jacobsen, *B.* 14, 2628).

Properties.—Oil, solidifying in a freezing-mixture at −28°. Unlike *m*- and *p*- xylene it does not yield a solid nitro- derivative with a cold mixture of H_2SO_4 and HNO_3. It is completely oxidised by chromic acid mixture.

Reactions.—1. Dilute HNO_3 forms *o*-toluic acid.—2. Boiling aqueous $KMnO_4$ oxidises it to phthalic acid.—3. PCl_5 at 200° reacts, forming $C_6H_4(CCl_3).CHCl_2$ (Colson a. Gautier, *Bl.* [2] 45, 507).—4. *Bromine* in the dark forms bromo-*o*-xylene $C_6H_3Me_2Br$ [1:2:4]. In direct sunshine the products are $C_6H_4Me.CH_2Br$ and $C_6H_4(CH_2Br)_2$ (Schramm, *B.* 18, 1278).—5. $AlCl_3$ and gaseous HCl at 100° yield benzene, *m*- and a little *p*-xylene, ψ-cumene and mesitylene (Hesse a. Töhl, *A.* 270, 168).

***m*-Xylene** $C_6H_4Me_2$ [1:3]. V.D. 3·68 (calc. 3·67) (Schiff, *A.* 220, 92). (139°). S.G. $\frac{0}{0}$ ·8812 (Pinette, *A.* 243, 50); $\frac{12\cdot8}{4}$ ·8715 (S.); $\frac{20}{4}$ ·8655 (Brühl, *A.* 235, 13); $^{22\cdot5}$ ·864 (Gladstone, *C. J.* 59, 290). C.E. (0°–10°) ·00096. μ_α 1·495 (B.); μ_A 1·4876, μ_H 1·5277. S.V. 139·8. H.C. 1,084,168 (Stohmann, *J. pr.* [2] 35, 41). M.M. 12·73 at 20°–30° (Schönrock, *Z. P. C.* 11, 758). *Critical temperature*: 346° (A.). Occurs in coal-tar (*v. o*-XYLENE).

Formation.—1. From *m*-iodo-toluene, MeI, and Na (Wroblewsky, *A.* 192, 200).—2. From (1,3,4)-xylidine and amyl nitrite (Staedel a. Holz, *B.* 18, 2919).—3. From toluene, MeCl, and $AlCl_3$ (Friedel a. Crafts, *A. Ch.* [6] 1, 461; Ador a. Rilliet, *B.* 11, 1627).—4. By distilling mesitylenic and xylylic acids with lime (Fittig, *A.* 148, 10; 156, 236).

Properties.—Liquid. Not attacked by dilute HNO_3. Conc. HNO_3 on warming forms tri-nitro-xylene [176°], sl. sol. alcohol.

Reactions.—1. Oxidised by *chromic acid mixture* to isophthalic acid.—2. PCl_5 at 200° forms a hexachloride (Colson a. Gautier, *Bl.* [2] 45, 508).—3. *Bromine* in the dark forms $C_6H_3Me_2Br$ [1:3:4], while in direct sunshine $C_6H_4Me(CH_2Br)$ and $C_6H_4(CH_2Br)_2$ are produced (Schramm, *B.* 18, 1277; *M.* 8, 305).—4. $AlCl_3$ and gaseous HCl at 100° form benzene, mesitylene, and some *p*-xylene and ψ-cumene (Heise a. Töhl, *A.* 270, 168). On boiling with $AlCl_3$ the products are benzene, toluene, a little *p*-xylene, ψ-cumene, mesitylene, and durene (Anschütz, *A.* 235, 182).—5. On heating with MeI and I at 250° it yields ψ-cumene, mesitylene, and $C_{10}H_{14}$ (Rayman a. Preis, *A.* 223, 320).—6. *Ethyl-malonyl chloride* at 60° in presence of $AlCl_3$ forms the ketone $C_{13}H_{14}O_2$ [63°] (Béhal a. Auger, *Bl.* [3] 3, 122).—7. *Benzoyl peroxide* forms dixylylene $C_{16}H_{18}$ (265°), S.G. $\frac{22}{}$ ·9984 (Lippmann, *M.* 7, 528).—8. CrO_2Cl_2 added to its solution in CS_2 ppts. chocolate brown $C_6H_4Me_2 2CrO_2Cl_2$, which is converted by water into *m*-toluic aldehyde and at 200° yields $C_6H_4Me.CH(CrO_2Cl)_2$ (Étard, *A. Ch.* [5] 22, 244).—9. CH_2Cl_2 and $AlCl_3$ form tetra-methyl-anthracene [163°] (Friedel a. Crafts, *A. Ch.* [6] 11, 268).—10. PH_4I forms C_8H_{14} on heating (Baeyer, *Z.* [2] 4, 455). HIAq and P at 280° form *m*-xylene hexahydride.

***p*-Xylene** $C_6H_4Me_2$ [1:4]. [13°] (Reissert, *B.* 23, 2242); [15°] (Jannasch). (138°). S.G. $\frac{0}{0}$ ·8801 (R.); $\frac{23\cdot7}{}$ ·860 (Gladstone, *C. J.* 59, 290). C.E. (0°–10°) ·00098 (Pinette, *A.* 243, 51). μ_A 1·4854. μ_H 1·5253. S.V. 140 (Schiff). H.C. 1,084,274 (Stohmann, *J. pr.* [2] 35, 41). M.M. 12·79 at 20°–30° (Schönrock, *Z. P. C.* 11, 753). *Critical temperature*: 344°. Occurs in coal-tar (*v. supra*) and in Galician petroleum (Pawlewski, *B.* 18, 1915). Formed by the action of MeI and sodium on *p*-bromo-toluene (Fittig, *A.* 136, 303; Jannasch, *A.* 171, 79) and on *p*-di-bromo-benzene (V. Meyer, *B.* 3, 753). Monoclinic prisms; $a:b:c = 2\cdot32:1:2\cdot34$; $\beta = 69\cdot5°$ (Baeyer, *A.* 245, 141).

Reactions.—1. Dilute HNO_3 forms *p*-toluic acid.—2. *Chromic acid mixture* yields terephthalic acid.—3. PCl_5 at 190° gives $C_6H_4(CH_2Cl)_2$ and at 200° $C_6H_4(CCl_3)_2$ (Colson a. Gautier, *Bl.* [2] 45, 6, 507).—4. *Bromine* in the dark forms $C_6H_3BrMe_2$, while in direct sunshine the products are $C_6H_4Me.CH_2Br$ and $C_6H_4(CH_2Br)_2$ (Schramm, *B.* 18, 1276).—5. $AlCl_3$ and HCl at 100° act in the same way as with o-xylene.

References.—Bromo-, Bromo-nitro-, Chloro-, Dichloro-nitro, Di-iodo-, Nitro-, and Oxy-xylenes.

XYLENE-AZO- compounds *v.* Azo- compounds.

XYLENE CARBOXYLIC ACID *v.* Di-methyl-benzoic acid and Mesitylenic acid.

***m*-XYLENE DICARBOXYLIC ACID** $C_{10}H_{10}O_4$ *i.e.* $C_6H_2Me_2(CO_2H)_2$ [1:3:4:6]. *Dimethyl-iso-phthalic acid.*

(α)-*Cumidic acid.* Mol. w. 194. [above 320°]. Formed by heating di-bromo-*m*-xylene dissolved in ether under pressure with $ClCO_2Et$ and sodium-amalgam. Formed also, together with (β)-cumidic acid, by oxidation of durene with dilute HNO_3 or of durylic acid with $KMnO_4$ (Schnapauff, *B.* 19, 2508). Minute prisms (from water) or plates (by sublimation).—BaA″ 1½aq: crystals, v. sol. water. Yields *m*-xylene on distilling with lime.

Methyl ether Me_2A''. [76°]. Crystals.

***m*-Xylene dicarboxylic acid** $C_6H_2Me_2(CO_2H)_2$ [1:3:4:5]. *Dimethyl-phthalic acid. Isocumidic acid.* [280°]. Formed by oxidation of (β)- and (γ)-isodurylic acid (Jacobsen, *B.* 15, 1857). Small crystals. May be sublimed. Yields *m*-xylene on distillation with lime. The Ca salt crystallises in small plates. The Ba salt is amorphous.

***p*-Xylene dicarboxylic acid** $C_6H_2Me_2(CO_2H)_2$ [1:4:2:5]. *Di-methyl-terephthalic acid.* (β)-*Cumidic acid.* Formed, together with (α)-cumidic acid, by oxidation of *s*-durene with dilute HNO_3 or of durylic acid with $KMnO_4$ (S.). Minute six-sided prisms (from alcohol). Sublimes in small plates without melting. Nearly insol. hot water. Yields *p*-xylene on distilling with lime.—BaA″ 2½aq: tables, v. sol. water.

Methyl ether Me_2A''. [114°]. (c. 297° cor.).

Xylene dicarboxylic acid $C_6H_3Me(CO_2H)CH_2.CO_2H$ [3:2:1]. [178°]. Formed by oxidation of $C_6H_3Me(CO.Et)CH_2.CO_2H$ (Béhal a. Auger, *C. R.* 109, 972). Gives off CO_2 on fusion.

Xylene di-ω-carboxylic acid *v.* Phenylene-diacetic acid.

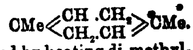
Reference.—Oxy-xylene carboxylic acid.

XYLENE GLYCOL *v.* Di-oxy-xylene.

***o*-XYLENE DIHYDRIDE** *v.* Cantharene.

***m*-Xylene dihydride** C_8H_{12}. (133°). S.G. $\frac{22}{}$ ·828. V.D. 3·74 (calc. 3·88). μ_D 1·4675. Formed, together with a polymeride $C_{16}H_{24}$ (280°–285°) S.G. $\frac{20}{}$ ·832, by heating the ketone $C_8H_{14}O$ with $ZnCl_2$. The ketone itself is obtained by distilling the anhydride $C_{10}H_{14}O_4$ which is got by the action of Ac_2O on cineolic acid, formed by oxidation of eucalyptol (Wallach, *A.* 258, 327). Liquid, smelling like xylene. Yields on nitration $C_6H_3Me_2(NO_2)$ [1:3:4].

***p*-Xylene dihydride**



$CMe\langle{}^{CH.CH_2}_{CH_2.CH}\rangle CMe$. (134°) at 720 mm. Formed by heating di-methyl-quinite dibromide $C_8H_{14}Br_2$ with quinoline (Baeyer, *B.* 25, 2122). Smells like turpentine. Forms a crystalline compound with HBr.

***m*-Xylene tetrahydride** $C_6H_8Me_2$. (119°). S.G. $\frac{0}{}$ ·814; $\frac{14}{}$ ·794.

Formation.—1. By heating oxycamphoric anhydride $C_{10}H_{14}O_4$ with water at 180° or with HI at 150° (Wreden, *A.* 163, 336).—2. By heating camphoric acid with syrupy phosphoric acid at 200°.—3. By distilling camphoric acid with $ZnCl_2$ (Ballo, *A.* 197, 322).—4 By heating camphoric acid with HIAq at 200° (Wreden, *A.* 187, 171).

Properties.—Oil. Oxidised by chromic acid mixture to acetic, *m*-toluic, isophthalic, and terephthalic acids. HNO_3 forms tri-nitro-*m*-xylene.

Xylene tetrahydride C_8H_{14}. (131°). S.G. $\frac{22}{}$ ·816. Occurs among the products of the distillation of colophony (Renard, *A. Ch.* [6] 1, 236). Slightly dextrorotatory liquid. Yields oily di- and tri- bromo- derivatives. Sulphuric acid forms an oily polymeride $C_{16}H_{28}$, which is oxidised by fuming HNO_3 to succinic and oxalic acids. Absorbs oxygen. Does not reduce ammoniacal $AgNO_3$. In ethereal solution it combines with Br, forming $C_8H_{14}Br_2$.

m-Xylene tetrahydride (?) C_8H_{14}. (120°). *Octonaphthylene.* Formed by the action of moist Ag_2O on $C_8H_{15}I$, which is got by the action of CaI_2 at 60° on $C_8H_{15}Cl$ (175°), a product of the chlorination of octonaphthene (Jakowkin, *J. R.* 16, ii. 294). Oil, smelling like turpentine. Combines with Br (2 atoms). An isomeric octonaphthylene (123°–129°) is got by distilling $C_8H_{15}Cl$ obtained by chlorination of iso-octonaphthene (Putochin, *J. R.* 16, ii. 295).

m-Xylene hexahydride C_8H_{16} *i.e.* $C_6H_{10}Me_2$ [1:3]. *Octonaphthene.* (118°). S.G. $\frac{0}{0}$ ·7814 (Lossen, *A.* 225, 110); $\frac{20}{0}$ ·7706 (A.). C.E. (0°–26°) ·001072. V.D. 3·87. S.V. 164·8. $\mu_D = 1·419$ at 22° (Wallach, *B.* 25, 923). Occurs in Baku petroleum (Beilstein a. Kurbatoff, *B.* 13, 1820; Markownikoff a. Spady, *B.* 20, 1850), and among the products of the distillation of colophony (Renard, *A. Ch.* [6] 1, 229). Formed by heating heptanaphthene carboxylic acid with HIAq and P (Aschan, *B.* 24, 2718). Prepared by heating camphoric acid or *m*-xylene with HIAq at 200° (Wreden, *A.* 187, 157). Liquid. Not oxidised by aqueous $KMnO_4$. H_2SO_4 and HNO_3 form tri-nitro-*m*-xylene. Sulphur at 220° forms *m*-xylene.

Isomeride C_8H_{16}. *Iso-octonaphthene.* (122°). S.G. $\frac{0}{0}$ ·7767 $\frac{17.5}{0}$ ·7637. Occurs in Caucasian petroleum (Putochin, *J. R.* 16, ii. 295). Liquid.

p-Xylene hexahydride $C_6H_{10}Me_2$[1:4]. (138° cor.). V.D. 4·01 (obs.). S.G. $\frac{4}{4}$ ·7956. Formed by heating bromo-camphor with $ZnCl_2$ (R. Schiff, *B.* 13, 1407; *G.* 10, 320). Liquid, yielding tri-nitro-*p*-xylene [137°] on nitration.

m-XYLENE PHOSPHINIC ACID

Chloride $C_6H_3Me_2.PCl_2$ [1:3:4]. (257°). Got from mercuric dixylyl $Hg(C_6H_3Me_2\ [4:1:3])_2$ and PCl_3 at 235° (Weller, *B.* 20, 1720). Liquid, converted by water into the acid $C_6H_3Me_2P(OH)_2$. Chlorine forms the compound $C_6H_3Me_2.PCl_4$, which is converted by water into $C_6H_3Me_2PO(OH)_2$ [194°].

m-Xylene-phosphinic acid $C_6H_3Me_2P(OH)_2$ [98°] (Michaelis, *A.* 212, 237). Formed by the action of water on the chloride. Needles (from alcohol). Probably a mixture.

Chloride $C_6H_3Me_2.PCl_2$ (256°). S.G. ^{12} 1·24. Formed from *m*-xylene, PCl_3, and $AlCl_3$ (Weller, *B.* 20, 1720). It is a mixture of the preceding body and the 1,3,5 isomeride. Readily absorbs chlorine, forming $C_6H_3Me_2PCl_4$, whence SO_2 forms $C_6H_3Me_2.POCl_2$ (280°–300°).

p-Xylene phosphinic acid $C_6H_3Me_2P(OH)_2$. *p-Xylene phosphinous acid.* Formed by treating the chloride with hot water (Weller, *B.* 21, 1494). Crystallises with difficulty.

Chloride $C_6H_3Me_2PCl_2$. [–30°]. (254°). S.G. $\frac{15}{15}$ 1·25. Formed by heating *p*-xylene (150 g.) with $AlCl_3$ (30 g.) and PCl_3 (200 g.) for 36 hours with inverted condenser (Michaelis a. Paneck, *A.* 212, 236). Strongly refracting liquid.

m-XYLENE *s*-PHOSPHONIC ACID $C_6H_3Me_2PO(OH)_2$. *m-Xylene (α)-phosphinic acid.* [194°]. S. 1·5 at 20°; 6·9 at 100°. Formed by boiling the chloride $C_6H_3Me_2PCl_4$ (*v. supra*) with water (Weller, *B.* 20, 1721). Needles, v. e. sol. alcohol. Decomposed into *m*-xylene and phosphoric acid on heating with alkalis. Br added to dilute solutions forms bromo- and di-bromo-*m*-xylene. Yields two nitro- derivatives [182°] and [100°].

Salts. — BaA″aq. Plates. — $CdH_2A''_2$aq. Plates, more sol. cold than hot water. — $NiH_2A''_2$aq.—Ag_2A'': white pp.

m-Xylene *s*-phosphonic acid $C_6H_3Me_2.PO(OH)_2$. *m-Xylene (β)-phosphinic acid.* [161°]. S. 1·8 at 15°; 117·3 at 100°. Prepared by boiling with water the mixture of chlorides $C_6H_3Me_2.POCl_2$ (280°–300°) which is got by the action of SO_2 on the mixture of tetrachlorides $C_6H_3Me_2.PCl_4$ formed by combination of chlorine with the mixture of chlorides $C_6H_3Me_2PCl_2$ obtained by heating *m*-xylene with PCl_3 and $AlCl_3$ (W.). Plates or needles, v. e. sol. alcohol and ether. Decomposed by alkalis into *m*-xylene and phosphoric acid.

p-Xylene phosphonic acid $C_6H_3Me_2.PO(OH)_2$. [180°]. Formed by the action of water on $C_6H_3Me_2.PCl_4$ [c. 60°] which is got by passing Cl through the product of the action of PCl_3 on *p*-xylene in presence of $AlCl_3$ (Weller, *B.* 21, 1494). Needles, m. sol. water, v. sol. alcohol, sl. sol. ether. Conc. HNO_3 forms the compound $C_6H_2(NO_2)Me_2PO(OH)_2$ [224°]. $KMnO_4$ yields $C_6H_3Me(CO_2H).PO_3H_2$ [278°].

Salts.—KHA″.—BaA″. Pearly plates, more sol. cold than hot water.

Chloride $C_6H_3Me_2.POCl_2$. (281°). S.G. $\frac{18}{18}$ 1·31. Oil. Formed by the action of SO_2 on $C_6H_3Me_2.PCl_4$.

Reference.—Nitro-xylene phosphonic acid.

XYLENE PHTHALOYLIC ACID *v.* Phenyl xylyl ketone carboxylic acid.

o-XYLENE SULPHINIC ACID $C_8H_{10}SO_2$ *i.e.* $C_6H_3Me_2.SO_2H$ [1:2:4]. [83°]. Formed by the action of zinc-dust on *o*-xylene sulphochloride (Jacobsen, *B.* 10, 1011). Plates (from water).

m-Xylene sulphinic acid $C_6H_3Me_2(SO_2H)$ [1:3:4]. [c. 50°]. Formed by reducing the sulphonic chloride $C_6H_3Me_2.SO_2Cl$ (Jacobsen; *cf.* Lindoff a. Otto, *A.* 146, 233). Crystalline.

p-Xylene sulphinic acid $C_6H_3Me_2(SO_2H)$ [1:4:2]. [85°]. Groups of needles (Jacobsen, *B.* 11, 22).

o-XYLENE SULPHONIC ACID $C_8H_{10}SO_3$ *i.e.* $C_6H_3Me_2(SO_3H)$ [1:2:4]. Formed by warming *o*-xylene with H_2SO_4 (Jacobsen, *B.* 10, 1011; 11, 22). Tables (containing 2aq) (from dilute H_2SO_4).—NaA′ 5aq.—BaA'_2 2aq. S. 5·8 at 0°; 33·6 at 100°.

Chloride $C_6H_3Me_2.SO_2Cl$. [52°]. Prisms.

Amide $C_6H_3Me_2.SO_2NH_2$. [144°]. Yields two acids $C_6H_3Me(CO_2H).SO_2NH_2$ on oxidation by $KMnO_4$.

o-Xylene *c*-sulphonic acid $C_6H_3Me_2.SO_3H$ [1:2:3]. Formed by the action of sodium-amalgam on $C_6H_2Me_2Cl(SO_3H)$ [1:2:6:3] (Krüger, *B.* 18, 1760).

Amide $C_6H_3Me_2.SO_2NH_2$. Granules.

m-Xylene *c*-sulphonic acid $C_6H_3Me_2(SO_3H)$ [1:3:2]. *m-Xylene (β)-sulphonic acid.* Formed, together with a larger quantity of the (1,3,4)-isomeride, by dissolving *m*-xylene in fuming H_2SO_4 (Jacobsen, *A.* 184, 188; *B.* 11, 18). It remains in the acid liquor after pp. the (1,3,4)-isomeride by the proper quantity of water. Potash-fusion yields *p*-xylenol [74·5°] (Jacobsen, *B.* 21, 2828). Its K salt heated with sodium formate forms an acid $C_9H_{10}O_2$ [99°].—KA'.—BaA'$_2$: minute needles.—CuA'$_2$aq.

Chloride $C_6H_3Me_2.SO_2Cl$. Oil.

Amide $C_6H_3Me_2.SO_2NH_2$. [96°]. Needles.

***m*-Xylene sulphonic acid** $C_6H_3Me_2(SO_3H)$ [1:3:4]. *m-Xylene (a)-sulphonic acid.* Formed as above. Long flat prisms (containing 2aq). Its K salt heated with sodium formate yields xylylic acid.—NaA'.—BaA'$_2$. Small plates.—ZnA'$_2$ 9aq.—CuA'$_2$ 6aq.

Chloride $C_6H_3Me_2.SO_2Cl$. [34°].

Amide [137°]. Needles (from water). BzCl at 160° forms $C_6H_3Me_2.SO_2NHBz$ [151°] Mahon, *Am.* 4, 194), which yields crystalline Ba$(C_{15}H_{14}NSO_3)_2$aq and BaA'$_2$, sl. sol. water.

***p*-Xylene sulphonic acid** $C_6H_3Me_2(SO_3H)$ [1:4:2]. Formed by sulphonating *p*-xylene (Beilstein a. Wahlforss, *A.* 133, 38; Fittig a. Glinzer, *A.* 136, 305; Jacobsen, *B.* 10, 1009; 11, 22; Remsen a. Emerson, *Am.* 8, 265). Plates or prisms (containing 2aq). Oxidised by alkaline KMnO$_4$ to sulpho-terephthalic and two sulpho-*p*-toluic acids.—NaA'aq. [148°]. Trimetric plates; *a*:*b*:*c* = 1·077:1:1·498 (Moody a. Nicholson, *C. J.* 57, 978).—KA'aq.—BaA'$_2$. S. 2·27 at 0°; 5·53 at 100°.—CuA'$_2$ 8aq. Light-blue triclinic prisms.—ZnA'$_2$ 10aq.

Chloride $C_6H_3Me_2.SO_2Cl$. [26°]. Prisms.

Amide [148°]. Needles, m. sol. hot water.

***o*-Xylene disulphonic acid** $C_6H_2Me_2(SO_3H)_2$. Formed by heating (1,2,4)-xylene sulphonic acid with ClSO$_3$H at 150° (Pfannenstill, *J. pr.* [2] 46, 155).—K$_2$A''aq.—BaA''3aq.—PbA''3aq. Prisms.

Chloride $C_6H_2Me_2(SO_2Cl)_2$. [79°]. Prisms.

Amide $C_6H_2Me_2(SO_2NH_2)_2$. [239°].

***m*-Xylene disulphonic acid** $C_6H_2Me_2(SO_3H)_2$ [1:3:4:2]. Formed by heating *m*-xylene with fuming H$_2$SO$_4$ at 150° (Wischin, *B.* 23, 2113), and by heating (1,3,4)-xylene sulphonic acid with SO$_3$ at 150° (P.). Deliquescent needles, converted by potash-fusion into $C_6H_2Me_2(OH)_2$ [146°].—(NH$_4$)$_2$A''.—NaHA'' 3aq.—K$_2$A'' 2aq.—BaA''3aq. Needles, v. sol. water.—PbA'' 3aq.—CuA''. Gummy mass.

Ethyl ether Et$_2$A''. Plates.

Chloride $C_6H_2Me_2(SO_2Cl)_2$. [129°]. Converted by PCl$_5$ at 180° (2,4,1,3)-di-chloro-xylene (220°).

Amide $C_8H_{12}N_2S_2O_4$ [249°]. Needles. Oxidised by KMnO$_4$ to $C_6H_2\left(\left\langle{}^{CO}_{SO}\right\rangle NH\right)_2$ [225°].

Ethylamide $C_6H_2Me_2(SO_2NHEt)_2$. [135°].

***m*-Xylene disulphonic acid** $C_6H_2Me_2(SO_3H)_2$ [1:3:2:6?]. Formed in small quantity, together with the preceding isomeride, by heating (1,3,2)-xylene sulphonic acid with ClSO$_3$H at 150° (Pfannenstill, *J. pr.* [2] 46, 154). Needles.

Chloride $C_6H_2Me_2(SO_2Cl)_2$. Oil.

Amide. [210°]. More sol. water than its isomeride.

***p*-Xylene disulphonic acid** $C_6H_2Me_2(SO_3H)_2$ [1:4:2:6?]. Formed by heating (1,4,2) $C_6H_3Me_2(SO_2Cl)$ with fuming H$_2$SO$_4$ (Holmes, *Am.* 13, 372; Pfannenstill, *J. pr.* [2] 46, 156). Needles, v. e. sol. water.—BaA'' 3aq.—CaA'' 4aq.—MgA'' 7aq.—PbA'' 3aq.—Ag$_2$A''aq.

Chloride $C_6H_2Me_2(SO_2Cl)_2$. [75°].

Amide $C_6H_2Me_2(SO_2NH_2)_2$. [295°].

References.—BROMO-, BROMO-NITRO-, NITRO-, and NITRO-AMIDO-, XYLENE SULPHONIC ACID.

XYLENE THIOSULPHONIC ACID. *Xylyl ether* $C_8H_9.SO_2S.C_8H_9$. *Xylyl disulphoxide.* Formed by heating xylene sulphinic acid with water at 150°–160° (Otto a. Lindoff, *A.* 146, 239). Oil, v. sol. alcohol and ether.

XYLENIC ALCOHOL is TOLYL-CARBINOL.

XYLENIC DIBROMIDE *v.* DI-ω-BROMO-XYLENE.

XYLENIC GLYCOL *v.* DI-ω-OXY-XYLENE.

***o*-XYLENOL** $C_8H_{10}O$ *i.e.* $C_6H_3Me_2.OH$ [1:2:4]. Mol. w. 122. [62°]. (225° i.V.). H.F.p. 61,566 (Stohmann, *J. pr.* [2] 34, 316). Obtained by potash-fusion from the sulphonic acid (Jacobsen, *B.* 11, 28), and by the diazo-reaction from (1,2,4)-xylidine (Jacobsen, *B.* 17, 161). Long needles (from water). SiCl$_4$ yields Si(OC$_8$H$_9$)$_4$, crystallising in prisms (350°–360° at 120 mm.) (Hertkorn, *B.* 18, 1691). Ammoniacal ZnBr$_2$ at 300° from xylidine and dixylylamine.—NaOC$_8$H$_9$. Flat needles, v. sl. sol. NaOHAq.

Benzoyl derivative [57°]. H.F. 77,768 (Stohmann, *J. pr.* [2] 36, 8).

***o*-Xylenol** $C_6H_3Me_2(OH)$ [1:2:3]. [75°]. (218° i.V.). Occurs in coal-tar (Schulze, *B.* 20, 410). Formed by the action of nitrous acid on *c-o*-xylidine (Töhl, *B.* 18, 2562; Nölting a. Forel, *B.* 18, 2673). Slender needles. Its aqueous solution gives a blue colour with FeCl$_3$.

***c-m*-Xylenol** $C_6H_3Me_2(OH)$ [1:3:2]. [49°]. Obtained from the crude xylidine, or by the action of HCl on *p*-oxy-mesitylenic acid (Nölting; Jacobsen, *B.* 21, 2829). *p*-Xylenol is got instead of *m*-xylenol by potash-fusion from (1,3,2)-xylene sulphonic acid (Jacobsen, *B.* 11, 26; 21, 2828).

***m*-Xylenol** $C_6H_3Me_2(OH)$ [1:3:4]. [26°] (Jacobsen, *B.* 18, 3463); [[illegible]8°] (Staedel a. Hölz, *B.* 18, 2919). (211·5° i.V.). S.G. $\frac{0}{4}$ 1·0362. H.F.p. 59,501 (Stohmann, *J. pr.* [2] 34, 316).

Formation.—1. From *m*-xylene sulphonic acid by potash-fusion (Jacobsen, *B.* 11, 24, 375; *cf.* Wroblewsky, *Bl.* [2] 10, 286; Wurtz, *J.* 1868, 459).—2. By heating oxy-mesitylenic acid with conc. HClAq at 200° (Jacobsen, *B.* 11, 2052).—3. By reduction of nitro-*m*-xylene and treatment of the resulting xylidine with nitrous acid (Harmsen, *B.* 13, 1558; S. a. S.; Hodgkinson a. Limpach, *C. J.* 63, 104).

Properties.—Needles, v. sl. sol. water, miscible with alcohol and ether. Volatile with steam. FeCl$_3$ colours its aqueous solution blue and its alcoholic solution green, being changed to bright blue on dilution with water. Yields the corresponding xylidine and di-xylyl-amine when heated with ZnBr$_2$, ammonia, and NH$_4$Br at 315° (Müller, *B.* 20, 1041). Potash-fusion forms (4,1,3)-oxy-toluic acid. Yields oily PO(OC$_8$H$_9$)$_3$ (Kreysler, *B.* 18, 1703). SiCl$_4$ forms Si(OC$_8$H$_9$)$_4$ (455°) (Hertkorn, *B.* 18, 1690).

Salt.—NaOC$_8$H$_9$. V. sol. water and conc. NaOHAq (unlike Na salts of other xylenols).

Methyl ether MeOC$_8$H$_9$ (192° i.V.) (J.); (186°) (S.). H.F.p. 46,336 (Stohmann, *J. pr.* [2] 35, 24).

Acetyl derivative C$_8$H$_9$OAc. (226° i.V.).

***s*-Xylenol** $C_6H_3Me_2(OH)$ [1:3:5]. [64°] (T.); [68°] (N. a. F.) (220°). Occurs in coal-tar (Schulze, *B.* 20, 410). Formed by the action of nitrous acid on *s*-xylidine (Thöl, *B.* 18, 362; Nölting a. Forel, *B.* 18, 2679). Slender needles (from water). Not coloured by $FeCl_3$.—$NaOC_8H_9$. Plates, sl. sol. NaOHAq.

p-**Xylenol** $C_6H_3Me_2(OH)$ [1:4:2]. [74·5°]. (211·5° i.V.). H.F.p. 61,362 (Stohmann, *J. pr.* [2] 34, 316). S.G. ^{21} ·971. Formed by potash-fusion from *m*- and from *p*-xylene sulphonic acid and from oxy-mesitylenic acid (Wurtz, *A.* 147, 378; Jacobsen, *B.* 11, 26). Formed also from *p*-xylidine by diazotisation followed by boiling with water (Nölting, Witt, a. Forel, *B.* 18, 2665). Long flat needles (from dilute alcohol). Volatile with steam. Its aqueous solution is not coloured by $FeCl_3$.

Potash-fusion gives (3,4,1)-oxy-toluic and oxy-terephthalic acids. KNO_2 and HOAc yield a nitroso- derivative $C_6H_2Me_2(OH)(NO)$[1:4:3:6] [163°], which is the oxim of *p*-xyloquinone (Oliveri, *G.* 12, 162; Goldschmidt a. Schmid, *B.* 18, 568).

Salt.—$NaOC_8H_9$. Large plates, sl. sol. cold NaOHAq.

Methyl ether $MeOC_8H_9$. (194° i.V.). Oil.

Ethyl ether $EtOC_8H_9$. (199°) (S.); (205°) (N. W. a. F.). Oil. H.F.p. 54,150.

Acetyl derivative C_8H_9OAc. (237° i.V.). S.G. $\frac{15}{4}$ 1·0264. Oil, not solid at −20°.

Xylenol. (220°). Occurs in beechwood-tar (Marasse, *A.* 152, 75; Tiemann a. Mendelssohn, *B.* 10, 57). Oil. Yields C_8H_9OMe (220°). On boiling with aqueous $KMnO_4$ it yields an acid which is converted by potash-fusion into *u*-oxy-isophthalic acid [300°].

References.—BROMO- and NITRO- XYLENOLS.

XYLENOLIC ACID *v.* OXY-DI-METHYL-BENZOIC ACID.

o-**XYLENOL SULPHONIC ACID** $C_8H_{10}SO_4$ *i.e.* $C_6H_2Me_2(OH).SO_3H$. Formed by sulphonation of (1,2,4)-xylenol (Jacobsen, *B.* 11, 24). $FeCl_3$ gives a violet colour in neutral solutions.—NaA′. Slender prisms or small laminæ.—BaA'_2. Nodular groups of minute laminæ, sl. sol. cold water.

m-**Xylenol (α)-sulphonic acid.** Formed, together with the (β)-isomeride, by dissolving (1,3,4)-xylenol in H_2SO_4 (J.). $FeCl_3$ gives a violet-blue colour.—NaA′. Tables.—KA′. Plates.—BaA'_2. Leaflets.

m-**Xylenol (β)-sulphonic acid**
$C_6H_2Me_2(OH).SO_3H$ [1:3:4:2] (Jacobsen, *A.* 195, 283). Formed as above. Coloured violet-blue by $FeCl_3$. Converted by potash-fusion into (2,5,1)-oxy-toluic acid. — NaA′ 4aq. Laminæ. —BaA'_2. Minute needles, less soluble than the Ba salt of the (α)-acid. By sulphonating (1,3,4)-xylenol by $ClSO_3H$, Hodgkinson (*C. J.* 63, 110) obtained a xylenol sulphonic acid yielding BaA'_2aq.

m-**Xylenol sulphonic acid**
$C_6H_2Me_2(OH).SO_3H$ [1:3:6:4]. Formed from $C_6H_2Me_2(NH_2).SO_3H$ by the diazo-reaction (Sartig, *A.* 230, 336). Slender needles, v. sol. water and alcohol. The acid and its salts give with $FeCl_3$ a bluish-violet colour turned green by alcohol.—KA′.—BaA'_2 aq. Needles, v. e. sol. water.—PbA'_2 2aq.

Ethyl derivative $C_6H_2Me_2(OEt).SO_3H$. Formed by heating diazo-*m*-xylene sulphonic acid with alcohol under pressure. Minute tables, v. sol. water and alcohol.—BaA'_2 3aq. Minute plates, v. sol. water.

p-**Xylenol sulphonic acid.** Formed by dissolving *p*-xylenol in warm H_2SO_4. Hydrated leaflets.—NaA′5aq. Tables.—BaA'_2. Minute needles.

Reference.—NITRO-XYLENOL SULPHONIC ACID.

XYLENYL-AMIDOXIM *v.* DI-METHYL-BENZOIC ACID.

XYLENYL ALCOHOL *v.* DI-OXY-XYLENE.

XYLENYL CHLORIDE *v.* TETRA-ω-CHLORO-XYLENE.

XYLETIC ACID is OXY-DI-METHYL-BENZOIC ACID.

XYLIC ACID is DI-METHYL-BENZOIC ACID.

XYLIDIC ACID is TOLUENE DICARBOXYLIC ACID.

c-o-**XYLIDINE** $C_6H_3Me_2(NH_2)$ [1:2:3].—*Di-methyl-phenyl-amine. Amido-xylene.* Mol. w. 121. (223° i.V.) at 739 mm. S.G. ^{15} ·991. Obtained by reducing di-bromo-*o*-xylidine $C_6HMe_2Br_2(NH_2)$ [1:2:4:5:3] with sodium-amalgam in the cold (Töhl, *B.* 18, 2562). Got also by heating (1,2,4)-xylenol with NH_4Br and ammonio-zinc bromide at 300° (Müller, *B.* 20, 1039). Prepared from *o*-xylene by nitration and reduction (Nölting a. Forel, *B.* 18, 2671; Wroblewski, *B.* 18, 2904). Oil. When oxidised by $K_2Cr_2O_7$ and H_2SO_4 it yields a small quantity of *o*-xyloquinone [55°]. Converted by the diazo-reaction into *o*-xylenol [73°]. H_2SO_4 and HNO_3 give (4,1,2,3)-nitro-xylidine [114°] and (6,1,2,3)-nitro-xylidine [65°] (Nölting a. Stoecklin, *B.* 24, 567). —Salts: B′HClaq. Plates. Begins to sublime at 100°.—$B'HNO_3$. Needles.—$B'_2H_2SO_4$. Large plates, sl. sol. water.

Acetyl derivative $C_6H_3Me_2NHAc$. [134°] (N. a. F.); [131°] (T.; W.). Slender needles.

i-o-**Xylidine** $C_6H_3Me_2(NH_2)$ [1:2:4]. [49°]. (226°). S.G. $^{17\cdot5}$ 1·0755. Prepared from *o*-xylene by nitration and reduction (Jacobsen, *B.* 17, 159). Got also by heating *m*-toluidine hydrochloride with MeOH at 300° (Limpach, *B.* 21, 643). Monoclinic crystals, not coloured by exposure to light and air. Gives no colour with bleaching powder. Its solutions colour pine-wood yellow. On nitration it yields (6,1,2,4)-nitro-xylidine [137°] and an isomeride [80°] (N. a. S.). Yields a saffranine on oxidation together with di-amido-di-phenyl-amine (Nietzki, *B.* 19, 3163).—Salt: B′HCl aq. Prisms, v. sol. water. Yields ψ-cumidine when heated with MeOH at 310° (N. a. F.).

Acetyl derivative $C_6H_3Me_2(NHAc)$. [99°].

c-m-**Xylidine** $C_6H_3Me_2(NH_2)$ [1:3:2]. (β)-*Xylidine* (214° i.V.) at 739 mm. (N. a. F.). S.G. ^{20} ·9942 (W.). Formed by distilling *p*-amido-mesitylenic acid with lime (Schmitz, *A.* 193, 179) and by reducing *c*-nitro-*m*-xylene (Grevingk, *B.* 17, 2430). Obtained from commercial xylidine by crystallisation of the sulphate; the last mother-liquor depositing crystals which are converted into the acetyl derivative by distillation with HOAc. The acetyl derivative is saponified by treatment with dilute (25 p.c.) H_2SO_4 (Nölting a. Pick, *B.* 21, 3150; *cf.* Wróblewsky, *B.* 12, 1226). Gives *m*-xyloquinone [73°] on oxidation (Nölting a. Forel, *B.* 18, 2676). Yields (4,1,3,2)-nitro-xylidine [82°] on nitration (Nölting a. Stoecklin, *Bl.* [3] 5, 381).—Salts: B′HCl.—B′HCl ½aq. S. 9·7 at 18°. Monoclinic plates. Yields mesidine on heating with MeOH at 310°.—$B'HNO_3$. S. 8·2. Needles.—$B'_2H_2SO_4$. Very soluble needles. —$B'H_2SO_4$ 2½aq. S. 60.

Acetyl derivative [174°] (G.); [176·5°] (N. a. F.). Needles.

Benzoyl derivative [140°]. Needles. Yields benzoyl-nitro-xylidine [178°] on nitration (Hübner, *A.* 208, 318).

***s-m*-Xylidine** $C_6H_3Me_2(NH_2)$ [1:3:5]. (222° i.V.). S.G. $\frac{15}{15}$ ·972. Formed by reduction of *s*-nitro-*m*-xylene [71°] (Thöl, *B.* 18, 362; Nölting a. Forel, *B.* 18, 2678). On oxidation by $K_2Cr_2O_7$ and H_2SO_4 it gives *m*-xyloquinone [73°]. By boiling the diazo-compound with water xylenol [68°] is formed. $ClCO_2Et$ forms $C_6H_3Me_2NH.CO_2Et$ [77·5°] (Frentzel, *C. C.* 1888, 1361).—B'HCl. MeOH at 250°–300° yields isocumidine $C_6H_2Me_3(NH_2)$ [5:4:3:1] (Limpach, *B.* 21, 643).—$B'H_2SO_4$aq.—$B'HNO_3$. S. 4·66 at 13°.

Acetyl derivative [140·5°] (N. a. F.); [138°] (T.); [144·5°] (W.). Colourless plates (from alcohol or ether).

***i-m*-Xylidine** $C_6H_3Me_2(NH_2)$ [1:3:4]. (*a*)-*Xylidine.* (215°) at 745 mm. (G.). S.G. $\frac{15}{15}$ ·9184 (H.). S.V. 148·3.

Formation.—1. By reducing *i*-nitro-*m*-xylene (Deumelandt, *A.* 144, 273; Tavildaroff, *B.* 2, 553; Wroblewsky, *A.* 192, 215; 207, 91; Grevingk, *B.* 17, 2430; Wallach, *A.* 258, 331). It may be isolated from commercial xylidine by conversion into hydrochloride and several crystallisations from water; the yield being about 40 p.c. (Nölting a. Forel, *B.* 18, 2677).—2. By heating *o*- and *p*-toluidine hydrochloride with MeOH at 300° (Hofmann, *B.* 9, 1295; Limpach, *B.* 21, 640).—3. By distilling (4,3,1,5)-amido-mesitylenic acid with lime (Schmitz, *A.* 193, 177).—4. By heating *i-m*-xylenol with ammonium-zinc bromide and NH_4Br (Müller, *B.* 20, 1039).

Reactions.—1. When dissolved in H_2SO_4 (10 pts.) it yields $C_6H_2Me_2(NH_2)(NO_2)$ [1:3:4:6] [123°] on nitration (Nölting a. Collin, *B.* 17, 265).—2. The hydrochloride heated with MeOH at 310° yields mesidine.—3. $ClCO_2Et$ forms $C_6H_3Me_2.NH.CO_2Et$ [57°] (Frentzel, *C. C.* 1888, 1361).—4. When mixed with di-amido-di-phenylamine it yields a saffranine on oxidation (Nietzki, *B.* 19, 3163).—5. When *m*-xylidine (4 pts.) is heated with S (1 pt.) at 190° it gives off H_2S and forms a base $C_{16}H_{16}N_2S$ [107°] (283° at 14 mm.) which crystallises from alcohol in yellowish-white prisms and yields $C_{16}H_{15}AcN_2S$ [227°] (Anschütz a. Schultz, *B.* 22, 582). By further heating with sulphur a homologue of primuline is formed.—6. *Œnanthol* forms oily $C_{15}H_{25}NO$ (Leeds, *B.* 16, 288).—7. *Acrolein* yields $C_{11}H_{13}N$, a reddish-yellow mass which on distillation yields cryptidine $C_{11}H_{11}N$ (270°) (Leeds, *A. C. J.* 5, 1).

Salts.—B'HCl. Monoclinic prisms.—B'HCl ½aq. Plates (Staedel a. Hölz, *B.* 18, 2919).—$B'_2H_2PtCl_6$.—B'HBr.—Trimetric plates.—$B'HNO_3$.—$B'_2H_2SO_4$ 4½aq. Cubes. Loses xylidine on evaporation of its solution (Nölting a. Pick, *Bl.* [2] 50, 606).—$B'H_3PO_4$. Only phosphate formed (Lewy, *B.* 19, 2728)—$B'H_2C_2O_4$. S. 3·32 at 18°.—B'_2ZnCl_2 (Lachovitch, *M.* 9, 514).—$B'HgH_2(SO_3)_2$aq.—$B'_2Cu_2H_2(SO_3)_2$ (Denigès, *C. R.* 112, 870).

Formyl derivative $C_6H_3Me_2NH.CHO$. [111°] (G.); [114°] (G. a. M.). Got by heating the base (12 g.) with formic acid (5 g.) at 150° (Gasiorowski a. Merz, *B.* 18, 1011; Gudemann, *B.* 21, 2549). Crystals (from water). Converted by P_2S_5 at 100° into the thioformyl derivative [105°].

Mono-acetyl derivative $C_6H_3Me_2(NHAc)$. [129°]. Needles or plates (from dilute alcohol). P_2S_5 forms the compound $C_6H_3Me_2NH.CSMe$ [95°] (Jacobsen a. Ney, *B.* 22, 907).

Di-acetyl derivative $C_6H_3Me_2NAc_2$. [60°]. Formed, together with the mono-acetyl derivative, by boiling the base with Ac_2O (Wallach, *A.* 258, 301).

Benzoyl derivative $C_6H_3Me_2NHBz$. [192°]. Needles (Hübner, *A.* 208, 318). Converted by HNO_3 into the nitro-benzoyl derivative [184°] which is reduced by tin and HOAc to $C_6H_2Me_2{<}\genfrac{}{}{0pt}{}{NH}{N}{>}CPh$ [195°].

Phthalyl derivative [158°]. Prisms (from alcohol).

***p*-Xylidine** $C_6H_3Me_2(NH_2)$ [1:4:2]. [15·5°] (Michael, *B.* 26, 39). (215° i.V.) at 739 mm. (N. a. F.); (213·5° uncor.) (M.); (220°) (S.). S.G. $\frac{15}{15}$ ·980. Obtained from *m*-xylene by nitration and reduction (Schaumann, *B.* 11, 1537; Nölting a. Forel, *B.* 18, 2664; 19, 2680). Occurs to the extent of about 25 p.c. in commercial xylidine, from which it may be isolated by dissolving in warm H_2SO_4 and pouring into hot water. The sparingly soluble *m*-xylidine sulphonic acid crystallises out, and the mother-liquor, after successive treatment with $CaCO_3$ and Na_2CO_3, yields on evaporation sparingly soluble, pearly plates of sodium *p*-xylidine sulphonate, which on distillation with lime give *p*-xylidine almost without loss. May also be got from crude xylidine by means of its benzylidine derivative.

Reactions.—1. Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to *p*-xyloquinone [123°], the yield being 70 p.c.—2. Converted by the diazo-reaction into *p*-xylenol [75°] (210°).—3. On heating with *sulphur* it yields $C_{16}H_{16}N_2S$ [144°], which crystallises from alcohol in yellowish needles, and yields an acetyl derivative [212°] (Anschütz a. Schultz, *B.* 22, 585).—4. The hydrochloride heated with MeOH at 290° under pressure forms ψ-cumidine (Limpach, *B.* 21, 646).—5. *Benzoic aldehyde* forms $C_6H_3Me_2.N{:}CHPh$ [102°] (Pflug, *A.* 255, 168). The same body [96°] is got by adding benzoic aldehyde to an alcoholic solution of thionyl-*p*-xylidine (Michaelis, *A.* 274, 237).

Salts.—B'HCl aq. Leaflets, subliming at 125°–130° in needles.—$B'HNO_3$. Needles.—$B'H_2SO_4$. Plates, sl. sol. water.—$B'_2H_2C_2O_4$.

Formyl derivative $C_9H_{11}NO$. [112°]. Needles (Pflug, *A.* 255, 168).

Acetyl derivative $C_6H_3Me_2NHAc$. [139°]. Prisms. Yields on nitration acetyl-nitro-*p*-xylidine [192°].

Bromo-acetyl derivative $C_6H_3Me_2.NH.CO.CH_2Br$. [145°]. Formed from bromo-acetyl bromide and *p*-xylidine in benzene (Abenius, *J. pr.* [2] 40, 435). Needles (from dilute alcohol). Boiling alcoholic potash converts it into an azine and the compound $C_6H_3Me_2NH.CO.CH_2.OEt$ [50°].

Oxalyl derivative $(C_6H_3Me_2NH)_2C_2O_2$. Formed by heating the oxalate at 130°. Needles, subliming at 125°. An oxalyl-xylidine [204°] was obtained by Genz (*B.* 3, 227) from crude, commercial xylidine.

Benzoyl derivative $C_6H_3Me_2NHBz$. [140°]. Needles.

References.—Bromo-, Chloro-, and Nitro-xylidine.

XYLIDINE SULPHONIC ACID *v.* Amido-xylene sulphonic acid and Bromo- and Nitro-xylidine sulphonic acids.

XYLIDINIC ACID *v.* Toluene dicarboxylic acid.

XYLINDEÏN. C, 65·5 p.c.; H, 4·7 p.c.; N, 1·0 p.c. A green colouring matter in green decayed wood (Rommier, *C. R.* 66, 108; Liebermann, *B.* 7, 1102). Extracted by phenol and ppd. by alcohol or ether. Four-sided blue plates, with coppery lustre. H_2SO_4 forms a green solution. Rideal (*C. N.* 53, 277) finds that the blue substance in decayed birch-wood is soluble in chloroform, while the blue resin obtained from coniferin by successive treatment with H_2SO_4 and water is insol. chloroform.

XYLITONE $C_{12}H_{18}O$. *Xylite oil.* (252°) (Pinner, *B.* 15, 580; 16, 1729); (c. 240°) (Claisen a. Ehrhardt, *B.* 22, 1013). S.G. ·935. A product of the action of HCl on acetone (P.). Formed also by the action of NaOEt on mesityl oxide in ether, and in the preparation of acetyl-acetone by the action of boiling EtOAc and NaOAc on acetone (C. a. E.). Oil, easily resinified by strong acids.

Dixylitone $C_{12}H_{20}O_2$. (310°–320°). A product of the action of HCl on acetone (Pinner).

XYLOHYDROQUINONE *v.* Hydroxyloquinone.

XYLOÏC ACID *v.* Di-methyl-benzoic acid.

XYLONIC ACID $C_5H_{10}O_6$. $[\alpha]_D = 17 \cdot 48°$. Formed by oxidising xylose with bromine (Tollens, *A.* 260, 367). Dextrorotatory. Its Ca, Zn, and Ag salts are amorphous.—SrA'_2. $[\alpha]_D = +12 \cdot 14°$.

XYLONITRILE *v.* *Nitrile* of Di-methyl-benzoic acid.

o-**XYLOQUINONE** $C_8H_8O_2$ *i.e.* $C_6H_2Me_2O_2$[1:2:3:6]. [55°]. Formed by oxidation of *c*-*o*-xylidine by $K_2Cr_2O_7$ and H_2SO_4, the yield being about 10 p.c. (Nölting a. Forel, *B.* 18, 2673). Yellow needles (by sublimation), v. sl. sol. water, m. sol. alcohol and ether.

m-**Xyloquinone** $C_6H_2Me_2O_2$ [1:3:2:5]. [73°]. Formed by oxidation either of *c*-*m*- or *s*-*m*-xylidine with $K_2Cr_2O_7$ and H_2SO_4 (Nölting a. Forel, *B.* 18, 2679). Got also by oxidation of mesidine (Nölting a. Baumann, *B.* 18, 1151). Yellow needles.

p-**Xyloquinone** $C_6H_2Me_2O_2$ [1:4:2:5]. *Phlorone. Metaphlorone.* Mol. w. 136. [124°].

Formation.—1. Occurs, together with toluquinone and other bodies, among the products of the action of MnO_2 and H_2SO_4 on coal-tar and beechwood-tar (Rommier a. Bouilhon, *C. R.* 55, 214; Gorup-Besanez a. von Rad, *Z.* [2] 4, 560; Carstanjen, *J. pr.* [2] 23, 425).—2. By oxidation of *p*-xylylene-diamine (Nietzki, *B.* 13, 472; *A.* 215, 168).—3. By oxidation of ψ-cumenol (Carstanjen, *J. pr.* [2] 23, 430).—4. By oxidation of ψ-cumidine by CrO_3 (Nölting a. Th. Baumann, *B.* 18, 1151; Sutkowski, *B.* 20, 977). 5. By distilling xylidine (213°) with H_2SO_4 and MnO_2; the yield being 5 p.c. (C.).—6. By oxidation of *p*-xylidine with $K_2Cr_2O_7$ and H_2SO_4, the yield being over 70 p.c. (Nölting, Witt, a. Forel, *B.* 18, 2667).—7. By heating diacetyl with dilute NaOHAq (Van Pechmann, *B.* 21, 1420).

Preparation.—1. Commercial xylene (130°–140°) is heated with H_2SO_4 at 100° for six days; the product poured into water; neutralised by $CaCO_3$; treated with K_2CO_3; and the K salts of the sulphonic acids fused with potash. The product is dissolved in water, acidified, and extracted with ether; and the mixture of xylenols so obtained is dissolved in warm H_2SO_4, and then diluted with water and distilled with MnO_2. Crystals of *p*-xyloquinone appear in the condenser and receiver (Carstanjen, *J. pr.* [2] 23, 427).—2. 'Yellow carbolic acid' or 'creosote,' the mother-liquor from which phenol has crystallised, is dissolved in H_2SO_4, diluted with water, and then distilled with MnO_2. The solid found in the receiver is crystallised from alcohol when the first crop of crystals is xyloquinone (E. Carstanjen, *J. pr.* [2] 23, 423).

Properties.—Long yellow needles (from benzene), sl. sol. water and cold alcohol, v. sol. ether. May be sublimed. Volatile with steam.

Reactions.—1. Distilled with *zinc-dust* gives a hydrocarbon that oxidises to terephthalic acid.—2. Reduced by aqueous SO_2 to hydroxyloquinone.—3. Conc. HCl converts it into a mixture of mono- and di-chloro-hydro-xyloquinones, $C_6HClMe_2(OH)_2$ [147°] and $C_6Cl_2Me_2(OH)_2$ [175°].

Mono-oxim $C_6H_2Me_2O(NOH)$. *Nitroso-p-xylenol.* [168°]. Formed by heating *p*-xyloquinone (2 pts.) with an alcoholic solution of hydroxylamine hydrochloride (1 pt.) (Goldschmidt a. Schmid, *B.* 18, 568; Sutkowski, *B.* 20, 978). Obtained also by adding KNO_2 and excess of HOAc to an alkaline solution of *p*-xylenol (Oliveri, *G.* 12, 162). Yellowish needles (from alcohol), v. sol. alcohol, ether, and benzene, insol. cold water. Alkalis form a deep orange-red solution. Reduced by $SnCl_2$ to amido-*p*-xylenol. Oxidised by alkaline K_3FeCy_6 to nitro-*p*-xylenol.

Di-oxim $C_6H_2Me_2(NOH)_2$. [272°]. Formed by boiling the quinone (1 mol.) with an alcoholic solution of hydroxylamine hydrochloride (2 mols.) (Sutkowski, *B.* 20, 977). V. sl. sol. alcohol, acetic acid, and benzene, insol. water. Dissolves in alkalis with a yellow colour. By tin and HCl it is reduced to xylylene-*p*-diamine. Its *di-acetyl derivative* $C_6H_2Me_2(NOAc)_2$ crystallises from acetic acid in small yellow prisms, [170°], v. sol. alcohol and benzene.

References.—Di-bromo- and Chloro-xyloquinone.

XYLORCIN *v.* Di-oxy-xylene.

XYLOSE *v.* p. 538.

XYLOSTEÏN. A glucoside in the berries of *Bonicera Xylosteum* (Hübschmann, *J.* 1856, 691; Enz, *C. C.* 1856, 393). Crystalline, insol. water, sol. alcohol and ether.

XYLOYL-BENZOIC ACID *v.* Phenyl xylyl ketone carboxylic acid.

XYLOYL-FORMIC ACID *v.* Xylyl-glyoxylic acid.

pp-**DIXYLYL** $C_{16}H_{18}$ *i.e.* [4:1:3] $C_6H_3Me_2.C_6H_3Me_2$ [3:4:1]. [125°]. Prepared by distilling mercury di-*p*-xylyl (Jacobsen, *B.* 14, 2112). Long needles (from alcohol).

Dixylyl. (290°–295°). Formed from bromo-*m* (?)-xylene and Na (Fittig, *A.* 147, 38). Liquid.

Di-xylyl (so-called). (295°) (Oliveri, *G.* 12, 158). Is got by warming *commercial* xylene with H_2SO_4, but never from xylene which has been made from xylene sulphonic acid. Hence it is probably not a benzene derivative (Armstrong, *C. J.* 45, 150). It is a colourless, fluorescent liquid, smelling like copaiba balsam.

XYLYL-ACETAMIDE *v. Acetyl derivative* of XYLIDINE and *Amide* of XYLYL-ACETIC ACID.

XYLYL-ACETIC ACID [1:3:4] $C_6H_3Me_2.CH_2.CO_2H$. [102°]. Formed from its amide, which is got by the action of yellow ammonium sulphide on xylyl methyl ketone (Willgerodt, *B.* 21, 534). Slender needles.

Amide $C_8H_9.CH_2.CO.NH_2$. [183°].

Reference.—OXY-XYLYL-ACETIC ACID.

XYLYL ALCOHOL is TOLYL-CARBINOL.

XYLYL-AMIDO-ACETIC ACID $C_{10}H_{13}NO_2$ *i.e.* [1:3:4] $C_6H_3Me_2.NH.CH_2.CO_2H$. [134°]. Formed by boiling *m*-xylidine (2 mols.) with water and chloro-acetic acid (1 mol.) (Ehrlich, *B.* 16, 205). Prisms (from dilute alcohol). Insol. water, v. sol. acids.

Xylide $C_8H_9.NH.CH_2.CO.NHC_8H_9$. [128°]. Formed by boiling xylidine (2 mols.) with chloro-acetic ether (1 mol.). Thick needles (from alcohol), insol. water and HClAq.

XYLYL-AMIDO-CROTONIC ETHER [1:3:4] $C_6H_3Me_2.NH.CMe:CH.CO_2Et$. Formed from *m*-xylidine and acetoacetic ether (Conrad a. Limpach, *B.* 21, 526). Decomposed on heating into (*Py.* 1, 3; *B.* 2, 4)-oxy-tri-methyl-quinoline, di-xylyl-urea, and alcohol.

XYLYL-AMIDO-ETHYL-PHTHALIMIDE [1:3:4] $C_6H_3Me_2.NH.C_2H_4.N:C_8H_4O_2$. [123°]. Formed by heating bromo-ethyl-phthalimide with *m*-xylidine at 140° (Newman, *B.* 21, 2197). Small needles, v. e. sol. benzene, sl. sol. cold alcohol.

DI-*m*-XYLYL-DI-AMIDO-DIAZTHIOLE $C_{18}H_{20}N_4S$ *i.e.* $S<\begin{matrix}C(NHC_8H_9):N\\C(NHC_8H_9):N\end{matrix}$. [79°]. Formed by oxidising (1,3,4)-xylyl-thio-urea with aqueous H_2O_2 (Hector, *B.* 23, 368). Insol. water. Forms a very soluble hydrochloride.—$B'_2H_2PtCl_6$. Decomposes at 214°–217°.—B'_2AgNO_3. Explodes on heating. Blackened by sunlight.—$B'C_6H_3N_3O_7$. [218°]. Yellow crystals, v. sol. alcohol. Cyanogen passed into its alcoholic solution forms $C_{18}H_{20}N_4SCy_2$ [103°].

Acetyl derivative $C_{18}H_{19}AcN_4S$. Needles.

Benzoyl derivative $C_{18}H_{19}BzN_4S$. [212°].

Nitrosamine $C_{18}H_{19}(NO)N_4S$. [146°].

XYLYLAMINE *v.* XYLIDINE and METHYL-BENZYL-AMINE.

Di-*o*-xylyl-amine $(C_8H_9)_2NH$. (330°–345°). Formed, together with xylidine, by heating (1,2,4)-xylenol with ammonio-zinc bromide and NH_4Br at 300° (Müller, *B.* 20, 1039). Liquid, solidified at a very low temperature.

Di-*m*-xylyl-amine. (305°–310°). Formed in like manner from *m*-xylidine. Oil.

Di-xylyl-amine. [162°]. Formed, together with a liquid isomeride, by heating xylidine with its hydrochloride (Girard a. Vogt).

XYLYL-BENZYL-AMINE $C_{15}H_{17}N$ *i.e.* $C_6H_3Me_2.NH.CH_2Ph$. (c. 205° at 15 mm.). Formed by heating *m*-xylidine with benzyl chloride at 160° (Joblin-Goffinet, *Bl.* [3] 6, 21). Yellowish oil, sol. alcohol and benzene.

***p*-Xylyl-benzyl-amine** [1:4:2]$C_6H_3Me_2.NH.CH_2Ph$. (322°) (Pflug, *A.* 255, 168).

***o*-XYLYL BENZYL KETONE** $C_{16}H_{16}O$ *i.e.* $C_6H_3Me_2.CO.CH_2Ph$. [95°]. (210°–220° at 25 mm.). Formed from *o*-xylene, phenyl-acetic chloride, and $AlCl_3$ (Wege, *B.* 24, 3540). Plates, sol. alcohol, v. sol. ether. Yields a crystalline oxim. NaOEt and benzyl chloride yield $C_6H_3Me_2.CO.CH(CH_2Ph)Ph$ [75°].

***m*-Xylyl benzyl ketone** [1:3:4] $C_6H_3Me_2.CO.CH_2Ph$. (350°). Formed, together with a smaller quantity of an isomeride [93°], by the action of $AlCl_3$ on a mixture of *m*-xylene and phenyl-acetic chloride (Söllscher, *B.* 15, 1681). Yields $C_6H_3Me(CO_2H)_2$ [3:4:1] on oxidation. NaOEt and benzyl chloride form oily $C_8H_9.CO.CHPh.CH_2Ph$ (365°–375°).

***p*-Xylyl benzyl ketone** $C_8H_9.CO.CH_2Ph$. (220°–230° at 26 mm.). Formed in like manner from *p*-xylene (Wege). Yields an oxim [99°] and a phenyl-hydrazide [96°]. NaOEt and benzyl chloride yield $C_8H_9.CO.CHPh.CH_2Ph$ [60·5°].

***m*-XYLYL-BENZYL-THIO-UREA** $C_8H_9NH.CS.NHCH_2Ph$. [85°]. Formed from benzyl-thiocarbimide and *m*-xylidine in alcohol (Dixon, *C. J.* 59, 558). Monoclinic prisms, v. sol. boiling alcohol and chloroform.

XYLYL BROMIDE *v.* BROMO-XYLENE.

XYLYL-*tert*-BUTANE $C_6H_3Me_2.CMe_3$. (201°). Formed from *m*-xylene, isobutyl bromide, and $AlCl_3$ (Baur, *B.* 24, 2840). Got also from isobutyl alcohol, *m*-xylene, and H_2SO_4 or $ZnCl_2$ (Nölting, *B.* 25, 791). Oil, yields mesitylenic and trimesic acids on oxidation.

XYLYL-BUTYL ALCOHOL [2:4:1] $C_6H_3Me_2.CHPr.OH$. (above 270°). Got by reducing xylyl propyl ketone with zinc-dust and KOHAq, or with sodium-amalgam (Claus, *J. pr.* [2] 46, 474). Oil, v. sol. alcohol and ether.

Tri-xylyl-butyl alcohol $(C_8H_9)_3C.CMe_2.OH$. (above 300°). Formed from -xylene, tri-chloro-*tert*-butyl alcohol, and $AlCl_3$ (Willgerodt a. Genieser, *J. pr.* [2] 37, 361). Oil, smelling like mushrooms.

***m*-XYLYL-*n*-BUTYRIC ACID** [1:3:4]$C_6H_3Me_2.CH_2.CH_2.CH_2.CO_2H$. [70°]. Formed by saponifying the amide (Claus, *J. pr.* [2] 46, 476). Needles, v. sol. hot water. May be sublimed.—BaA'_2 4aq.—CaA'_2 4aq. Prisms, v. sol. water and alcohol.

Amide $C_6H_3Me_2.C_3H_6.CO.NH_2$. [124°]. Got by heating xylyl propyl ketone with S and ammonium sulphide in sealed tubes at 250°. Flat silky needles. May be sublimed.

***p*-Xylyl-*n*-butyric acid** [1:4:2]$C_6H_3Me_2.CH_2.CH_2.CH_2.CO_2H$. [70°]. Needles, sl. sol. cold water.—BaA'_2 4aq.—CaA'_2 4aq. Needles, sol. water and alcohol.

Amide $C_8H_9.C_3H_6.CO.NH_2$. [125°]. Formed from *p*-xylyl propyl ketone (C.). Flat needles, v. sol. hot water.

***m*-Xylyl-isobutyric acid** [1:3:4] $C_6H_3Me_2.CH_2.CHMe.CO_2H$. [70°]. Flat pearly needles, sol. hot water, alcohol, and ether. May be sublimed.

Amide $C_8H_9.C_3H_6.CO.NH_2$. [120°]. Got by heating xylyl isopropyl ketone with S and ammonium sulphide at 235° (Claus, *J. pr.* [2] 46, 483). Needles, sol. hot water.

XYLYL-CARBAMIC ACID [1:3:4] $C_6H_3Me_2.NH.CO_2H$. *Ethyl ether* EtA′. [58°]. Formed from *m*-xylidine and chloroformic ether (Hofmann, *B.* 3, 657; Frentzel, *C. C.* 1888, 1361). Needles.

Xylyl-carbamic acid [1:3:5] $C_6H_3Me_2.NH.CO_2H$. *Ethyl ether* EtA′. [77·5°] (Frentzel).

DI-*p*-XYLYL-CARBINOL ([2:5:1] $C_6H_3Me_2)_2CH.OH$. [131°]. Formed by reducing di-*p*-xylyl ketone with zinc-dust and KOH (Elbs, *J. pr.* [2] 35, 484; *B.* 19, 408). White needles (from alcohol), nearly insol. Aq.

XYLYL CYANATE [1:3:4] $C_6H_3Me_2.N:CO$. (205°) (Frentzel, *C. C.* 1888, 1361).

Xylyl cyanate [1:3:5] $C_6H_3Me_2.N:CO$. (208·5°).

XYLYL CYANURATE [1:3:4] $(C_6H_3Me_2)_3N_3C_3O_3$. [162°] (Frentzel, *C. C.* 1888, 1861).

XYLYLENE ALCOHOL *v.* Di-oxy-xylene.

XYLYLENE-DI-ALLYL-DI-THIO-DI-UREA $(CH_3)_2C_6H_2(NH.CS.NH.C_3H_5)_2$ [1:4:2:6]. [112·5°]. Made from *p*-xylylene diamine and allyl thiocarbimide (Lellmann, *A.* 228, 252). Needles (from alcohol). Not decomposed on melting.

***m*-XYLYLENE-*m*-DIAMINE** $C_6H_2(CH_3)_2(NH_2)_2$ [1:3:4:6]. *m-Di-amido-m-xylene* [105°]. Formed by reduction of nitro-xylidine [123°] or of di-nitro-xylene [93°] (Fittig, *A.* 147, 18; Grevingk, *B.* 17, 2426; Witt, *B.* 21, 2419). White crystals. Sublimable. Does not yield a eurhodine on boiling with nitroso-dimethyl-aniline, NaOAc, and HOAc. — B″2HCl. — $B''H_2SnCl_4$.—$B''H_2SO_4$. Crystalline, v. sol. Aq.

***m*-Xylylene-*o*-diamine** $C_6H_2Me_2(NH_2)_2$ [1:3:5:6] [78·5°]. Formed by reduction of [2:4:1] $C_6H_3Me_2.N_2.C_6H_2Me_2.NH_2$ [1:3:5:6] (Nölting a. Forel, *B.* 18, 2683) and also by the action of tin and HClAq on di-bromo-di-nitro-*m*-xylene [191°] (Jacobsen, *B.* 21, 2821), and on (5,1,3,6)-nitro-xylidine (Hofmann, *B.* 9, 1298). Plates (from water), sl. sol. cold benzene, sol. ether.

***m*-Xylylene-*m*-diamine** $C_6H_2Me_2(NH_2)_2$ [1:3:4:2]. [64°]. Formed by reduction of nitro-xylidine [78°] or of di-nitro-*m*-xylene [82°] (Grevingk, *B.* 17, 2426). White needles. Gives a Bismarck brown with nitrous acid and a chrysoïdine with diazobenzene.

***p*-Xylylene-*o*-diamine** $C_6H_2Me_2(NH_2)_2$ [1:4:2:3]. [75°]. Formed by reduction of *c*-di-nitro-*p*-xylene (Lellmann, *A.* 228, 251; Nölting, *B.* 19, 145). White needles (by sublimation). Gives a deep-red colour with $FeCl_3$.

***p*-Xylylene-*m*-diamine** $C_6H_2Me_2(NH_2)_2$ [1:4:2:6]. [102°]. Formed by reducing (2,6,1,4)-di-nitro-xylene (L.; N.). Needles (by sublimation). Behaves like a *m*-diamine.

***p*-Xylylene-*p*-diamine** $C_6H_2Me_2(NH_2)_2$ [1:4:2:5]. [142°] (S.); [147°] (N. a. F.); [150°] (N.). *Formation.*—1. By reduction of xylene-azoxylidine (amido-azo-xylene) [2:5:1] $C_6H_3Me_2.N_2.C_6H_2Me_2.NH_2$ [1:2:5:4] by zinc and HClAq (Nietzki, *B.* 13, 471; Nölting a. Forel, *B.* 18, 2685).—2. By reduction of nitro-*p*-xylidine [142°] (Nölting, Witt, a. Forel, *B.* 18, 2666; von Kostanecki, *B.* 19, 2318; Marckwald, *B.* 23, 1021).—3. By reduction of the di-oxim of *p*-xyloquinone $C_6H_2Me_2(NOH)_2$ with tin and HCl (Sutkowski, *B.* 20, 979).

Properties.— Colourless needles, sol. hot water and alcohol, m. sol. benzene and ether. Yields xyloquinone [123°] on oxidation. Not oxidised by exposure to air. May be sublimed.

Salts.—B″2HCl. Colourless leaflets. — $B''H_2SO_4$. Crystalline meal.

***o*-Xylylene *exo*-diamine** [1:2] $C_6H_4(CH_2.NH_2)_2$. Formed by heating the phthalimide $C_6H_4(CH_2.N:C_2O_2:C_6H_4)_2$ with conc. HClAq at 200° (Strassmann, *B.* 21, 579). Alkaline liquid, smelling strongly like ammonia. Absorbs CO_2. Gives with $FeCl_3$ a pp. of yellowish-red needles.—B″2HCl.—$B''2HAuCl_4$. Yellow plates.—$B''2C_6H_3N_3O_7$. Yellow needles, decomposing above 170° without melting.

Acetyl derivative $C_8H_{10}Ac_2N_2$. [146°].

Benzoyl derivative $C_8H_{10}Bz_2N_2$. [168°].

***m*-Xylylene-*exo*-diamine** [1:3] $C_6H_4(CH_2.NH_2)_2$. (247°). Formed by the action of conc. hydrochloric acid at 220° on the $C_6H_4(CH_2.N:C_8H_4O_2)_2$ [237°], which is got by heating potassium phthalimide with di-ω-bromo-*m*-xylene (Brömme, *B.* 21, 2705). Liquid, sol. water, miscible with alcohol and ether. Absorbs CO_2. — B″2HCl. Needles (from water). — $B''2H_2PtCl_6$.—$B''C_6H_3N_3O_7$. Yellow spangles, decomposing at 187°.

Acetyl derivative $C_6H_4(CH_2.NHAc)_2$. [119°]. Crystalline mass, v. sol. hot water.

Reference.—Nitro-xylylene-diamine.

XYLYLENE-BENZENYL-AMIDINE *v.* Benzenyl-xylylene-diamine.

XYLYLENE BROMIDE *v.* Di-bromo-xylene.

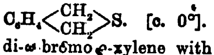
XYLYLENE-CHLORO-MALONIC ETHER *v.* Chloro-xylylene-malonic ether.

Xylylene-*exo*-di-chloro-malonic ether *v.* Di-chloro-phenylene-di-methyl-di-malonic ether.

XYLYLENE-ETHENYL-AMIDINE $C_{10}H_{12}N_2$ *i.e.* $CMe\left<{NH \atop N}\right>C_6H_2Me_2$. Formed by reducing $C_6H_2Me_2(NO_2)(NHAc)$ [1:3:5:4] with tin and HCl (Hobrecker, *B.* 5, 922). Resinous mass.—B′HCl. Large needles.—$B'_2H_2PtCl_6$.—$B'HNO_3$ Long needles.

XYLYLENE IODIDE *v.* Di-iodo-xylene.

XYLYLENE-DI-MALONIC ACID *v.* Phenylene-di-methyl-di-malonic acid.

***o*-XYLYLENE SULPHIDE** C_8H_8S *i.e.*  $C_6H_4\left<{CH_2 \atop CH_2}\right>S$. [c. 0°]. Formed by heating di-ω-bromo-*o*-xylene with K_2S (Leser, *B.* 17, 1824; Hjelt, *B.* 22, 2904). Oil, smelling like mercaptan. Very unstable, quickly turning into a black resin.—B'_2HgCl_2. Long needles.

Methylo-iodide B′MeI. [155°].

Di-xylylene disulphide [1:3:4:5] $C_6H_2Me_2:S_2:C_6H_2Me_2$ [5:4:3:1]. [118°]. Formed by heating xylylene-diazosulphide at 200°–250° (Jacobsen a. Ney, *B.* 22, 911). Conc. H_2SO_4 forms a blue liquid, remaining blue on dilution.

***u*-DI-XYLYL-ETHANE** $C_{18}H_{22}$ *i.e.* $CH_3.CH(C_8H_9)_2$. (314°). S.G. $\frac{20}{4}$ ·966. Formed from ethylidene chloride, *m*-xylene, and $AlCl_3$ (Anschütz, *B.* 18, 665; *A.* 235, 326). Oil.

Reference.—Chloro-di-xylyl-ethane.

DI-XYLYL-ETHYLENE $C_{18}H_{20}$ *i.e.* $C_6H_3Me_2.CH:CH.C_6H_3Me_2$. *Tetra-methyl-stilbene.* [106°]. (325°–340°). Formed by distilling

$C_6H_3Me_2.CH_2.CH_2Cl$, which is got from di-chloro-di-ethyl oxide, *m*-xylene, and H_2SO_4 (Hepp, *B.* 7, 1416). Spangles (from alcohol), sol. ether and CS_2. Unites with bromine. Oxidised by dilute HNO_3 to (1,3,4)-di-methyl-benzoic acid [122°].

Di-xylyl-ethylene $C_6H_3Me_2.CH{:}CH.C_6H_3Me_2$. [157°]. Formed in like manner from *p*-xylene. Plates (from alcohol). Less soluble than the preceding isomeride.

Tetra-xylyl-ethylene $(C_6H_3Me_2)_2C{:}C(C_6H_3Me_2)_2$. [245°]. Formed from xylene, $CHCl_3$, and $AlCl_3$ (Schwarz, *B.* 14, 1528). Yellow plates.

***m*-XYLYL-ETHYLENE-DIAMINE** $C_6H_3Me_2NH.C_2H_4.NH_2$. (274°). Formed from *m*-xylyl-amido-ethyl-phthalimide and HCl (Newman, *B.* 24, 2197).—B'HCl. [173°].—$B'_2H_2PtCl_6$.—$B'C_6H_3N_3O_7$. [141°]. Reddish-yellow needles, v. e. sol. alcohol.

DI-*m*-XYLYL-ETHYLENE DIKETONE $C_2H_4(CO.C_6H_3Me_2\,[4{:}3{:}1])_2$. [129°]. Formed from *m*-xylene, succinyl chloride, $AlCl_3$ and CS_2 (Claus, *B.* 20, 1375). Needles, insol. water, v. sol. alcohol and ether. Dilute HNO_3 oxidises it to (1,3,4)-di-methyl-benzoic acid.

Oxim $C_2H_4(C(NOH).C_8H_9)_2$. [140°].

Phenyl-hydrazide $C_2H_4(C(N_2HPh).C_8H_9)_2$. [189°]. Crystals.

Di-*p*-xylyl ethylene diketone $C_2H_4(CO.C_6H_3Me_2\,[2{:}4{:}1])_2$. [123°]. Formed from *p*-xylene, succinyl chloride, $AlCl_3$, and CS_2 (Claus). Needles.

***m*-XYLYL ETHYL KETONE** [1:3:4] $C_6H_3Me_2.CO.C_2H_5$. (239°). Light oil, with aromatic odour, not solid at −10° (Claus, *J. pr.* [2] 43, 140). Yields (1,3,4)-di-methyl-benzoic acid on oxidation.

Phenyl-hydrazide [126°]. Plates, v. sol. hot water, alcohol, and ether.

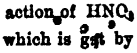
***p*-Xylyl ethyl ketone** [4:1:2] $C_6H_3Me_2.CO.C_2H_5$. (238° uncor.). Formed from *p*-xylene, $AlCl_3$, and propionyl chloride (Claus a. Fickert, *B.* 19, 3182). Oil. Oxidised by $KMnO_4$ to $C_6H_3Me_2.CO.CH_2.CO_2H$ [132°] and some (4,1,2)-di-methyl-benzoic acid.

***m*-XYLYL ETHYL KETONE CARBOXYLIC ACID** [4:2:1] $C_6H_3Me_2.CO.CH_2.CH_2.CO_2H$.

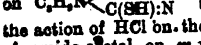
Di-methyl-benzoyl-propionic acid. [108°]. Formed from *m*-xylene, succinyl chloride, $AlCl_3$, and CS_2 (Claus, *B.* 20, 1376). Needles, v. sol. hot water, insol. cold.—NH_4A'.—KA' 4aq. V. sol. water.—NaA' 4aq. Needles.—BaA'_2 3aq. Needles.—PbA'_2: white pp.—AgA': white crystalline pp.

***p*-Xylyl ethyl ketone carboxylic acid** [4:1:2] $C_6H_3Me_2.CO.CH_2.CH_2.CO_2H$. [84°]. Formed from *p*-xylene in like manner (C.). Colourless needles.

XYLYL-DI-ETHYL-PHOSPHINE $C_6H_3Me_2.PEt_2$. (260°). Formed by the action of $ZnEt_2$ on $C_6H_3Me_2.PCl_2$ (Czimatis, *B.* 15, 2016). Thick, colourless oil. Yields B'MeI [90°], $B'_2Me_2PtCl_6$ [202°], and B'EtI [136°].



$C_8H_9N\left<\begin{array}{l}CH{:}CH\\CH{:}N\end{array}\right.$



$C_8H_9N\left<\begin{array}{l}CH=CH\\C(SH){:}N\end{array}\right.$

***m*-XYLYL-GLYOXALINE** $C_8H_9N\left<\begin{array}{l}CH{:}CH\\CH{:}N\end{array}\right.$ [82°]. (279°). Formed by the action of HNO_3 on $C_8H_9N\left<\begin{array}{l}CH=CH\\C(SH){:}N\end{array}\right.$ [192°], which is got by the action of HCl on the product of the action of amido-acetal on *m*-xylyl-thio-urea (Marckwald, *B.* 25, 2368). Sl. sol. water.—*Aurochloride* [165°].—*Picrate.* [159°]. Yellow needles, m. sol. chloroform.

***o*-XYLYL-GLYOXYLIC ACID** [4:3:1] $C_6H_3Me_2.CO.CO_2H$. [92°]. Formed by oxidising *o*-xylyl methyl ketone with alkaline K_3FeCy_6 (Buchka a. Irish, *B.* 20, 1766).—BaA'_2.

***m*-Xylyl-glyoxylic acid** [4:2:1] $C_6H_3Me_2.CO.CO_2H$. [54°]. Formed by oxidising *m*-xylyl methyl ketone with $KMnO_4$ (Claus, *B.* 19, 231; *J. pr.* [2] 43, 142). Flat prisms. Yields (4,2,1) di-methyl-benzoic acid on boiling with dilute HNO_3. Gives rise to $C_8H_9.CH(OH).CO_2H$ [119°] on reduction.—CaA'_2 2aq. Needles.—BaA'_2 2aq.—AgA'. Needles, sol. hot water.

***p*-Xylyl-glyoxylic acid** [5:2:1] $C_6H_3Me_2.CO.CO_2H$. [70°–80°]. Formed by oxidation of *p*-xylyl methyl ketone by aqueous $KMnO_4$ (Claus a. Wollner, *B.* 18, 1859). Crystalline, v. sol. alcohol, ether, and HOAc, v. sl. sol. water. Splits up above 200° into CO_2 and di-methyl-benzoic aldehyde. Oxidised by HNO_3 to $C_6H_3Me_2.CO_2H$. Ac_2O and NaOAc yield di-methyl-cinnamic acid.—BaA'_2 6aq: small felted needles.—CaA'_2 3aq.—AgA': crystalline pp.

Ethyl ether EtA'. Oil.

XYLYL GLYOXYLIC ALDEHYDE [1:3:4] $C_6H_3Me_2.CO.CHO$. *Oxim* [95°]. Formed from xylyl methyl ketone, NaOEt, and $C_5H_{11}NO_2$ (Söderbaum, *B.* 25, 3463). Needles (from benzene-ligroïn). Acetic anhydride gives the acetyl derivatives of the *syn*-oxim $C_8H_9.CO.CH{:}NOAc$ [54°] decomposed by alkalis with formation of $C_6H_3Me_2.CO_2H$ [126°] and by hot Ac_2O yielding $C_6H_3Me_2.CO.CN$ [47°]. AcCl converts the oxim into $C_6H_3Me_2.C(OH)_2.CH{:}NOAc$ [142°], whence cold NaOH forms $C_6H_3Me_2.CH(OH).CO_2H$ [103°], while NaOHAq at 50° forms 'xylyl formoin' $C_8H_9.CO.CH(OH).CO.CO.C_8H_9$ [155°].

DI-XYLYL-GUANIDINE $HN{:}C(NH.C_8H_9\,[1{:}2{:}4])_2$. [158°]. Formed by the action of PbO and alcoholic ammonia on di-xylyl-thio-urea (Hofmann, *B.* 9, 1295). Needles, (from alcohol).

XYLYL-HYDRAZINE [4:2:1] $C_6H_3Me_2NH.NH_2$. [85°]. Formed from xylidine by diazotisation followed by reduction with Na_2SO_3, the resulting $C_8H_9.N_2H_2.SO_3Na$ ½aq being then treated with zinc-dust and HOAc (Klauber, *M.* 11, 282). Pale-yellow needles, v. sl. sol. water, v. sol. alcohol. Reduces Fehling's solution on warming. On heating with aceto-acetic ether it yields a crystalline body [203°] reduced in alcoholic solution by Na to oxy-xylyl-methyl-pyrazole.

Salt.—C'HCl 2aq. [183°]. Small needles.

Di-*o*-xylyl-hydrazine [3:2:1] $C_6H_3Me_2NH.NHC_6H_3Me_2$ [1:2:3]. [141°]. *c-Hydrazo-o-xylene.* Got by heating nitro-*o*-xylene (20 g.) with NaOH (20 g.), alcohol (100 c.c.) and zinc-dust (25 g.), and reducing the product with alcoholic ammonium sulphide (Nölting a. Stricker, *Bl.* [2] 50, 613). White needles, sol. alcohol and ether. Easily oxidised by air.

***u*-Di-*o*-xylyl-hydrazine** $N_2H_2(C_6H_3Me_2[1{:}3{:}4])_2$. [107°]. Formed by reducing nitro-*o*-xylene with sodium-amalgam (N. a. S.). Yellowish white needles, sol. alcohol.

Di-*m*-xylyl-hydrazine $N_2H_2(C_6H_3Me_2[1:3:5])_2$. [125°]. Obtained from *s*-nitro-*m*-xylene (N. a. S.). Needles, easily oxidised by air.

***u*-Di-*m*-xylyl-hydrazine** $N_2H_2(C_6H_3Me_2[1:2:4])_2$. [122°]. Got by warming nitro-*m*-xylene (30 g.) with NaOH (30 g.), zinc-dust (40 g.), and alcohol (250 c.c.) and treating the xylene-azo-xylene so obtained with alcoholic ammonia and H_2S (N. a. S.). White needles, sol. alcohol and ether.

Di-*p*-xylyl-hydrazine $N_2H_2(C_6N_3Me_2[1:2:5])_2$. [145°]. Formed from nitro-*p*-xylene (N. a. S.). Needles, not affected by air.

XYLYLIC ACID *v.* Di-methyl-benzoic acid.

α-Xylylic acid *v.* Tolyl-acetic acid.

***p*-XYLYLIDENE-DI-IMINE** $C_6H_4(CH:NH)_2$ [1:4]. Formed by the action of alcoholic NH_3 or dry NH_3 gas upon terephthalic aldehyde (Oppenheimer, *B.* 19, 576). Glassy brittle crystals. V. sl. sol. alcohol and ether.

DI-XYLYL-KETONE $CO(C_6H_3Me_2)_2$. (c. 340°). Obtained from (*m*?)-xylene, $COCl_2$, and $AlCl_3$ (Ador a. Rilliet, *B.* 11, 399). Liquid, not solid at −60°. Split up by long boiling into H_2O and $C_{17}H_{16}$.

Di-*p*-xylyl ketone [2:5:1] $C_6H_3Me_2.CO.C_6H_3Me_2$ [1:2:5]. (327° uncor.). Formed from *p*-xylene, CS_2, and $COCl_2$ in closed vessels; the yield being 55 p.c. (Elbs, *J. pr.* [2] 35, 481). Oil. Quickly decomposed by distillation into H_2O and (*B.* 2, 1′,4′)-tri-methyl-anthracene [227°]. Reduced by zinc-dust and alcoholic KOH to di-*p*-xylyl-carbinol [131°].

Di-xylyl-tetraketone $C_8H_9.CO.CO.CO.CO.C_6H_3Me_2$ [4:3:1]. [180°]. Formed by the action of cold HNO_3 (S.G. 1·4) on $C_8H_9.CO.CH(OH).CO.CO.C_8H_9$ (Söderbaum, *B.* 25, 3475). Scarlet needles (from CS_2). On dissolving in HOAc and ppg. by water it yields a dihydrate [100°] $C_{20}H_{22}O_6$.

XYLYL MERCAPTAN $C_6H_3Me_2.SH$. (214°). S.G. ^{15} 1·036. Got by treating xylene sulphonic chloride with Zn and dilute H_2SO_4 (Yssell, *Z.* 1865, 360), and also by heating xylyl ethyl xanthate with alcoholic potash (Leuckart, *J. pr.* [2] 41, 192). Liquid. — $Hg(S.C_8H_9)_2$. — $Pb(S.C_8H_9)_2$. Yellow powder.

TRI-*p*-XYLYL-METHANE $CH\{C_6H_3Me_2\}_3$. [188°]. (above 360°). From di-*p*-xylyl-carbinol, *p*-xylene, and P_2O_5 by boiling for four hours (Elbs, *J. pr.* [2] 35, 484). Crystalline grains (from alcohol), v. sol. ether and benzene.

***o*-XYLYL METHYL KETONE** [4:3:1] $C_6H_3Me_2.CO.CH_3$. (246°). Formed from *o*-xylene, AcCl, and $AlCl_3$ (Claus, *B.* 18, 1856; 19, 232; *J. pr.* 1890, 410). Oil, smelling like coumarin (Armstrong a. Kipping, *C. J.* 63, 81). Yields (4,3,1)-di-methyl-benzoic acid on oxidation. Conc. HClAq forms $C_{20}H_{22}O$ [114°]. P_2O_5 gives a body melting at 165°. Zinc-dust reduces the ketone to $C_8H_9.CH(OH).CH_3$ (257°).

Oxim $C_8H_9.C(NOH).CH_3$. [85°]. Prisms (from dilute alcohol), converted by AcCl into $C_8H_9.C(NOAc).CH_3$ [72°].

Phenyl-hydrazide. Colourless prisms.

***m*-Xylyl methyl ketone** [4:2:1] $C_6H_3Me_2.CO.CH_3$. (228°). Formed from *m*-xylene, AcCl, and $AlCl_3$ (Claus, *B.* 19, 230). Obtained also by boiling *m*-xylene with HOA $ZnCl_2$, and $POCl_3$ (Frey, *J. pr.* [2] 43, 120). Oi smelling like peppermint. Not condensed b HClAq. Yields $C_{10}H_9Br_3O$ [69°]. Reduction b HI yields $C_6H_3Me_2.CH_2.CH_3$ (184°) (Claus, *J. p* [2] 45, 830). HNO_3 gives $C_{20}H_{18}N_2O_4$ [108 (Claus, *J. pr.* [2] 41, 492).

***p*-Xylyl methyl ketone** [5:2:1] $C_6H_3Me_2.CO.CH_3$. (225° uncor.). S.G ^{15} ·9962. V.D. 4·93. Formed from *p*-xylen AcCl, and $AlCl_3$ (Claus a. Wollner, *B.* 18, 1856 Oil, v. sol. alcohol and ether. Oxidised by sol aqueous $KMnO_4$ to *p*-xylyl-glyoxylic acid. Dilut HNO_3 forms di-methyl-benzoic and methyl phthalic acids.

Oxim $C_8H_9.C(NOH).CH_3$. [58°].

XYLYL METHYL KETONE CARBOXYLI ACID *v.* Methyl-benzoyl-acetic acid.

XYLYL-DI-METHYL-PHOSPHINE $C_6H_3Me_2.PMe_2$. (230°). Formed from ZnMe and $C_6H_3Me_2.PCl_2$ (Czimatis, *B.* 15, 2016). Oil. Unites with CS_2, forming a compound [115°].

XYLYL-METHYL-THIOHYDANTOÏN

[1:3:4] $C_6H_3Me_2.N\left<\begin{matrix}CO.CH_2\\CS.NH\end{matrix}\right.$. [165°]. Formed from xylyl-thiocarbimide and alanine (Marckwald, *B.* 24, 3282). Needles, v. sol. alcohol.

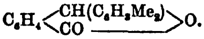
XYLYL PENTADECYL KETONE $C_6H_3Me_2.CO.C_{15}H_{31}$. [37°]. (269° at 15 mm.). Formed from *m*-xylene, palmityl chloride, and $AlCl_3$ (Krafft, *B.* 21, 2269). Small plates, yielding di-methyl-benzoic acid [126°] on oxidation.

XYLYL PHENYLAMYL KETONE $C_6H_3Me_2.CO.CHPh.C_4H_9$. [91·5°]. Formed by Friedel and Craft's method (Wege, *B.* 24, 3541).

XYLYL-PHENYL- *v.* Phenyl-xylyl-.

TRI-XYLYL PHOSPHATE $PO(OC_6H_3Me_2)_3$. The *o*- and *p*- compounds are formed by heating *o*- and *p*-xylenol with $POCl_3$ (Kreysler, *B.* 18, 1702). They are oils, v. sol. ether, alcohol, and benzene.

***m*-XYLYL-PHTHALIDE**



$C_6H_4\left<\begin{matrix}CH(C_6H_3Me_2)\\CO\end{matrix}\right>O$. [84°]. Got by heating $C_6H_3Me_2.CO.C_6H_4.CO_2H$ with zinc and HCl (Gresly, *A.* 234, 237). Needles (from alcohol), sl. sol. benzene.

XYLYL-PROPIONIC ACID [1:3:4] $C_6H_3Me_2.CH_2.CH_2.CO_2H$. [105°]. Formed by saponifying the amide. Silky needles, v. sol. hot water.—BaA'_2 6aq. Plates, m. sol. water.—CaA'_2 4aq.—AgA'. White powder.

Amide $C_6H_3Me_2.C_2H_4.CO.NH_2$. [107°]. Got by heating the oxim of *m*-xylyl ethyl ketone with yellow ammonium sulphide under pressure (Claus, *J. pr.* [2] 46, 477). Needles, sol. hot water.

***m*-XYLYL PROPYL KETONE** $C_{12}H_{16}O$ i.e. [4:2:1] $C_6H_3Me_2.CO.Pr$. (251°). Formed from *m*-xylene, butyryl chloride and $AlCl_3$ (Claus, (*J. pr.* [2] 46, 474). Oil, v. sol. alcohol and ether. Yields *m*-xylyl-glyoxylic acid [54°] on oxidation with $KMnO_4$.

Oxim. Crystals, v. e. sol. alcohol.

***p*-Xylyl propyl ketone** [5:2:1] $C_6H_3Me_2.CO.Pr$. (249°). Formed in like manner from *p*-xylene. Light oil.

Oxim [47°]. Colourless needles.

***o*-Xylyl isopropyl ketone** [4:3:1] $C_6H_3Me_2.CO.Pr$. (258°). Oil, smelling like turpentine (Claus, *J. pr.* [2] 46, 484). Yields di-methyl-benzoic acid [163°] on oxidation.

Oxim [68°]. Large prisms.

***m*-Xylyl isopropyl ketone** [4:2:1] $C_6H_3Me_2.CO.Pr$. (245°). Oil, yielding *m*-xylyl-glyoxylic acid on oxidation by $KMnO_4$.

Oxim [97°]. Prisms (from alcohol).

Phenyl-hydrazide [129°]. Crystals.

***p*-Xylyl isopropyl ketone** [5:2:1] $C_6H_3Me_2.CO.Pr$. (240°). Formed from *p*-xylene, isobutyryl chloride, and $AlCl_3$ (Claus, *J. pr.* [2] 46, 484). Oil, smelling like mushrooms.

Oxim [76°]. Plates and prisms.

TETRA-*o*-XYLYL SILICATE $Si(OC_6H_3Me_2)_4$. (c. 460°). Formed by heating *o*-xylenol with $SiCl_4$, the yield being 85 p.c. of the theoretical amount (Hertkorn, *B.* 18, 1691). Large prisms.

Tetra-*m*-xylyl silicate $Si(OC_6H_3Me_2)_4$. (453°–457°). Formed, in like manner, from *m*-xylenol. Oil.

***m*-XYLYL THIOCARBIMIDE** C_9H_9NS *i.e.* [4:2:1] $C_6H_3Me_2.N:CS$. Formed from di-xylyl-thio-urea and P_2O_5 (Hofmann, *B.* 9, 1295). Crystals. Converted by PhOEt and $AlCl_3$ into $C_8H_9NH.CS.C_6H_4.OEt$ [140°] (Gattermann, *B.* 25, 3530).

XYLYL ETHYL DITHIOCARBONATE $CS(OEt).SC_6H_3Me_2$. Formed from potassium xanthate and *m*-diazo-xylene chloride (Leuckart, *J. pr.* [2] 41, 192). Oil, converted by heating with alcoholic potash into xylyl mercaptan (214°).

DI-XYLYL-THIO-UREA $CS(NH.C_6H_3Me_2[1:2:4])_2$. [153°]. Formed by digesting xylidine with CS_2 as long as H_2S escapes (Hofmann, *B.* 9, 1295). Crystals (from alcohol).

XYLYL-UREA $NH_2.CO.NHC_6H_3Me_2[1:2:4]$. [186°]. Formed from crude xylidine sulphate and potassium cyanate (Genz, *B.* 8, 226). Needles (from alcohol).

***s*-Xylyl urea** $NH_2.CO.NH.C_6H_3Me_2[1:3:5]$. [162°] (Frentzel, *C. C.* 1888, 1361).

Di-*s*-xylyl-urea $CO(NHC_6H_3Me_2[1:3:5])_2$. [275°] (F.); [251°] (G. a. C.). Formed from *s*-xylidine and $COCl_2$ (F.). Formed also from *m*-xylyl cyanate and xylidine (Gattermann a. Cantzler, *B.* 25, 1089). Needles.

Di-*m*-xylyl-urea $CO(NH.C_6H_3Me_2[1:2:4])_2$. [263°]. A product of the distillation of *m*-xylyl-amido-crotonic acid (Conrad a. Limpach, *B.* 21, 527). Sublimes when melting.

Di-xylyl-urea $CO(NHC_6H_3Me_2)_2$. Formed by heating urea (1 pt.) with crude xylidine (8 pts.). Felted needles (from hot alcohol), not melted at 250° (Genz, *B.* 3, 226).

Reference.—METHYL-BENZYL-UREA.

Y

YTTERBIUM. Yb. At. w. c. 173. This name is given to the metal, not yet isolated, of an earth separated by Marignac, in 1878, from crude erbia obtained from *gadolinite* or *euxenite*. The claim of ytterbia to rank as a definite homogeneous compound is not yet satisfactorily established.

The discovery of a new earth in a mineral from Ytterby in Sweden was announced in 1788 by Gadolin; in 1797 Eckeberg confirmed the discovery. The new earth was named *yttria*, and the mineral from which it was obtained was called *gadolinite*. Researches into the nature of yttria were conducted by Berzelius in 1819 (*v. Lehrbuch* [5th ed.] 2), Mosander in 1839 and 1843 (*J. pr.* 30, 27), Scheerer in 1842, Clève and others. In 1878 Marignac made a careful examination of erbia (*A. Ch.* [5] 14, 247); he fractionally decomposed erbium nitrate by heat, and obtained an earth which he called *ytterbia*. The erbia used by Marignac was pink, and gave, in solution, an absorption spectrum; the new earth was white and showed no absorption spectrum. Nilson (*B.* 12, 554; 13, 1439 [1879–80]) prepared ytterbia, but found a reacting weight for the earth different from that assigned to it by Marignac. By repeated fractional decomposition by heat of the nitrate of ytterbium, Nilson separated another earth which he called scandia (*cf.* SCANDIUM, this vol., p. 431). Nilson (*B.* 13, 1430) in 1879 made a fuller examination of ytterbia, and determined the at. w. of the metal of this earth, and the properties of several salts of the metal. In this memoir Nilson asserted that *erbia* was separable into seven distinct earths: erbia proper, scandia, terbia, thulia, ytterbia, yttria, and Soret's X (afterwards called holmia). (*cf.* ERBIUM, vol. ii. p. 456; and METALS, RARE, vol. iii. p. 245).

Occurrence.—Along with erbia, scandia, yttria, &c., in very small quantities in a few rare Scandinavian minerals, chiefly in *gadolinite* and *euxenite*. Nilson (*l.c.*) obtained c. 20 g. ytterbia from 6–7 kilos. of the crude earths prepared from c. 15 kilos. gadolinite.

Preparation of ytterbia.—Nilson (*B.* 13, 1430) mixed finely powdered *euxenite* or *gadolinite*, c. 400 g. at a time, with four times its weight of $KHSO_4$, fused over a powerful burner, pulverised the fused mass, and thoroughly exhausted with cold water; he ppd. the aqueous solution by ammonia, washed the ppd. hydrated oxides, and dissolved in HNO_3Aq; after boiling the solution for some time, and filtering, he ppd. by oxalic acid, washed the pp., dried it, and heated strongly until it was decomposed. The crude earths thus obtained were freed from K_2CO_3 by boiling with water, and were then dissolved in HNO_3Aq; the solution was evaporated to dryness, and the residue was fused until red vapours began to come off. The reddish-yellow, opaque solid was then treated with boiling water, whereby a reddish-yellow pp. was formed, which was filtered off by means of a suction-pump. (This pp. contained oxide of Th, along with oxides of Ce, Fe, and U.) The reddish filtrate was evaporated to dryness, and the solid nitrates thus obtained were partly decomposed by heating, the soluble (undecomposed) portion removed by solution in water, the residue dissolved in HNO_3Aq, the solution evaporated to dryness, the residue partly decomposed by heating, the undecomposed nitrates were removed by washing with water, the residue was dissolved in HNO_3Aq, and so on. After thirty repetitions of this process a solution was obtained that showed merely a trace of red colour after thirty-five repetitions the solution was quite colourless, and showed only two faint absorption bands, one in the green and the other in the red; after forty repetitions a solution was obtained which gave only the red band; and when the process of partial decomposition by heat had been repeated sixty-eight times a solution in HNO_3Aq was obtained which showed no trace of an absorption spectrum. This solution was saturated with H_2S, the small yellowish-brown pp. of PtS_2 was filtered off, the filtrate was ppd. by pure oxalic acid, the pp. was washed, dried, and decomposed by heating strongly, and pure ytterbia was thus obtained. For a modification of this method of separating ytterbia from accompanying earths *v.* Auer von Welsbach (*M.* 4, 630).

Atomic weight of ytterbium.—The metal has not been isolated; the at. w. was determined by Nilson (*B.* 13, 1433) by dissolving pure Yb_2O_3 (*v. supra*) in HNO_3Aq, adding a suitable quantity of H_2SO_4Aq, evaporating on a water-bath to drive off HNO_3, then on a sand-bath, and finally over a flame until all free H_2SO_4 was removed, weighing the $Yb_2(SO_4)_3$ thus obtained, and analysing it. Nilson dissolved pure Yb_2O_3 in HNO_3Aq, evaporated to dryness, partially decomposed the nitrate by heat, treated with water, &c., as described *supra*, and in this way obtained seven fractions, each of which was converted into sulphate. The results are presented in the following table:—

Weight of Yb_2O_3 taken	Weight of sulphate formed	Pctge. composition of sulphate		Atomic w. of Yb.
		Yb_2O_3	SO_3	
1·0063	1·6186	62·171	37·829	173·21
1·0139	1·6314	62·149	37·851	173·03
·8509	1·3690	62·155	37·845	173·08
·7371	1·1861	62·145	37·855	173·00
1·0005	1·6099	62·147	37·853	173·01
·8090	1·3022	62·126	37·874	172·84
1·0059	1·6189	62·134	37·866	172·91
Mean		62·147	37·853	173·01

Chemical relations of ytterbium.—If Yb is really a homogeneous substance, it must be placed in Series 10 of Group III. in the periodic classification of the elements. This group contains the following elements:—

Even series—

2	4	6	8	10	12
B (11)	Sc (44)	Y (89)	La (139)	Yb (173)	—

Odd series—

3	5	7	9	11
Al (27)	Ga (70)	In (114)	—	Tl (204)

A comparison of the position of Yb with the positions of elements placed in Series 10 (*v.* table on p. 811 of vol. iii.) shows that Yb ought to be decidedly more metallic than B, and somewhat more metallic than Al, Ga, or In; the data, however, are too meagre to allow a detailed comparison to be made. Little is known of the properties of compounds of Yb; but what is known broadly confirms the conclusions drawn from the position of the element in the periodic scheme of classification (*cf.* EARTHS, METALS OF THE, vol. ii. p. 424).

Ytterbium oxide Yb_2O_3. (*Ytterbia.*) A very heavy, white, infusible powder; slowly acted on by acids when cold or gently warmed, but readily dissolved by dilute acid solutions when boiling. Solutions in acids are colourless, and show no absorption spectra. The emission spectrum of a solution in HClAq, obtained by help of the spark, shows several lines, the most conspicuous of which have the wave-lengths 6221, 5556, 5476, 5352, and 5334 (*v.* Lecoq de Boisbaudran, *C. R.* 88, 1342). S.G. 9·175. S.H. (0°–100°) ·0646 (Nilson, *l.c.*).

Hydrated ytterbium oxide. A white, gelatinous, but heavy pp. obtained by adding NH_3Aq to a solution of a salt of Yb; shrinks much when dried, and absorbs CO_2 from the air. Easily soluble in acids (Nilson, *l.c.*).

Ytterbium salts. Nilson (*l.c.*) prepared an oxalate, an acid selenite, and a sulphate; and Marignac (*C. R.* 87, 578) prepared a formate.

Ytterbium oxalate $Yb_2(C_2O_4)_3.10aq$. A white, microscopically crystalline powder; insoluble in water, scarcely soluble in dilute acids; unchanged in air; gives up part of its water at 100°. Prepared by adding oxalic acid to a warm solution of the sulphate.

Ytterbium selenite $Yb_2O_3.4SeO_2.5aq$. Obtained by adding Na_2SeO_3Aq to a solution of $Yb_2(SO_4)_3$, washing the ppd. normal selenite, dissolving in water containing a large excess of H_2SeO_3, evaporating nearly to dryness, and washing the residue with water. A white crystalline salt, insoluble in water. Loses $4H_2O$ at 100°.

Ytterbium sulphate $Yb_2(SO_4)_3$. Prepared by dissolving Yb_2O_3 in HNO_3Aq, adding H_2SO_4Aq, evaporating on a water-bath to drive off HNO_3, then on a sand-bath, and finally over a flame at low redness till all H_2SO_4 is removed. An opaque, white solid. Dissolves in water when a large quantity is added at once; if a little is added much heat is produced, the salt combines with the water, and then dissolves very slowly when more water is added. Decomposed at a red heat, fully at a white heat. S.G. 3·793. S.H. ·1039 at 0° to 100°.

A *hydrated sulphate* $Yb_2(SO_4)_3.8aq$ was obtained by Nilson in large, white, lustrous prisms by evaporating a solution of $Yb_2(SO_4)_3$ in water at a gentle heat.

M. M. P. M.

YTTRIUM. Y. At. w. c. 89·6. The name yttrium is given to the metal of an earth obtained from a few rare Swedish minerals. The separation of a new earth from a mineral found at Ytterby, in Sweden, was made by Gadolin in 1788. The existence of the new earth was confirmed in 1797 by Eckeberg, and the earth was called by him *yttria*. Subsequent researches carried on by Berzelius, Mosander, Scheerer, Berlin, Delafontaine, Popp, Bahr a, Bunsen, Marignac, and others showed that the yttria of Gadolin and Eckeberg was a mixture of many oxides (*cf.* ERBIUM, vol. ii. p. 456; SCANDIUM, vol.

iv. p. 401; Ytterbium, this vol. p. 879; and v. *infra*, *Homogeneity of Yttria*).

Occurrence.—About 30 to 35 p.c. of yttria, in combination with SiO_2, is found in the exceedingly rare Swedish mineral *gadolinite*; some specimens of *orthite* also contain yttria, and the earth has also been found, in combination with Nb_2O_5 and Ta_2O_5, in specimens of *euxenite*. The oxides that generally accompany yttria in these rare minerals are ceria, didymia, erbia, lanthana, lime, magnesia, soda, and oxide of iron.

Preparation of yttria.—The crude oxides of yttrium, erbium, &c., are separated from *gadolinite* by the method of Bahr a. Bunsen described under Erbium (vol. ii. p. 457). Marignac (*A. Ch.* [5] 14, 247) converted the oxides into nitrates, heated the nitrates in a Pt basin until red fumes came off freely; treated the residue with water, and separated the solution, which contained much Yt nitrate, from insoluble basic nitrates of Er, &c. He then evaporated the solution to dryness, heated again until partial decomposition was effected, again treated with water, poured off the solution, evaporated it to dryness, partially decomposed the solid nitrates by heat, and so on. After some hundred repetitions of these processes, approximately pure yttria was obtained. Auer von Welsbach (*M.* 4, 630) separated approximately pure yttria from the crude earths obtained from *gadolinite* by a long-continued series of operations based on the facts (1) that yttrium nitrate is less readily decomposed to basic salts than erbium nitrate when a fairly conc. solution of these nitrates is heated with the oxides of the metals made into a paste with water, and (2) that basic yttrium nitrates dissolve in a solution of the normal nitrates of Y and Er more readily than basic erbium nitrates.

References.—Gadolin (*Crell's Annal.* 1796 [1] 313); Eckeberg (*Scher. J.* 3, 187); Klaproth (*Scher. J.* 5, 531); Vauquelin (*Scher. J.* 5, 552); Berzelius (*Scher. J.* 16, 250, 404; and *Lehrbuch* [5th ed.], 2, 177); Berlin (*P.* 43, 105); Scheerer (*P.* 56, 483); Mosander (*P. M.* 23, 251); Popp (*A.* 131, 179); Delafontaine (*Ar. Sc.* [2] 21, 97; 22, 30; 25, 112; 51, 48; 61, 273); Bahr (*A.* 135, 376); Bahr a. Bunsen (*A.* 137, 1); Cleve a. Höglund (*Bl.* [2] 18, 193, 279); Cleve (*Bl.* [2] 21, 344).

Preparation of yttrium.—The metal has not been obtained pure. Wöhler in 1828 (*P.* 13, 580) obtained impure yttrium by reducing the chloride by sodium. In 1864 Popp (*A.* 131, 179) dissolved yttria in HClAq, added NH_4ClAq, evaporated, separated and dried the double chloride of yttrium and ammonium thus formed, mixed this with Na, the double salt and the Na being arranged in alternate layers, heated the mixture in a closed crucible till action began and then allowed the reaction to proceed; washed the fused mass with water, separated unreduced yttria by levigation, washed the dark-grey powder that remained with water, and then with alcohol, and dried it over H_2SO_4. In 1890 Winkler (*B.* 23, 787) obtained a black powder that decomposed water by heating yttria and finely-divided Mg in the ratio Y_2O_3:3Mg (*cf.* Yttria, p. 882). Popp describes yttrium as a dark-grey powder resembling *ferrum redactum*, decomposing cold water slowly and hot water rapidly, easily dissolved by dilute acids, including acetic acid, decomposing boiling KOHAq, and NH_4ClAq at the ordinary temperature, with evolution of H and NH_3; the metal burns brilliantly when heated on Pt foil; when heated in O it burns with a very dazzling light.

An examination of the emission spectrum of yttrium was made by Thalén: the most prominent lines observed had the wave-lengths 6191, 6131, 5987, 5971, 5662, 5496, 5402, 5205, 5200, 5088, 4900, 4881, 4854, 4374, and 4309 (*Kongl. Sv. Vetens. Acad. Handl.* 12).

The atomic weight of yttrium was determined by Berzelius, Delafontaine, Popp, Bunsen a. Bahr (*v. supra*, *References*) by analyses of the sulphate, or by transforming yttria into the sulphate; the values varied from 92·2 to 102·3. In 1873 Cleve a. Höglund (*v. B.* 6, 1467) made more accurate determinations by analysing purer specimens of $Yt_2(SO_4)_3$, and obtained the value 89·6.

Chemical relations of yttrium.—Assuming yttrium to be a homogeneous element with at. w. c. 89, it must be placed in Series 6 of Group III. in the periodic arrangement of the elements. This group contains the earth metals; yttrium is preceded in the even series family by B and Sc, and is succeeded by La and Yb. A consideration of the position given to Y in the periodic classification shows that the element ought to closely resemble the other metals of the earths. Too little is known of the properties of many of the earth metals to allow of a detailed comparison of them one with another. A general account of the relations of these metals will be found in Earths, metals of the (vol. ii. p. 424).

The homogeneity of yttria.—The properties described as belonging to yttria before 1885 were the properties of a mixture of at least five, and perhaps six, different bodies, according to Crookes (*C. N.* 54, 13, 155). Crookes subjected 'yttria' to a prolonged process of fractionation by ammonia (for a description of this method *v.* Earths, vol. ii. p. 423), and he then examined the phosphorescence spectra of various fractions. Crookes concludes that yttrium is a compound, or perhaps a very intimate mixture, of simpler bodies. For details of the phosphorescence spectra of the substances obtained by fractionating 'yttria' *v.* Metals, rare (vol. iii. p. 248). By thirty-two fractionations of 'yttria' by ppn. with NH_3Aq, followed by twenty-six fractionations by ppn. with oxalic acid, Lecoq de Boisbaudran (*C. R.* 103, 649 [1887]) obtained a white specimen of yttria which gave no phosphorescence spectrum when mixed with lime, and which, when converted into chloride, gave a spark spectrum, showing only the lines of yttrium.

Yttrium, bromide of, $YBr_3.9H_2O$. Colourless, very deliquescent tablets; obtained by dissolving Y_2O_3 in HBrAq and concentrating (Cleve, *Bl.* [2] 18, 193). The anhydrous salt is obtained by Duboin (*C. R.* 107, 99, 248) by heating Y_2O_3 to redness on a support of gas-carbon in a current of CO and Br vapour. Very soluble in water or alcohol; insoluble in ether.

Yttrium, chloride of, $YCl_3.6H_2O$. Obtained by dissolving yttria in HClAq, evaporating to dryness on a water-bath, dissolving in alcohol, and evaporating over H_2SO_4 (Cleve, *l.c.*). Crystallises in large, colourless, very deliquescent, rhombic prisms (C., *l.c.*). The anhydrous compound is formed by heating yttria to redness on a support of gas-carbon in a slow stream of CO and Cl (Duboin, *l.c.*). By evaporating a solution of yttria in HClAq with addition of NH_4Cl a *double compound* of YCl_3 and NH_4Cl is obtained; double compounds with KCl and NaCl are formed by fusing the constituent chlorides together. Popp (*A.* 131, 179) described the double compound $YCl_3.3HgCl_2.9H_2O$. Cleve (*Bl.* [2] 31, 195) described $YCl_3.SnCl_4.8H_2O$.

Yttrium, fluoride of, $2YF_3.H_2O$. Obtained as a gelatinous pp. by adding HFAq, or solution of an alkali fluoride, to solution of a salt of yttrium (Cleve, *Bl.* [2] 18, 193).

Yttrium, iodide of, (?YI_3). Deliquescent crystals, soluble in alcohol; obtained by evaporating a solution of yttria in HIAq (Berlin, *P.* 43, 105; no analyses given).

Yttrium, oxides of. Besides yttria, Y_2O_3, there probably exists another oxide containing more oxygen.

YTTRIA Y_2O_3. (*Yttrium sesquioxide.*) A *hydrate*, probably $Y_2O_3.6H_2O$ (Popp, *l.c.*), is obtained, as a gelatinous pp. closely resembling hydrated alumina, by ppg. the solution of a salt of yttrium by ammonia. The oxide is formed by strongly heating this hydrate; also by decomposing by heat the carbonate, nitrate, or oxalate of yttrium in presence of air. Yttria is described as a heavy, white or almost white powder, S.G. 5·078 (Cleve, *l.c.*); 5·046 (Nilson a. Pettersson, *B.* 13, 1459). S.H. (0°–100°) ·1026 (N. a. P., *l.c.*). By heating amorphous yttria with $CaCl_2$ for some hours, and washing with warm water, Duboin (*C. R.* 107, 99, 243) obtained highly refractive crystals of Y_2O_3, scarcely acted on by acids or by fused Na_2CO_3. Yttria is a markedly basic oxide; it absorbs CO_2 from the air, and decomposes solutions of ammonium salts, giving off NH_3. Yttria is insoluble in water; it dissolves slowly in cold HClAq, HNO_3Aq, or H_2SO_4Aq, but more rapidly on warming. By heating a mixture of yttria and finely-powdered Mg, in the ratio Y_2O_3:3Mg, Winkler (*B.* 23, 787) obtained a black powder which slowly gave off H from cold water, rapidly from hot water, and dissolved in dilute HClAq, with violent evolution of H.

YTTRIUM PEROXIDE. By adding H_2O_2Aq and NH_3Aq to a solution of sulphate or nitrate of yttrium, Cleve (*Bl.* [2] 43, 53) obtained a white gelatinous pp. to which he gave the composition Y_4O_9; but this formula cannot be regarded as final.

Yttrium, salts of. The salts which are formed by replacing the H of acids by yttrium belong to the form Y_2X_3, where X = $2ClO_3$, $2NO_3$, SO_3, SO_4, CO_3, $\frac{2}{3}PO_4$, &c. Almost all the yttrium salts of oxyacids that have been prepared are normal salts; a basic nitrate, and an acid orthophosphate and selenate, are known. Many of the salts are obtained by dissolving yttria in acids and evaporating; those salts which are insoluble, or but slightly soluble, in water are formed by ppn. from the nitrate or sulphate. The salts formed by ppn. are the *arsenate*, *borate*, *carbonate*, *chromate*, *iodate* and *periodate*, *oxalate*, *phosphates*, *selenite* and *sulphite*; besides these salts, the following salts of oxyacids are known, and are soluble in water: *bromate*, *chlorate* and *perchlorate*, *nitrate*, *selenate*, *sulphate*, *thiosulphate* and *tungstate*. A few *double salts* are known; the principal are $Y_2(CO_3)_3.M_2CO_3.xH_2O$,
$Y_2(C_2O_4)_3.3M_2C_2O_4.xH_2O$, and
$Y_2(SO_4)_3.mM_2SO_4.xH_2O$, where M = an alkali metal. Duboin (*C. R.* 107, 99, 243) obtained a *silicate* $Y_2O_3.SiO_2$ by very strongly heating a mixture of 3 pts. yttria with 30 pts. $CaCl_2$, and washing with water. The yttrium salts of oxyacids have been examined, chiefly by Cleve (*Bl.* [2] 18, 193, 289; 21, 344; *v.* also Berlin, *P.* 43, 105; Högbom, *Bl.* [2] 42, 2; Popp, *A.* 131, 179).

Yttrium, sulphide of. No compound of yttrium and sulphur has been isolated with certainty. Addition of $(NH_4)_2SAq$ or NH_4HSAq to a solution of a salt of yttrium ppts. hydrated oxide. By fusing yttria, S, and an alkali carbonate, and washing the fused mass with water, a yellowish-green solid is obtained that is insoluble in water, but is partly decomposed thereby to hydrated oxide and H_2S; this solid dissolves in acids, giving off H_2S. The same solid seems to be obtained by strongly heating yttria in H laden with CS_2. No compound of yttrium and S was obtained by heating yttria with Na_2S_5. By heating YCl_3 in a stream of H_2S, HCl is given off, and a yellow powder remains, which is decomposed by water, with evolution of much H_2S (*v.* Popp, *A.* 131, 179). According to Popp (*l.c.*), the composition of this substance is Y_2S_3.

By passing dry H_2S over a mixture of YCl_3 with excess of NaCl, heated to c. 1000° in a boat of gas-carbon, Duboin (*C. R.* 107, 99, 243) obtained a greenish, crystalline solid, which when washed with water left transparent, greenish lamellæ of the *double compound* $Y_2S_3.Na_2S$.

M. M. P. M.

ZANZALOÏN *v.* ALOÏN.

ZEORIN $C_{13}H_{22}O$. [231°]. Occurs in the ethereal extract from *Zeora sordida* (Paterno, *G.* 7, 281, 508). Small pyramids with hexagonal base (from ether-alcohol), v. sl. sol. alcohol and ether, insol. water. Neutral. Not attacked by alkalis or dilute acids.

ZINC. Zn. At. w. c. 65·3 (*v. infra*). Mol. w. c. 65·3 at c. 1400°; probably the same in solution in Hg (*v. infra*). Melts at 419° (determined by air thermometer; V. Meyer a. Riddle, *B.* 26, 2443); at 417·57° (determined by platinum thermometer, Callendar a. Griffiths, *C. N.* 63, 1); for older determinations, giving m.p. from 340° to 450°, *v.* Carnelley's *Melting- and Boiling-point Tables* (1, 14). Boils between 930° and 954° (Deville a. Troost, *C. R.* 90, 773); at 930° (Violle, *C. R.* 94, 720; *cf.* Troost, *C. R.* 94, 788). S.G. c. 6·9 to 7·2 (*v.* Schiff, *A.* 107, 59; Kalischer, *B.* 14, 2750; Quincke, *P.* 135, 642; Spring, *B.* 16, 2724). V.D. 34·8 at c. 1400° (Mensching a. V. Meyer, *B.* 19, 3295). S.H. (0° to 100°) ·0935 (Bunsen, *P.* 141, 1); (19° to 47°) ·0932 (Kopp, *T.* 155, 71; *cf.* Schüller a. Wartha, *B.* 8, 1016). C.E.; if length of bar at $0^\circ = l^\circ$, then length at $t^\circ = (1+\beta t)$; if volume at $0^\circ = V_0$, then volume at $t^\circ = (1+3\beta t)$; $\beta =$ ·00002976 from 0° to 100° (Matthiessen, *P. M.* [4] 32, 472). Heat of fusion for 1 kilo = 28,130 (Person, *A. Ch.* [3] 24, 129). T.C. (Ag = 100) 28·1 (Wiedemann, *P. M.* [4] 19, 243). E.C. (Hg at 0° = 1) 16·1 at 0°, 16·92 at 100° (Bénoit, *P. M.* [4] 45, 314); 14·83 at 15° (Kirchoff a. Hausemann, *W.* 13, 406). Chief lines in emission spectrum 6360, 6100, 4924, 4911, 4809, 4722, 4679 (Huggins, *T.* 154, 139; *cf.* Thálen, *Détermin. des Longueurs d'Onde des Raies Métalliques* [Upsala, 1868]; and Ames, *P. M.* [5] 30, 33); for wave-lengths of lines of high refrangibility *v.* Hartley a. Adeney (*T.* 1884 [1]. 97). Zinc crystallises in tabular hexagonal plates, $a : c = 1·356425$ (Williams a. Burton, *Am.* 11, 219; *cf.* Stolba, *J. pr.* 89, 122; 96, 178; Sharples, *Am. S.* [3] 7, 223; Nöggerath, *P.* 39, 324; Nicklès, *A. Ch.* [3] 22, 37; G. Rose, *B. B.* 1852. 26; *P.* 107, 448; Storer, *P. Am. A.* 6; Cooke, *Am. S.* 31, 191). The metal is probably dimorphous. H.C. [Zn,O] = 85,430 (Thomsen, *Th.* 3, 275). Refraction equivalent = 9·8 (Gladstone, *Pr.* 18, 49).

Historical.—That copper acquired a reddish colour, and that its properties were modified, by melting with certain ores, was known to the ancients and the alchemists; the ore with which copper was generally melted to form brass was called *cadmia fossilis*. The fact that a lustrous solid could be obtained by heating *cadmia fossilis* seems to have been known to the ancient writers on mineralogy. According to Kopp (*Geschichte der Chemie*, 4, 116), the earliest use of the word *zinc* is found in a writing of the fifteenth century attributed to Basil Valentine. Paracelsus, in the sixteenth century, speaks of zinc as a definite metal-like substance, and assigns it to the class of bastard or semi-metals. The name 'zinc' was applied during the seventeenth and eighteenth centuries alike to zinc ores and to the metal-like substance obtained from these ores. Boyle speaks of zinc, and also uses the word *spelter*, or *splauter*, a term of Indian origin according to Kopp. Tolerably pure zinc seems to have been obtained from zinc ores about 1720, probably by Henckel (*v.* Percy's *Metallurgy*, 1, 520).

Occurrence. — Zinc is found in small quantities; Becker (*J. M.* 1857, 698) and Phipon (*C. R.* 55, 218) noticed the occurrence of native zinc in Victoria. Considerable quantities of compounds of zinc occur in many places; the commonest ores are *calamine* (carbonate), *siliceous calamine* (silicate), *blende* (sulphide), and *red zinc ore* (oxide); aluminate, arsenate, phosphate, and sulphate of zinc are also found, but in smaller quantities. Small quantities of Cd compounds occur in most zinc ores. The ash of a plant that grows on the waste heaps of the zinc works in Rhenish Prussia (*Viola calaminaria*) is said to contain compounds of zinc (Braun; *P.* 92, 175). Zinc compounds have been found in some springs (*v.* Hillebrand, *U. S. Geolog. Survey Bull.* No. 113 [1898]). Traces of zinc compounds have been found, according to Lechartier a. Bellamy (*C. R.* 84, 687), in the human liver, in calves' liver, in beef, hens' eggs, wheat, barley, maize, beans, and vetches.

Formation.—Zinc ore, generally carbonate or sulphide, is roasted in reverberatory calciners; the roasted ore is mixed with half its weight of powdered charcoal, coke, or anthracite, and heated in crucibles or retorts arranged so that the reduced metal distils from the impurities; the metal is condensed and collected in suitable vessels, and CO passes off. For details and descriptions of the different forms of apparatus *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 1042.

Preparation.—Commercial zinc generally contains from ·5 to 3·3 p.c. lead, with c. ·2 to ·5 p.c. iron and cadmium, and small traces of arsenic.

Pure zinc was prepared by Reynolds a. Ramsay (*C. J.* 51, 854 [1887]) by dissolving zinc sold as free from common impurities in dilute H_2SO_4Aq, evaporating, crystallising the sulphate several times, electrolysing a solution of this salt, the metal being deposited on an electrode of Pt wire, dissolving the metal in dilute HClAq, ppg. ZnO_2H_2 by NH_3Aq, dissolving the pp. in excess of NH_3Aq, and ppg. ZnS by H_2S; the ZnS was dissolved in HClAq, and again ppd. from an ammoniacal solution by H_2S; the pp. was well washed, dissolved in pure dilute H_2SO_4Aq, and the sulphate obtained on crystallisation was re-crystallised several times; an aqueous solution of this sulphate was then electrolysed, using a Pt wire as electrode, and the metal was melted in a tube of hard glass from which the air had been exhausted. By distilling this metal *in vacuo* in a tube of hard glass, very pure zinc was obtained. Pullinger (*C. J.* 57, 816 [1890]) distilled zinc sold as 'chemically pure' in a hard glass tube, bent slightly towards the closed end, placed in a combustion furnace, the open end being connected with a good water-pump. By melting the distilled zinc in a tube of hard glass with a small bulb blown on the end, the part of the tube between the bulb and the wider portion containing the zinc being capillary, and the open end being connected with a water-pump, he obtained the zinc in perfectly bright, smooth, lustrous spheres free from hollows; the pump was stopped while the zinc was molten, and the increased pressure caused the molten metal to filter through the capillary tube into the bulb. For the preparation of pure zinc by electrolysis of an ammoniacal solution of the sulphate, *v.* Myers (*C. R.* 74, 195).

Stolba (*C. C.* 1884. 419) says that zinc can be obtained free from As and nearly free from iron by the combined interaction of S and water vapour. He mixes burnt gypsum with one-fourth its weight of S powder, moulds the moistened mixture into spheres about 5 cm. diameter, and sinks these to the bottom of a crucible containing molten zinc; vapours of

H_2S and S are given off, and the molten metal is thereby briskly agitated. When the reaction is completed, the little balls are taken out, the upper crust is removed, and the operation is repeated if necessary.

Zinc-dust is obtained either in the distillation of the metal, or, in not such fine division, by crushing and powdering the metal in an iron mortar at a temperature somewhat below the m.p. of zinc. The ZnO_2H_2 always present in specimens of zinc-dust may be removed by digesting with NH_4ClAq and then with NH_3Aq, and drying on a porous tile *in vacuo* (Carnegie, *C. J.* 53, 471).

Properties.—Zinc is a white metal, with a slight shade of blue; it is very lustrous when polished. Commercial zinc is brittle at the ordinary temperature, but it becomes malleable between 100° and 150°; at 210° it again becomes brittle, and at that temperature it can be finely powdered in a mortar. Pure zinc is said to be malleable at the ordinary temperature. Commercial zinc that has been heated to 100°-150° retains its malleability when it cools. Kahlischer (*B.* 14, 2747) noticed that rolled zinc ceased to give a ringing sound when struck after it was heated to c. 160°-300°, that it could then be bent easily, and that when bent it emitted a sound like the 'cry' of tin; he found that the zinc became crystalline, and the crystalline structure was more decided the higher the temperature; the S.G. was very slightly increased, and the electrical resistance was reduced by c. 3 p.c. Zinc is a softer metal than copper; its hardness is increased by rolling. The tensile strength of zinc varies much with the mode of preparation. Zinc crystallises easily, especially when pure; the form is that of hexagonal plates (for references *v. supra*, beginning of this article). Zinc melts at c. 420°, and boils somewhat below 1000° (*v. supra*). Molten zinc expands somewhat during solidification. The metal can be distilled at a full red heat; the vapour takes fire in the air, and burns with formation of ZnO and the production of a bright white light. Zinc exposed to the ordinary air becomes very gradually covered with a thin film of a basic carbonate which protects the mass of the metal from further corrosion; in pure dry air zinc is unchanged. Zinc dissolves in dilute acids, generally with evolution of H (*v. infra, Reactions with sulphuric and nitric acids*); it also dissolves in solutions of caustic potash or soda. When impure zinc is amalgamated it resists the action of acids. Zinc is not acted on by mineral lubricating oils; some of the commoner animal oils attack it slightly (*v.* Redwood, *C. S. I.* 5, 362). Zinc ppts. most of the other metals from their solutions; if a piece of impure zinc is dissolved in an acid, most of the metallic impurities (As, Cd, Cu, Pb, &c.) remain undissolved as long as undissolved zinc is present. Zinc combines directly with O, S, Se, Te, the halogens, and P; it forms alloys with many metals. Pure zinc does not decompose boiling water, but the commercial metal reacts and gives off H. Zinc-dust usually contains some ZnO_2H_2; it is said also to contain H, produced by the interaction of Zn and ZnO_2H_2 (*v.* Greville Williams, *C. N.* 52, 205, 268).

Atomic and molecular weights of zinc. In **1809 Gay-Lussac (*Mém. S. d'A.*, 2, 174)** determined the weight of ZnO obtained by dissolving a determinate weight of zinc in nitric acid, evaporating to dryness, and strongly heating the residue; Berzelius in 1811 repeated the experiment of Gay-Lussac (*G. A.* 37, 400; *v.* also *P.* 8, 184); and in 1843 Erdmann made similar experiments (*v. Berzelius' Lehrbuch*, 3, 1219). The values obtained for the at. w. of zinc were 65·39 (G.-L.), 65·41 (B.), and 64·94 and 64·88 (E.). In 1844 Favre decomposed ZnC_2O_4 by heating in air, and determined the weights of ZnO and CO_2 produced; the value 65·88 was thus obtained for the at. w. of zinc. In the same year Favre obtained the value 65·78 by dissolving zinc in dilute H_2SO_4Aq, burning the H given off by passing it over hot CuO, and weighing the water thus produced (*A. Ch.* [3] 10, 163). In 1884 Marignac determined the Cl and the Zn in $ZnCl_2.2KCl$, and obtained the value 65·18 for the at. w. of zinc (*A. Ch.* [6] 1, 309; *v.* also Baubigny, *C. R.* 97, 908 [1883]). By dissolving zinc in dilute H_2SO_4Aq and measuring the H given off, van der Plaats concluded that the at. w. of zinc is 65·18 (*C. R.* 100, 52 [1885]). Reynolds a. Ramsay, in 1887, by measuring the H given off by the interaction between very pure zinc and H_2SO_4Aq, obtained the value 65·48 (*C. J.* 51, 854). By oxidising zinc to ZnO, by HNO_3Aq, in 1888, Morse a. Burton obtained the value 65·1 (*Am.* 10, 311). In 1889 Gladstone a. Hibbert (*C. J.* 55, 443) determined the ratio of zinc dissolved to silver deposited by one and the same electric current; taking the at. w. of silver as 107·66 (the value adopted in this *Dictionary*) the at. w. of zinc was found to be 65·29.

In 1886 Mensching a. V. Meyer (*B.* 19, 3295) found the V.D. of zinc at c. 1400° to be 34·3, a number which shows that the gaseous molecule of zinc is monatomic. Ramsay, in 1889, determined the lowering of the vapour pressure of Hg produced by dissolving zinc therein (*C. J.* 55, 521); assuming that equal volumes of dilute solutions contain equal numbers of molecules, and that the molecular weight of liquid Hg is 200, Ramsay's results indicate that the molecules of zinc in dilute solutions of this metal in Hg are monatomic. The experiments of Heycock a. Neville (*C. J.* 57, 376 [1890], and 61, 888 [1892]) on the lowering of the freezing-points of Bi, Cd, Pb, Sn, and Na by solution of zinc in these metals tend to confirm the conclusion that the molecule of zinc in dilute solutions in these metals is monatomic.

Chemical relations of zinc. Zinc is the second odd-series member of Group II. in the periodic classification of the elements. Zinc is preceded in the odd series of this group by Mg and is followed by Cd, —, and Hg; the members of the even series of Group II. are Be, Ca, Sr, Ba, —, —. Zinc is the second member of series 5; it is preceded in this series by Cu, and is succeeded by Ga, Ge, As, Se, and Br. The general chemical character of zinc is that of a metal; its oxide ZnO is basic, its chloride $ZnCl_2$ is volatilisable without decomposition. No acids are known containing zinc, and the molecule of the element is monatomic. The fact that compounds of ZnO and K_2O are obtained by dissolving ZnO_2H_2 in KOHAq and adding alcohol shows that the hydroxide of the metal has feebly marked acidic properties, and the isolation of a number of oxychlorides and basic carbonates, nitrates, and sulphates illustrates the fact that zinc is less positive than Mg, which is the first member of the zinc family of Group II. For a general account of the properties of the family of which zinc forms a member *v.* MAGNESIUM GROUP OF ELEMENTS, vol. iii. p. 163. The atom of zinc is divalent in the gaseous molecules of its compounds.

Reactions and Combinations.—1. Zinc is unchanged in pure dry *air*; in ordinary air the surface layers are slowly converted into a basic carbonate, which protects the metal beneath. Heated strongly in air or *oxygen*, zinc burns to ZnO.—2. Heating zinc in *bromine*, *chlorine*, or *iodine* produces $ZnBr_2$, $ZnCl_2$, or ZnI_2.—3. When zinc is heated in *phosphorus* vapour, phosphide of zinc (*q. v.*, p. 890) is formed.—4. By heating zinc with *selenion* vapour, a compound of Zn and Se is formed (*v.* ZINC SELENIDE, p. 890).—5. Zinc combines with *tellurium* when the elements are heated together (*v.* ZINC TELLURIDE, p. 891).—6. *Sulphur* and zinc combine when a mixture of these elements is very strongly compressed (Spring, *B.* 16, 1000).—7. Zinc decomposes *water* at a red heat. Commercial samples of zinc decompose water at 100° (L'Hôte, *C. R.* 101, 1153).—8. ZnS is formed by strongly heating zinc in a stream of *hydrogen sulphide*; when *hydrogen selenide* is used the product is ZnSe, and by heating the metal in *hydrogen telluride* ZnTe is formed (*v.* Margottet, *C. R.* 84, 1293).—9. Zinc is said to reduce *carbon monoxide* at a very high temperature.—10. Zinc is superficially oxidised by heating to dull redness in *nitric oxide* (Sabatier a. Senderens, *C. R.* 114, 1429). Oxidation in *nitrogen dioxide* (NO_2) is effected at 300° (S. a. S., *C. R.* 115, 236).—11. Many *metallic oxides* are reduced by heating with zinc.—12. Zinc reacts with *sulphurous acid solution*; according to Schweizer (*v. C. N.* 23, 293), the products are $ZnSO_3$, along with $H_2S_2O_4Aq$, $H_2S_3O_6Aq$, and S.—13. Zinc dissolves in *hydrochloric acid*, giving off H and forming $ZnCl_2$. Reynolds a. Ramsay (*C. J.* 51, 857) say that pure zinc scarcely reacts with boiling hydrochloric acid. For reactions of zinc with sulphuric and nitric acids, *v. infra.*—14. Zinc dissolves slowly in hot solutions of *caustic soda* or *potash*, giving off H, and forming $ZnO.xM_2O$ (*cf.* ZINC HYDROXIDE, p. 888); the reaction is much hastened by adding iron or Pt along with the zinc.—15. Many *metallic salts in solution* are reduced by zinc, with ppn. of the metals, *e.g.* salts of As, Cd, Cu, and Pb.—16. When zinc-dust is shaken with an aqueous solution of *ferric chloride*, the whole of the ferric salt is very rapidly reduced to ferrous chloride (for details of the application of this reaction in the estimation of ferric iron, *v.* Carnegie, *C. J.* 53, 468 [1888]).—17. According to Siersch (*J.* 1867. 257), zinc dissolves in *sodium chloride* solution, forming $ZnCl_2.2NaClAq$, ZnO, and H.—18. Poumarède (*J. pr.* 73, 496) says that nearly all *chlorides* and *fluorides* are reduced by reacting with vapour of zinc in an atmosphere of H.—19. By heating to redness a mixture of zinc filings and *sodium metaphosphate*, Hvoslef (*A.* 100, 99) probably obtained phosphides of zinc (*v.* ZINC PHOSPHIDES, p. 890).—20. Zinc reacts with *sodium hydrogen sulphite* solution, forming $ZnSO_3$, $Na_2S_2O_4Aq$, and Na_2SO_3Aq (*v.* HYPOSULPHITES, this vol. p. 592).—21. By heating zinc with *zinc sulphide* in an exhausted tube, some of the ZnS is carried forward and deposited in the front part of the tube; probably at a high temperature ZnS is decomposed, and there exist only Zn and S, and at a lower temperature these recombine to form ZnS (Morse a. White, *Am.* 11, 348). A similar phenomenon is noticed on heating zinc with *zinc oxide* (M. a. W., *l.c.* p. 258).—22. ZnS is formed by strongly heating zinc and *mercuric sulphide* or zinc and *potassium polysulphides* (*v.* ZINC SULPHIDE, p. 890).

When slips of zinc-foil are immersed in $CuSO_4Aq$, a deposit of finely-divided Cu is formed on the zinc. This *copper-zinc couple* is an energetic reducing agent; $KClO_3Aq$ is reduced to KClAq, KNO_3Aq to KNO_2Aq and NH_3Aq, K_3FeCy_6Aq to K_4FeCy_6Aq, SO_2Aq to S, As_2O_3Aq to AsH_3, $C_6H_5NO_2$ (in alcohol) to $C_6H_5NH_2$, &c. (*v.* Gladstone a. Tribe, *C. J.* 33, 306).

Reactions of zinc with sulphuric and nitric acids. Commercial zinc dissolves easily in dilute H_2SO_4Aq, with formation of $ZnSO_4Aq$ and evolution of H. In 1830 De la Rive noticed that very little action took place between approximately pure zinc and H_2SO_4Aq; this fact has been confirmed by other experimentors. Reynolds a. Ramsay (*C. J.* 51, 857 [1887]) found that zinc prepared by repeated electrolysis of the sulphate and distillation *in vacuo* scarcely reacted with H_2SO_4Aq; L'Hôte (*C. R.* 101, 1153) also asserted that pure zinc does not react with H_2SO_4Aq. Divers a. Shimidzu (*C. J.* 47, 598 [1885]) observed very great differences between the rate of action of the same H_2SO_4Aq on sheets of commercial zinc of the same size. Pullinger in 1890 (*C. J.* 57, 815), and Weeren in 1891 (*B.* 24, 1785), made somewhat elaborate investigations into the connections between the conditions and the rate of the interaction of zinc and H_2SO_4Aq.

Pullinger used 'pure' sulphuric acid diluted with three times its weight of water; and zinc prepared by distilling that sold as 'chemically pure' *in vacuo* and casting in balls under pressure to prevent the formation of cracks or hollows (*v. supra, Preparation of zinc*, p. 885). He found that when the surface of the zinc was very smooth this was best accomplished by immersing in *aqua regia* for 10 or 15 seconds, and washing with water—and the acid was boiled for some hours before the experiment, there was practically no reaction at 20°–25° (spheres of zinc weighing c. 2½ g. lost from 5 to 6 mgms. in 20 hours). Pullinger found that the presence of small quantities of H_2S, SO_2, or H_2S_2[illegible]Aq did not affect the weight of zinc dissolved by the boiled H_2SO_4Aq; addition of some H_2O_2 materially increased the rate of action; and H_2SO_4Aq that had been electrolysed before use dissolved from four to ten times more zinc than some of the same acid that had not been electrolysed; addition of a few drops of HNO_3Aq considerably increased the action; when a few drops of HIAq were added to the H_2SO_4Aq practically no action occurred. P. supposed that all the 'pure' acid used by him contained traces of an oxidising substance, probably $H_2S_2O_8$, and that the solvent action was due to this. P.

insists on the important connection between the rate of action and the smoothness or roughness of the surface of the zinc used. But he concludes that 'in all probability *pure* dilute sulphuric acid would, at ordinary temperatures, be entirely without action upon metallic zinc, whether the surface of the latter were rough or smooth.'

Weeren used zinc which he found to be chemically pure by analysis; he gives no account of his method of preparation nor any details of his analytical results. W. found that the weight of pure zinc dissolved by pure H_2SO_4Aq (1:20) at the ordinary temperature, and under a pressure of 10 mm., was c. ten times greater than the weight dissolved at 760 mm. pressure; but the weights of impure zinc dissolved at the two pressures were almost the same. The pure zinc used by W. dissolved fairly rapidly in boiling H_2SO_4Aq; in one case when 2·1 mgm. dissolved at 0° after thirty minutes' action, 122 mgm. dissolved in the boiling acid. W. found that the solubility of his pure zinc increased very slowly as temperature rose up to within 1° of the b.p. of the acid used, but that when ebullition actually began the solubility of the zinc suddenly increased; the weight of pure zinc dissolved by H_2SO_4Aq at 100° and boiling, was c. sixteen times greater than the weight of the same zinc dissolved by the same acid at 100° but kept from actually boiling by pressure. On the other hand, W. noticed that as much impure zinc dissolved at 100° when the acid was boiling as when it was prevented by pressure from boiling. Addition of oxidisers, CrO_3 or H_2O_2, enormously increased (c. 300 times) the solubility of pure zinc in H_2SO_4Aq at 18°-20°, but only slightly increased (c. six times) the solubility of impure zinc. W. supposes that when pure zinc is immersed in pure H_2SO_4Aq a slight reaction occurs, and that the H produced is attracted to and held firmly on the surface of the zinc, and that the reaction ceases because the surface of the metal is protected by the layer of H. Increase of temperature does not appreciably affect the rate of action, because the layer of H remains fixed to the surface of the zinc, but when the acid boils the H is removed and rapid dissolution occurs; any conditions which remove the layer of H increase the solubility of the zinc. W. supposes that the rate of dissolution of impure zinc in H_2SO_4Aq is not much affected by boiling, presence of oxidisers, &c., because H is not given off at the surface of the zinc, but at the surface of the more negative impurities. The rapid solution of zinc in HNO_3Aq is connected, according to W., with the rapid oxidation of the H produced at the surface of the zinc, and hence the production of a layer of water on the surface of the metal which destroys the attraction between the zinc and any H that may escape oxidation.

As regards the products of the interaction of zinc and sulphuric acid, when the acid is fairly concentrated (c. $H_2SO_4.H_2O$ to c. H_2SO_4) SO_2 is given off, and at moderately high temperatures H_2S and S are also produced (*v.* Calvert a. Johnson, *C. J.* [2] 4, 435 [1867]). A qualitative examination of the products by Pattison Muir a. Adie (*C. J.* 53, 47 [1888]) showed that $ZnSO_4$ is the only salt of zinc produced, with any concentration of acid, and at any temperature up to the b.p. of the acid used; that with approximately pure zinc little or no SO_2 or H_2S is formed unless the temperature be high; and that the purer the zinc the less is the quantity of S produced (*cf.* Ditte, *A. Ch.* [6] 19, 68).

The products of the interaction of zinc and nitric acid are $Zn(NO_3)_2Aq$, $Zn(NO_2)_2Aq$, NH_4NO_3Aq and NH_4NO_2Aq, and NO, N_2O, and N. Acworth found that when HNO_3Aq reacts with zinc in presence of $(NH_4)NO_3$ the chief gaseous product is N (along with some N_2O and NO) (*C. J.* 28, 828 [1875]). Acworth a. Armstrong studied the reaction of HNO_3Aq and Zn more fully in 1878 (*C. J.* 32, 54), and found that the only gaseous products were N, N_2O, and NO (*cf.* Deville, *C. R.* 70, 22, 550 [1870]). According to Divers (*C. J.* 43, 443 [1883]), a little NH_2OH is formed when cold HNO_3Aq (3 to 4 p.c.) is poured on to granulated zinc and quickly poured off again. Divers a. Shimidzu (*C. J.* 47, 597 [1885]) found that considerable quantities of NH_2OH are produced by the combined reaction of HNO_3Aq and H_2SO_4Aq, or HNO_3Aq and HClAq, on zinc (*v.* HYDROXYLAMINE, *Formation*, vol. ii. p. 734). Divers (*l.c.*) thought that zinc does not form $Zn(NO_2)_2$ by a direct reaction with HNO_3Aq, but by interacting with some of the $Zn(NO_3)_2$ formed by the primary action of the metal on the acid. The products of the interaction of zinc and HNO_3Aq have been examined recently by Montemartini (*G.* 22 [1], 277 [1892]), who says that free H is not produced (he also says that no NH_2OH is formed), and that in addition to nitrate and nitrite of zinc and ammonium, hyponitrite is also produced; the gaseous products, according to M., are N_2O, NO, NO_2, and N; there is no nitrous acid formed, says M., if the HNO_3Aq contains more than 30 p.c. HNO_3, and no NO_2 if less than 30 p.c. HNO_3 is present. M. also gives determinations of the quantities of the various products at different temperatures, and of the rate of reaction with different concentrations of HNO_3Aq (*Abstract* in *C. J.* 62, 1279 [1892]).

Zinc, alloys of. Alloys of zinc have been formed with most metals by fusing the constituents together; the alloys are generally hard, some of them are brittle. With *antimony*, two crystalline alloys are formed by melting the metals together, in the ratios 3Zn:2Sb and Zn:Sb, and allowing to cool very slowly; Cooke (*Am. S.* [2] 18, 229; 20, 222) formulates these alloys as Zn_3Sb_2 and Zn_2Sb_2 respectively. These alloys react with water and give off H. Alloys with *arsenic* are formed by heating together Zn and As, or Zn and As_2O_3, or by heating Zn in vapour of As and H; by the last method Descamps (*C. R.* 86, 1022, 1065) obtained crystals agreeing in composition with the formula Zn_3As_2. Spring (*B.* 16, 324) formed an alloy by compressing Zn and As, in the ratio 3Zn:2As, at 6,500 atmospheres. Zinc alloys with *bismuth* when the metals are melted together, but on cooling two layers are formed, the upper containing zinc with c. 2 p.c. Bi, and the lower Bi with from 8 to 14 p.c. zinc. An alloy of zinc with *bismuth and lead* (3 pts. Zn, 5 pts. Bi, and 5 pts. Pb) melts at 94·5°. For descriptions of alloys with *calcium* *v.* Caron (*C. R.* 48, 440; 50, 547); Wöhler (*A.* 138, 253); and Norton a. Twitchell

(*Am. J.* 10, 70). *Brass* is composed of alloys of zinc with *copper* (*v.* vol. ii. p. 254; and for details *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 1052). Alloys of zinc with *copper and nickel* form *German silver*; most modern *bronzes* are alloys of zinc with *copper and tin* (*v.* vol. ii. p. 254; and for details *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 838). Zinc alloys with *iron* (for details *v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 1051). For alloys with *lead v.* vol. iii. p. 125 (also Krant, *S. C. I.* 5, 537). Alloys with *lead and tin* are mentioned in vol. iii. p. 125 (*v.* also Wright a. Thompson, *Pr.* 48, 25). For alloys with *magnesium v.* Parkinson (*J. pr.* 101, 375). Zinc and *mercury* form a number of amalgams, which are brittle when a little Hg is present and pasty when much Hg is present (for references *v. S. C. I.* 9, 512). For alloys with *platinum v.* this vol. p. 288. For alloys with *silver v.* Wright a. Thompson (*Pr.* 48, 25).

For an account of the formation of zinc alloys by immersing zinc in various metallic solutions *v.* Mylius a. Fromm (*B.* 27, 630 [1894]).

Zinc, amide of, $Zn(NH_2)_2$. This compound was obtained by Frankland (*Pr.* 8, 502) by passing dry NH_3 into an ethereal solution of $ZnEt_2$. A white, amorphous powder; unchanged at 200°, but decomposed at a red heat to Zn_3N_2 (*v.* ZINC NITRIDE, p. 889) and NH_3; reacts with water to form ZnO_2H_2 and NH_3.

Zinc, bromide of, $ZnBr_2$. Formula probably molecular, from analogy of $ZnCl_2$. S.G. 3·643 at 10° (Bödeker). Melts at 394° (Carnelley, *C. J.* 33, 277). Boils at 695° to 699° (C. a. Williams, *C. J.* 33, 283); at 650° (Freyer a. V. Meyer, *B.* 25, 622). H.F. $[Zn,Br^2] = 75{,}930$ (*Th.* 3, 275).

Preparation.—1. Zinc filings are heated to dull redness in a stream of Br vapour.—2. Zinc, or ZnO_2H_2, is dissolved in a slight excess of HBrAq, the solution is evaporated to dryness, and the dry residue is sublimed out of contact with air.

Properties and Reactions.—White needles; very deliquescent. Easily soluble in water, alcohol, or ether (*v.* Berthemot, *J. Ph.* 14, 610). Thomsen gives $[ZnBr^2,Aq] = 15{,}030$ (*Th.* 3, 275). Aqueous solutions of $ZnBr_2$ of different concentrations have the following specific gravities according to Kremers (*P.* 108, 115):—

S.G. $ZnBr_2Aq$ at 19·5°.	P.c. $ZnBr_2$.
1·1849	18·3
1·3519	31·7
1·5276	43·2
1·7082	52·6
1·8525	59·1
2·1027	68·0

Combinations.—1. With *ammonia* to form a series of compounds. These compounds were examined by Rammelsberg (*P.* 55, 240), and, more recently, by André (*Bl.* [2] 39, 398 [1883]). By dissolving $ZnBr_2$ in NH_3Aq under different conditions, A. obtained (1) $ZnBr_2.2NH_3.H_2O$, (2) $3ZnBr_2.8NH_3.2H_2O$, (3) $3ZnBr_2.10NH_3.H_2O$, and (4) $ZnBr_2.5NH_3$; by saturating hot NH_4BrAq with ZnO, he obtained $3ZnBr_2.6NH_3.H_2O$.—2. With *cæsium bromide*, to form $ZnBr_2.3CsBr$ and $ZnBr_2.2CsBr$ (Wells a. Campbell, *Zeit. f. anorg. Chemie*, 5, 273).

Zinc, chloride of, $ZnCl_2$. Mol. w. c. 136. Melts at 262° (Braun, *P.* 154, 190). Boils at 708°–719° (Carnelley a. Williams, *C. J.* 33, 284); at 730° (Freyer a. V. Meyer, *B.* 25, 622). S.G. 2·753 at 13° (Bödeker). V.D. at 890° to 907° = 66 (F. a. M., *l.c.*). H.F. $[Zn,Cl^2] = 97{,}210$ (*Th.* 3, 275).

Formation.—1. By heating zinc filings in Cl.—2. By heating a mixture of 2 pts. $HgCl_2$ and 1 pt. zinc filings in a retort.—3. By distilling a mixture of equal pts. $ZnSO_4$ and $CaCl_2$, or a mixture of 1 pt. ZnO and 2 pts. NH_4Cl.—4. By dissolving zinc, or ZnO_2H_2, in HClAq, evaporating to dryness, and heating the residue in a retort.

Preparation.—1. Zinc filings are heated in a small retort in a stream of Cl; the product is distilled.—2. Zinc, or ZnO_2H_2, is dissolved in a slight excess of HClAq; the solution is evaporated to dryness, and the residue is distilled from a small retort.

Properties and Reactions.—A white, semi-transparent, crystalline, very caustic solid; very deliquescent. Easily soluble in water, also in alcohol. Thomsen gives $[ZnCl^2,Aq] = 15{,}630$ (*Th.* 3, 275). Sublimes at a red heat. An aqueous solution is partly decomposed on evaporation, giving oxychlorides (*q.v.*). Oxychlorides are also formed by heating a solution of $ZnCl_2$ in HClAq with ZnO, also with HgO or PbO. Kremers (*P.* 105, 360) gives the following data:

S.G. $ZnCl_2Aq$	P.c. $ZnCl_2$
1·1275	13·8
1·2466	25·8
1·3869	37·5
1·5551	49·2

A conc. solution of $ZnCl_2$ is often used as a bath for maintaining fairly high constant temperatures. Dry $ZnCl_2$ is used as a caustic; also as a dehydrating agent; a dilute aqueous solution is employed as an antiseptic.

Combinations.—1. With *water*. By keeping $ZnCl_2Aq$ containing 70·5 p.c. $ZnCl_2$ at 0° for 24 hours, Engel (*C. R.* 102, 111) obtained large crystals of the *trihydrate*, $ZnCl_2.3H_2O$, melting at 7°. When $ZnCl_2Aq$ containing 79·9 p.c. $ZnCl_2$ at 0° is kept for a long time it solidifies; on heating to 16° a part melts and a part remains solid; the liquid part is the *dihydrate* $ZnCl_2.2H_2O$, and the solid part is the hydrate $2ZnCl_2.3H_2O$ (E., *l.c.*). By heating a syrupy solution of $ZnCl_2$ with a little HClAq, Schindler (*Mag. Pharm.* 36, 45) obtained octahedral crystals of the *monohydrate* $ZnCl_2.H_2O$. According to Engel (*l.c.*), the hydrate obtained by S. was $2ZnCl_2.3H_2O$.—2. With *hydrogen chloride and water*. Engel (*M.* 5, 432) obtained the compounds $2ZnCl_2.HCl.2H_2O$ and $ZnCl_2.HCl.2H_2O$ by passing HCl gas into $ZnCl_2Aq$, and adding zinc from time to time, and, when the solution had the S.G. of 2·0, cooling to 0°.—3. Various compounds of $ZnCl_2$ with *ammonia* have been described; the formulæ $ZnCl_2.NH_3$, $ZnCl_2.2NH_3$, $2(ZnCl_2.2NH_3).H_2O$, $ZnCl_2.4NH_3.H_2O$, and $ZnCl_2.5NH_3.H_2O$ have been given to compounds obtained by dissolving $ZnCl_2$ in NH_3Aq, passing in NH_3, and evaporating under different conditions (*v.* Marignac, *Ann. M.* [5] 12, 1; Divers, *C. N.* 18, 13; Priwoznik, *P.* 142, 467; Davis, *C. N.* 25, 265; André, *A. Ch.* [6] 3, 84, 98; Thoms, *B.* 20, 743).—4. Lang (*B.* 21, 1578) described a compound with *pyridine*, $ZnCl_2.2C_5H_5N$.—5. $ZnCl_2$ combines with *alkali chlorides*. Compounds, $ZnCl_2.NH_4Cl.xH_2O$, $ZnCl_2.2NH_4Cl.xH_2O$, and $ZnCl_2.3NH_4Cl$ are described by Schindler (*Mag. Pharm.* 36, 45), Marignac (*J.* 1857. 217), Rammelsberg (*P.* 94, 508), and Hantz (*A.* 66, 287). A compound $ZnCl_2.2KCl$ is described by R. (*l.c.*) and M. (*l.c.*); and a compound $ZnCl_2.2NaCl.3H_2O$ by M. (*l.c.*). Wells a. Campbell (*Zeit. f. anorg. Chemie*, 5, 273) describe two compounds with CsCl, to which they give the formulæ $ZnCl_2.2CsCl$ and $ZnCl_2.3CsCl$.—6. With *zinc oxide*, *v. Oxychlorides*, p. 891.

A solution of zinc in conc. KClAq, to which as much NH_4Cl has been added as the weight of zinc dissolved, is used for cleaning the surfaces of metals that are to be soldered together; any oxide on the metallic surfaces reacts with the NH_4Cl present to form chloride which dissolves in the $ZnCl_2$ solution.

Zinc, cyanide of, and double zinc cyanides; *v.* vol. ii. p. 347. For details regarding the conditions of formation and the properties of *zinc-mercuric cyanide*, *v.* Dunstan, *C. J.* 61, 666 [1892].

Zinc, ferrocyanide of; *v.* vol. ii. p. 337.

Zinc, fluoride of, ZnF_2. Formula probably molecular, from analogy of $ZnCl_2$. Formed by heating zinc or ZnO to redness in a stream of dry HF; also by the interaction of fused $ZnCl_2$ and dry HF at 800° to 900°; also by heating the hydrated salt to redness in dry HF (Poulenc, *C. R.* 116, 581 [1893]). The *tetrahydrate* $ZnF_2.4H_2O$ is obtained by evaporating a solution of zinc in HFAq, and crystallising. The salt ZnF_2 crystallises in colourless needles, probably monoclinic. S.G. 4·84 at 15°; the crystals act strongly on polarised light (P., *l.c.*). Clarke (*Am. S.* [3] 13, 291) gives S.G. of ZnF_2 as 4·556 at 17°, and 4·612 at 12°; and the S.G. of $ZnF_2.4H_2O$ as 2·567 at 10° and 2·535 at 12°. ZnF_2 is slightly soluble in cold, more soluble in hot, water; it is insoluble in alcohol at 95°; soluble in boiling HClAq, H_2SO_4Aq, or HNO_3Aq (P., *l.c.*). Heated in air, or to redness in steam, it is wholly changed to ZnO; fusion with alkali carbonates produces ZnO and alkali fluorides; heating with H_2S forms ZnS, and with HCl forms $ZnCl_2$. It is reduced by H at a red heat (P., *l.c.*). ZnF_2 forms *double salts* with AlF_3 and with alkali fluorides. Berzelius (*P.* 1, 26) described the salts $ZnF_2.2AlF_3$ and $ZnF_2.2KF$; and Wagner (*B.* 19, 896) the salts $ZnF_2.2NH_4F.2aq$, $ZnF_2.KF$, and $ZnF_2.NaF$. The compound $ZnF_2.ZrF_4.6aq$ ($= ZnZrF_6.6aq$) is described by Marignac (*A. Ch.* [3] 60, 257); S.G. 2·255 at 12° (Topsöe, *C. C.* 4, 76). For $ZnF_2.SiF_4$ *v.* ZINC SILICOFLUORIDE, p. 890.

Zinc, hydrophosphide of, ZnPH. A white, friable solid having this composition was obtained by Drechsel a. Finkelstein (*B.* 4, 352) by passing dry PH_3 into a cooled ethereal solution of $ZnEt_2$. The compound can be kept in a closed vessel; in air it absorbs moisture and rapidly decomposes, giving off PH_3.

Zinc, hydrosulphide of. According to Thomsen (*B.* 11, 2044 [1878]), the pp. obtained by mixing NaHSAq and $ZnSO_4Aq$, in equivalent quantities, is probably a hydrosulphide of zinc (no analyses or formula given). Addition of two equivalents of NaSH in solution to an equivalent of $ZnSO_4$ in solution produces no pp., but the solution gives a pp. of ZnS or hydrosulphide on standing, or on addition of acid or soda (T., *l.c.*). According to von Zotta (*M.* 10, 807 [1890]), the pp. supposed by Thomsen to be zinc hydrosulphide has the composition $ZnS_2H_2.2ZnS$. When four equivalents of NaSH are added to one equivalent of $ZnSO_4$, both in solution, and the clear solution is boiled, or treated with acid or alkali, a pp. of $ZnS_2H_2.2ZnS$ is obtained (von Z., *l.c*). Linder a. Picton (*C. J.* 61, 130 [1892] obtained evidence in favour of the existence of compounds of Zn, S, and H, probably $7ZnS.H_2S$ and $12ZnS.H_2S$, by passing H_2S into water at 0° with ZnO_2H_2 in suspension; they failed to isolate a definite compound with certainty.

Zinc, hydroxide of, ZnO_2H_2. (*Zinc hydrate. Hydrated zinc oxide.*) Obtained, as a white flocculent pp., by adding to solution of a salt of zinc rather less KOHAq than is sufficient to decompose the whole of the salt, washing thoroughly, and drying at a low temperature. According to Ville (*C. R.* 101, 375), ZnO_2H_2 is obtained in crystals by shaking very finely-powdered $ZnCO_3$, or basic carbonate, with twice as much KOH in 10 p.c. solution as is theoretically required for the decomposition of the carbonate; formation of crystals of ZnO_2H_2 begins at once, and is complete after twenty to thirty minutes. ZnO_2H_2 is said to be obtained in lustrous rhombic prisms by immersing zinc in contact with iron or copper in NH_3Aq (Nicklès, *A. Ch.* [3] 22, 31; Cornu, *Bl.* 5, 64 [1863]). Bödeker (*A.* 94. 358) obtained the *monohydrated hydroxide* $ZnO_2H_2.H_2O$ in very lustrous octahedra by keeping a saturated solution of the hydroxide in NaOHAq in a closed vessel for some weeks. S.G. of ZnO_2H_2 is given by Nicklès (*l.c.*) as 2·677, and by Filhol (*A. Ch.* [3] 21, 415) as 3·053. Thomsen gives $[Zn,O,H^2O] = 82,680$ (*Th.* 3, 275). ZnO_2H_2 dissolves easily in acids, forming salts ZnX^I_2.

ZnO_2H_2 also dissolves in caustic alkali solutions, and in $(NH_4)_2CO_3Aq$. By adding alcohol to a solution of ZnO_2H_2 in KOHAq, Laux (*A.* 9, 183) obtained small lustrous crystals (?ZnO_2K_2); Fremy (*C. R.* 15, 1106) obtained (?) $ZnO_2K_2.ZnO$; by using NaOHAq Comey a. Jackson (*B.* 21, 1589 [1888]) obtained two compounds derived from ZnO_2H_2 by replacing H by Na. They shook a solution of ZnO_2H_2 in conc. NaOHAq with alcohol, separated the upper (alcoholic) layer and allowed it to crystallise, and treated the lower (watery) layer repeatedly with alcohol until it solidified. The crystals from the lower layer had the composition

$$Zn_3O_6Na_4H_2.17H_2O\ (= Zn_3(OH)_2(ONa)_4.17H_2O),$$

agreeing, except in water of crystallisation, with an ammonium compound described by Malaguti (*C. R.* 62, 413 [1866]); this compound melts at c. 70°, rapidly absorbs CO_2 from the air, loses $12H_2O$ at 100°, is insol. in ether, and is decomposed by water, but not in presence of excess of NaOH, with formation of ZnO and a little ZnO_2H_2. The crystals from the upper layer had the composition

$$2ZnO_2NaH.7H_2O = (2Zn(OH)(ONa).7H_2O),$$

corresponding with the compound described by Fremy (*l.c.*); this compound forms white radiating needles, which do not melt at 300°; it absorbs CO_2 from the air more slowly than the other compound, is decomposed by alcohol or water, and does not lose H_2O until heated above 200° (*v. Am.* 11, 145 [1889]). C. a. J. failed to obtain compounds derived from ZnO_2H_2 by replacing H by NH_4 or Mg. Compounds of ZnO with BaO, CaO, and MgO are described by Bertrand (*C. R.* 115, 939); these compounds are of the forms $2ZnO.MO.xH_2O$.

Zinc, iodide of, ZnI_2. Formula probably molecular, from analogy of $ZnCl_2$. Formed by heating together zinc and iodine, and subliming; also by digesting I with water and excess of zinc until the liquid is colourless and evaporating over H_2SO_4 (Rammelsberg, *P.* 43, 665). Crystallises in white octahedra; S.G. 4·696 (Bödeker); melts at c. 446° (Carnelley, *C. J.* 33, 278); and boils at c. 624° (C. a. Williams, *v.* Carnelley's *Melting- and Boiling-point Tables,* 1, 23). H.F. $(Zn,I^2) = 49,230$; $[Zn,I^2,Aq] = 60,540$ (*Th.* 3, 275). Heated in air ZnI_2 gives off I, and ZnO remains. Kremers (*P.* 111, 61) gives the following data:—

S.G. ZnI_2Aq	P.c. ZnI_2	S.G. ZnI_2Aq	P.c. ZnI_2
1·2340	23·1	1·9746	63·5
1·5121	42·6	2·3976	76·0
1·7871	56·3		

Hot ZnI_2Aq is said to dissolve zinc in contact with the air, and on filtering an oxyiodide is said to be deposited (Müller, *J. pr.* 26, 441). ZnI_2Aq also dissolves I; Baup (*J. Ph.* 9, 37 [1823]) says enough I is dissolved to form ZnI_4.

ZnI_2 combines with NH_3. By allowing a solution of ZnI_2 in NH_3Aq to evaporate, Rammelsberg (*P.* 48, 152) obtained lustrous, four-sided prisms of $ZnI_2.4NH_3$, decomposed by water with production of ZnO. Various *double compounds* with other iodides have been described: $ZnI_2.2MI$, where $M = NH_4$, K or Na (Rammelsberg, *l.c.*; also *P.* 43, 665); $ZnI_2.2CsI$ and $ZnI_2.3CsI$ (Wells a. Campbell, *Zeit. f. anorg. Chemie,* 5, 273); $2ZnI_2.BaI_2$ (R., *l.c.*); $ZnI_2.2BiI_3.12aq$ (Linau, *P.* 111, 240).

Zinc, nitride of, Zn_3N_2. Obtained by Frankland (*Pr.* 8, 502) by heating zinc amide ($Zn(NH_2)_2$; *v.* p. 887) to low redness. A grey, pulverulent solid; unchanged by heating to redness out of contact with air; reacts violently with water to give ZnO_2H_2 and NH_3.

Zinc, nitroprusside of, *v.* vol. ii. p. 341.

Zinc, oxides of. Besides the normal basic oxide ZnO, there seems to be another higher (? superoxide) of zinc.

ZINC OXIDE ZnO. Formula not certainly molecular.

Occurrence.—With oxides of Mn, and Fe, as *red zinc ore* and *franklinite.*

Formation.—1. By burning zinc in air or O. 2. By strongly heating ZnO_2H_2, $Zn(NO_3)_2$, $ZnCO_3$, or another salt of zinc with a volatilisable acid.

Preparation.—Pure $ZnSO_4$, prepared as described under Zinc, *Preparation* (p. 883), is dissolved in water, and the solution is *very slowly* added to a boiling solution of pure Na_2CO_3 containing rather less Na_2CO_3 than suffices to decompose all the $ZnSO_4$. The pp. of basic zinc carbonate is washed by decantation with boiling water until the washings are free from carbonates and sulphates; it is then dried, powdered, and heated either in a Hessian crucible, or, better, in a flask of hard glass, until a portion taken from the middle dissolves, when cold, in acid without effervescence. The solid is now finely powdered, sifted through a fine sieve, again heated and then rubbed up with water, and washed and dried. ZnO is prepared in crystals by heating $ZnCl_2$ to redness in steam (Daubrée, *C. R.* 39, 153); also by heating the amorphous oxide slowly in a stream of H (Regnault, *A. Ch.* [2] 62, 350; Deville, *A. Ch.* [3] 43, 477); also by heating the amorphous oxide to whiteness in a stream of O (Sidot, *C. R.* 69, 202); also by heating $Zn(NO_3)_2$ to redness (Brügelmann, *W.* 4, 283).

Properties.—A slightly yellow, powdery solid; becomes darker yellow when heated, but recovers its original colour on cooling. S.G. 5·5 to 5·7 (*v.* Brügelmann, *B.* 13, 1741; Filhol, *A. Ch.* [3] 21, 415; Herapath, *C. J.* 1, 42; Karsten, *S.* 65, 394). S.G. crystalline (at 15°) 5·782 (Brügelmann, *W.* 4, 286). ZnO crystallises in slightly yellow, lustrous, hemimorphous pyramids belonging to the hexagonal system (B., *l.c.*). Thomsen (*Th.* 3, 275) gives H.F. $[Zn,O] = 85,430$. Richards a. Rogers (*Am.* 15, 567 [1893]) found that ZnO, prepared by heating $Zn(NO_3)_2$, gave off some gas when dissolved in dilute acids; the maximum amount of gas from 10 g. ZnO was 20 c.c.; the gas consisted chiefly of N, with a little O; the higher the temperature to which the $Zn(NO_3)_2$ had been heated the less was the quantity of gas obtained; but some N always came off, even from ZnO which had been heated to the softening temperature of porcelain. Moissan (*C. R.* 115, 1034 [1892]) states that ZnO volatilises readily when heated in an electric furnace, and condenses again in transparent crystals. ZnO is not decomposed at c. 1750° (Read, *C. J.* 65, 313 [1894]).

Reactions and Combinations.—1. ZnO is a basic oxide. It interacts with most *acids* to form salts $ZnX(X = 2NO_3, SO_4, \frac{2}{3}PO_4$, &c.) and water.—2. With fairly conc. *caustic soda* or *potash*, salts are formed which are most simply regarded as derived from ZnO_2H_2, with H replaced by Na or K (*v.* ZINC HYDROXIDE, p. 888).—3. ZnO is reduced to Zn, with explosive violence, by heating with *magnesium* (*v.* Winkler, *B.* 23, 123).—4. Morse a. White (*Am.* 11, 258) heated a mixture of ZnO and *zinc* in an exhausted tube, and found that a deposit of ZnO formed in the front part of the tube. They suppose that some of the original ZnO is decomposed by the combined action of heat and zinc, and that zinc and O exist together in the hot part of the tube, but combine in the cooler parts of the tube to form ZnO.—5. Oxychlorides, oxybromides, and probably oxyiodides of zinc are formed by heating ZnO with *zinc chloride, bromide,* and *iodide* respectively.—6. ZnO is reduced to zinc by heating with *carbon* or in *carbon monoxide.*—7. ZnO does not directly interact with *water*; ZnO_2H_2 is produced by ppg. a zinc salt solution by an alkali (*v.* ZINC HYDROXIDE, p. 888).—8. By heating ZnO with *oxides of aluminium, chromium,* and *iron* along with B_2O_3 in a pottery furnace until the B_2O_3 was volatilised, Ebelmen (*A. Ch.* [3] 33, 34) obtained the compounds $ZnO.Al_2O_3$, $ZnO.Cr_2O_3$, and $ZnO.Fe_2O_3$.

Zinc peroxide. In 1818 Thénard (*A. Ch.* [2] 9, 55) obtained what he called 'deutoxide de zinc' by the action of H_2O_2Aq on gelatinous ZnO_2H_2, and also by adding KOHAq to a solution of ZnO_2H_2 in HClAq to which H_2O_2 had been added. In 1884 Haas (*B.* 17, 2249) obtained a white, tasteless, neutral, gelatinous pp. by adding H_2O_2Aq to solutions of zinc salts and then adding NH_3Aq; after washing and drying at 100°, the solids had approximately the compositions Zn_5O_8 and Zn_3O_5. H. thinks it probable that the substances obtained by him were compounds of ZnO and ZnO_2; the formula $2ZnO.3ZnO_2$ agrees well with some of his analyses.

Zinc, oxybromides of. Oxybromides of zinc are formed by heating solutions of $ZnBr_2$ with ZnO, and by partially ppg. $ZnBr_2$Aq by NH_3Aq. Several compounds have been described by André (*Bl.* [2] 39, 398 [1884]):
(1) $ZnBr_2.4ZnO.xH_2O$, $x = 10$, 13, and 19;
(2) $ZnBr_2.5ZnO.6H_2O$; (3) $ZnBr_2.6ZnO.35H_2O$.

Zinc, oxychlorides of. These compounds are formed by adding to $ZnCl_2$Aq a quantity of NH_3Aq less than sufficient for complete ppn.; also by boiling $ZnCl_2$Aq with ZnO, or with certain other metallic oxides. Schindler (*Mag. Pharm.* 36, 45) obtained $ZnCl_2.3ZnO.4H_2O$ by boiling $ZnCl_2$Aq with ZnO, and the same compound by partially ppg. $ZnCl_2$Aq by NH_3Aq. By adding to $ZnCl_2$Aq so much NH_3Aq that the pp. which formed at first partly dissolved, and also by treating $ZnCl_2.4NH_3$ with water, Kane (*A. Ch.* 72, 296) obtained $ZnCl_2.6ZnO.10H_2O$. André (*C. R.* 106, 854) obtained $2ZnCl_2.3ZnO.11H_2O$ by boiling $ZnCl_2$Aq with HgO and letting the solution cool; using PbO he obtained another oxychloride, probably $ZnCl_2.3ZnO$, combined with $ZnCl_2.PbO$.

Zinc, oxyiodides of. According to Müller (*J. pr.* 26, 441 [1842]), ZnI_2Aq dissolves zinc when warmed therewith in the air; on cooling, an oxyiodide, $ZnI_2.3ZnO.2aq$, is ppd.

Zinc, oxysulphides of. The compound 4ZnS.ZnO occurs native as *voltzite*, as spherical globules in some specimens of *galena*. A compound having the same composition was found in a furnace flue at Freiberg by Karsten (*S.* 57, 186). By heating dry $ZnSO_4$ to redness in H, Arfvedson obtained a yellow-coloured oxysulphide ZnS.ZnO (*P.* 1, 59).

Zinc, perbromoplatinocyanide of, *v.* vol. ii. p. 345.

Zinc, phosphides of. Zinc and P combine when heated together, forming a greyish, lustrous, somewhat malleable compound. By heating finely powdered zinc in vapour of P, Schrötter obtained a compound, with S.G. 4·76, having the composition Zn_3P_2 (*W. A. B.* 1859. 301). Vigier obtained the same compound by heating zinc in H until distillation began, and then passing H laden with vapour of P over the zinc. The same compound was formed by Regnault (*A. Ch.* [4] 9, 162) by heating to whiteness a mixture of $MgHPO_4$, ZnS and C; along with the Zn_3P_2 were formed crystals of another phosphide, probably ZnP; and by treating Zn_3P_2 with dilute acid, an amorphous, yellow solid remained which detonated when mixed with $KClO_3$ and struck, and which was perhaps ZnP_6. The compound Zn_3P_2 was obtained by Hvoslef (*A.* 100, 99) by strongly heating a mixture of ZnO, P_2O_5, and C. By heating a mixture of $NaPO_3$ and zinc shavings in a retort, H. (*l.c.*) obtained a yellowish red, loose sublimate which contained Zn and P; and by heating the fused mass in the retort with HClAq, grey lustrous tablets of ZnP_2 remained. Lüpke (*C. C.* 1890 [ii.] 642) formed zinc phosphide (? Zn_3P_2) by adding amorphous P to molten zinc covered with $(NH_4)_2CO_3$; this phosphide was not decomposed by water, but was slowly decomposed by dilute HClAq, giving off PH_3.

For the compound ZnPH *v.* Zinc hydrophosphide, p. 888.

Zinc, platinocyanide of, *v.* vol. ii. p. 344.

Zinc, salts of. Many salts are obtained by replacing the H of acids by zinc. The greater number of the salts of zinc are normal salts; several basic carbonates, nitrates, and sulphates are known. The following are the chief salts of zinc derived from oxyacids:—*Arsenite* and *arsenate*, *borate*, *bromate*, *carbonates*, *chlorate* and *perchlorate*, *chromates*, *iodate* and *periodates*, *molybdates*, *nitrates* and *nitrites*, *phosphates* and *phosphites*, *selenate* and *selenite*, *silicate*, *sulphates* and *sulphite*, *thiosulphate*, *tungstates*, *vanadates* (*v.* Carbonates, Nitrates, Sulphates, &c.).

Zinc, selenide of, ZnSe. This compound is formed, in reddish-yellow, regular crystals, S.G. 5·40, by heating zinc to redness in a stream of H_2Se, and then subliming in a slow stream of H (Margottet, *C. R.* 84, 1293).

Zinc, selenocyanide of, *v.* vol. ii. p. 348.

Zinc, silicofluoride of, $ZnSiF_6.6H_2O$. Obtained in hexagonal plates, easily sol. in water, by evaporating to a small bulk a solution of ZnO in H_2SiF_6Aq (Berzelius). S.G. 2·104 (Topsöe, *C. C.* 4, 76).

Zinc, stannifluoride of, $ZnSnF_6.6H_2O$; *v.* this vol., p. 724.

Zinc, sulphocyanide of, *v.* vol. ii. p. 353.

Zinc, sulphide of, ZnS. This compound is not formed by heating together zinc and S, as the S volatilises before the temperature of combination is reached.

Occurrence.—As *zinc blende.*

Preparation.—1. By repeatedly subjecting a mixture of zinc and S, in the ratio Zn:S, to a great pressure; the product resembled zinc blende (Spring, *B.* 16, 1,000).—2. By rapidly heating a mixture of zinc filings and cinnabar in a retort; formation of ZnS occurs with detonation; Hg distils off.—3. By heating ZnO with S.—4. By heating ZnO, or ZnO_2H_2, in a stream of H_2S; in the case of ZnO_2H_2 formation of ZnS takes place very slowly (*v.* Wagner, *D. P. J.* 197, 334).—5. ZnS is also formed by heating dry $ZnSO_4$ with S and C.—6. ZnS is obtained by passing H_2S into a neutral or alkaline solution of a zinc salt, or into a solution in a weak acid, such as acetic acid, washing the pp., drying it at 100°, and heating in a stream of dry H_2S. The pp. dried at 100° is said to be $2ZnS.H_2O$ (Geiger a. Reimann, *Mag. Pharm.* 31, 178; *cf.* Souchay, *Fr.* 7, 78).

Properties and Reactions.—S.G. of ZnS = 3·93 (Karsten, *S.* 65, 394); S.G. of *blende* = 4·03 to 4·07 (*v.* Neumann, *P.* 23, 1). Thomsen (*Th.* 3, 276) gives H.F. of $ZnS.xH_2O$ as $[Zn,S,xH^2O] = 41,580$. ZnS prepared by ppn. is a yellowish solid; easily sol. in acid, forming salts of Zn and giving off H_2S. Zinc blende is a grey to black crystalline solid; slowly acted on by acids. By repeatedly washing ppd. ZnS, also by passing H_2S into water containing pure ZnO_2H_2 in suspension, Winssinger (*Bl.* [2] 49, 452 [1888]) obtained colloidal ZnS, sol. in water; the solution could be boiled until all excess of H_2S was expelled without ppn. of ZnS. ZnS prepared by adding excess of NH_3Aq to $ZnCl_2$Aq, ppg. all the zinc as ZnS by H_2S, washing and drying the pp., and then heating nearly to whiteness in a Hessian crucible inside a plumbago crucible, is very phosphorescent (*v.* Henry, *C. R.* 115, 503).

By heating ZnS with zinc in a vacuous tube, Morse a. White (*Am.* 11, 348) found that some of the ZnS was carried forward and deposited on the cooler part of the tube; they supposed that some of the ZnS was decomposed, and that Zn and S existed in the hottest part of the tube and combined in the cooler portions. By heating *blende* with I and a little water some $ZnSO_4$ is formed (Filhol a. Melhies, *A. Ch.* [4] 22, 58; Lasaulx, *J.* 1870, 1272).

According to Schiff (*A.* 115, 74), a *polysulphide of zinc*, probably ZnS_5, is formed by ppg. a neutral solution of a salt of zinc by K_2S_5Aq, and drying the pp. over H_2SO_4. Spring (*B.* 16, 1000) thought that a polysulphide of zinc was probably formed by strongly compressing a mixture of zinc with excess of S.

Zinc, telluride of, ZnTe. Obtained, in large ruby-red, regular crystals, by strongly heating zinc in a stream of H_2Te, and then subliming in a slow current of H (Margottet, *C. R.* 84, 1293).

Zinc, titanifluoride of, $ZnTiF_6$; *v.* this vol., p. 742.

M. M. P. M.

ZINC, ORGANIC COMPOUNDS OF.

Zinc methyl or **Zinc methide** ZnC_2H_6 *i.e.* $ZnMe_2$. Mol. w. 95. V.D. 3·29 (calc. 3·30). [−40°] (Haase, *B.* 26, 1053). (46°). S.G. $^{14.5}$ 1·386.

Formation.—1. By heating methyl iodide with zinc in sealed tubes at 150°. The compound IZnMe is formed as an intermediate product. The reaction takes place more easily when the MeI is mixed with two-thirds of its volume of ether and heated to 100°, but it is then difficult to separate the ether from the $ZnMe_2$ (Frankland, *A.* 85, 346; 111, 62; Wanklyn, *C. J.* 13, 124; Butlerow, *A.* 144, 2; Ladenburg, *A.* 173, 147).—2. By heating finely granulated zinc with $HgMe_2$ in a sealed tube for 24 hours at 120°, and distilling the product (Frankland a. Duppa, *C. J.* 17, 30).—3. IZnMe is formed in 24 hours if MeI is left in contact with a large amount of copper-zinc couple (Gladstone, *C. J.* 35, 109).

Preparation.—Zinc filings (9 pts.) are heated with reduced copper (1 pt.) till the copper-zinc couple is produced, and the product treated with MeI (Gladstone, *C. J.* 35, 569).

Properties.—Colourless mobile liquid, taking fire on exposure to air. Decomposed by water into CH_4 and $Zn(OH)_2$. By very careful oxidation it appears to yield $Zn(OMe)_2$ and crystalline $ZnMe(OMe)$, which is split up by water into $Zn(OH)_2$, methyl alcohol, and CH_4.

Reactions.—1. *Acetyl chloride* (1 mol.) forms $CH_3.CCl(OZnMe).CH_3$, which is slowly converted, by further treatment with $ZnMe_2$, into $CH_3.CMe(OZnMe).CH_3 + ClZnMe$, crystallising in prisms, and converted by water into *tert-butyl* alcohol, CH_4, zinc chloride, and $Zn(OH)_2$. The compound $CH_3.CCl(OZnMe).CH_3$ yields acetone on addition of water (Butlerow, *Z.* 1864, 365, 702; Pawlow, *N. Petersb. Acad. Bull.* 22, 497; Bogomoletz, *A.* 209, 88).—2. *Bromo-acetyl bromide*, followed by water, yields methyl-iso-propyl-carbinol (Winogradoff, *A.* 191, 127).—3. In ethereal solution *secondary hexyl iodide* has no action at 100°; but at 125° the products appear to be CH_4, ethyl iodide, and hexylene (Purdie, *C. J.* 39, 464).—4. *Chloral* followed by water forms $CCl_3.CHMe.OH$, while butyric chloral yields $C_3H_4Cl_3.CHMe.OH$.—5. *Nitric oxide* passed into $ZnMe_2$ forms $CH_3N_2O_2(ZnMe)$, which is decomposed by water, yielding crystalline $(CH_3N_2O_2)_2Zn$ aq, from which the Na salt $CH_3N_2O_2Na$ aq of 'di-nitro-methylic' acid may be obtained (Frankland, *A.* 99, 369).

Zinc ethyl or **Zinc ethide** $ZnEt_2$. Mol. w. 123. [−28°] (Haase, *B.* 26, 1053). (118°). S.G. ^{18} 1·182. H.F. −31,800 (Guntz, *C. R.* 105, 673). V.D. 4·26 (obs. and calc.).

Formation.—1. By heating zinc or zinc-sodium alloy with EtI or a mixture of EtI and ether (Frankland, *C. J.* 2, 297; 3, 44; *Tr.* 142, 431; 145, 259; *A.* 95, 28; Wanklyn, *C. J.* 13, 121; Pebal, *A.* 118, 22; 121, 105; Rieth a. Beilstein, *A.* 123, 245; 126, 248; Chapman, *Laboratory*, 1, 195; Alexejeff a. Beilstein, *C. R.* 63, 171; Rathke, *A.* 152, 220; Wichelhaus, *J.* 1868, 425).—2. By heating granulated zinc with $HgEt_2$ in sealed tubes for 36 hours at 100° (Frankland a. Duppa, *C. J.* 17, 3).—3. From zinc filings and EtBr (Wichelhaus, *A.* 152, 321).

Preparation.—Clean zinc filings (180 g.) are mixed with copper (20 g.) reduced from the oxide at a dull-red heat by coal gas; the mixture is rapidly heated over a very large Bunsen flame, and is well shaken meanwhile. As soon as the filings begin to cake together and the copper is no longer visible, the copper-zinc couple has been made. The flask is now connected with an inverted condenser, inclined slightly upwards, and when it is cold ethyl iodide (175 g.) is added. Dry CO_2 is passed through the apparatus, and the flask heated by a water-bath; in half an hour the EtI ceases to run back from the condenser, for it has been converted into IZnEt. The apparatus is now tilted so that the condenser is inclined downwards, and heated in a bath of paraffin. The reaction $2IZnEt = ZnI_2 + ZnEt_2$ now takes place, and $ZnEt_2$ (60 g.) is collected in a receiver kept full of CO_2 (Gladstone a. Tribe, *C. J.* 26, 445; 35, 569).

Properties.—Colourless, mobile liquid, fuming in the air, and quickly taking fire, burning with a luminous green-edged flame, and giving off clouds of ZnO. Immediately decomposed by water into $Zn(OH)_2$ and ethane. In like manner it attacks organic compounds containing hydroxyl or amidogen, with elimination of ethane. It causes india-rubber to swell remarkably.

Reactions.—1. Gradually treated with dry *oxygen* it appears to produce $ZnEt(OEt)$ and $Zn(OEt)_2$ successively (Frankland). According to Demuth a. Meyer (*B.* 23, 894), the passage of oxygen through a solution of $ZnEt_2$ in ligroin

(7 vols.) yields EtZn.O.O.Et, which is decomposed by heat, sometimes with explosive violence. The compound EtZn.O.OEt sets free I from a solution of KI and yields alcohol when distilled with dilute H_2SO_4.—2. *Sulphur* forms zinc mercaptide $Zn(SEt)_2$. Se appears to act in like manner (Chabrié, *Bl.* [3] 2, 788).—3. *Iodine* forms IZnEt and ZnI_2 successively, together with EtI. Bromine acts in like manner. Zinc ethyl takes fire in chlorine.—4. Dry *ammonia* forms $Zn(NH_2)_2$ and ethane (Frankland, *Pr.* 8, 502).—5. *Nitric oxide* is absorbed by an ethereal solution of $ZnEt_2$ forming crystalline $ZnEt_2(NO)_2$ which melts below 100° and is split up by water into ethane and $C_2H_5.N_2O_2.ZnOH$. Carbon dioxide passed into an aqueous solution of this salt ppts. zinc carbonate, while zinc 'dinitroethylate' $(C_2H_5N_2O_2)_2Zn$ remains in solution (Frankland, *Tr.* 1857, 59; *A.* 99, 342; *C. J.* 37, 570). The salt $(C_2H_5N_2O_2)_2Zn$ aq crystallises in prisms, yields NH_3 and NH_2Et on treatment with sodium-amalgam (Zuckschwerdt, *A.* 174, 302), and HNO_3 and NH_2Et on treatment with alcoholic potash (Zorn, *B.* 15, 1008). The dinitroethylates NaA′, BaA'_2, $CaA'_2$3aq, MgA'_2, $CuA'_2\frac{1}{2}$aq, AgA′, and $Ag_2A'(NO_3)$ were prepared by Frankland.—6. SO_2 forms zinc ethane sulphinate (Hobson, *C. J.* 10, 455).—7. PCl_3 yields PEt_3 (Hofmann a. Cahours, *Tr.* 1857, 578).—8. $SiCl_4$ gives $SiEt_4$.—9. Heated with EtI at 170° it forms *n*-butane and ZnI_2. Ethane and ethylene are also formed (Brodie, *C. J.* 3, 405). $ZnEt_2$ does not act on amyl iodide.—10. Displaces halogens in organic compounds by ethyl.—11. Adds itself to a carbonyl group. Thus with *di-ethyl-ketone* it forms $Et_2C(OZnEt).Et$, which is converted by water into tri-ethyl-carbinol. *Di-propyl ketone* forms, in like manner, ethyl-di-propyl-carbinol. Ketones containing the group $CO.CH_3$ act differently, forming condensation-products; thus acetone yields mesityl oxide and phorone (A. Saytzeff, *J. pr.* [2] 31, 319). Zinc ethyl has no action on paraldehyde (Wedensky, *J. pr.* [2] 39, 568). With acetic aldehyde it forms $CH_3.CHEt.OZnEt$, which is converted by water into *sec*-butyl alcohol.—12. In some cases it can add ZnEt and H to a carbonyl group, C_2H_4 being evolved. Thus $ZnEt_2$ converts *chloral*, dissolved in pure ether, into crystalline $CCl_3.CH_2.OZnEt$, which is converted by water into tri-chloro-ethyl alcohol (Delacre, *Bl.* [2] 48, 784). Further action of zinc ethide on chloral yields $(CCl_3.CH_2O)_2Zn$, a white powder. In like manner butyric chloral is converted into $C_3H_4Cl_3.CH_2.OH$. In this splitting off of an olefine, $ZnEt_2$ differs from $ZnMe_2$, but resembles zinc propyl and zinc isobutyl (Garzarolli, *A.* 223, 162).—13. Can displace oxygen by two ethyl radicles; thus it converts *oxalic ether* into $CO_2Et.CEt_2.CO_2Et$ (Frankland a. Duppa, *A.* 142, 1; *Pr.* 12, 396).—14. Can displace ethoxyl by ethyl. Thus it converts *formic ether* into HCEt(OZnEt).OEt and then into HCEt(OZnEt).Et, which is turned by water into di-ethyl-carbinol (Wagner a. Saytzeff, *A.* 175, 351).—15. Can displace chlorine by hydrogen. Thus with *chloro-benzoic acid* the first product is probably $C_6H_4(ZnEt).CO_2Et$, which is converted by water into benzoic ether, C_2H_6, and ZnO.—16. With *benzonitrile* at 150°, and subsequent treatment with alcohol, cyaphenine is formed (Frankland a. Evans, *C. J.* 37, 568). It polymerises phenyl-acetonitrile in the same way, forming cyanbenzine.—17. *Cyanogen* forms $ZnCy_2$ and EtCN (Frankland a. Graham, *C. J.* 37, 740).—18. *Azobenzene* is reduced by $ZnEt_2$, followed by water, to aniline (Frankland a. Louis, *C. J.* 37, 563).—19. Acts on primary and secondary amines, giving off ethane, but has no action on tertiary amines (Frankland, *Pr.* 8, 502; Gal, *J. Ph.* [5] 7, 484). $ZnEt_2$ has no action on nicotine or quinoline, but forms with many alkaloids containing O compounds from which the alkaloids are regenerated by water.—20. *Acetamide* gives $(AcNH)_2Zn$, while oxamide gives $C_2O_2(NH)_2Zn$.—21. Acts on $HgCl_2$, forming ClHgEt and $HgEt_2$ (Buckton, *A.* 109, 218). Hg_2Cl_2 yields $HgEt_2$, mercury, and $ZnCl_2$.—22. AgCl forms $ZnCl_2$, silver, and butane.—23. CCl_4 forms EtCl, ethylene, and propylene (Rieth a. Beilstein, *A.* 124, 242).—24. *Chloroform* yields amylene (R. a. B.), while bromoform gives propylene and EtBr (Alexejeff a. Beilstein, *C. R.* 58, 172). $CHCl_2I$ produces ethylene, butane, and hydrogen (Borodine, *A.* 126, 239).

Zinc bromo-ethide ZnBrEt. [62°]. Formed by the action of the copper-zinc couple on EtBr at 100° (Gladstone a. Tribe, *C. J.* 27, 410). Pearly scales, decomposed by heat partly into $ZnBr_2$ and $ZnEt_2$ and partly into Zn, $ZnBr_2$, C_2H_4, and C_2H_6.

Zinc iodo-ethide ZnIEt. Formed in like manner. Crystalline. Split up by heat into ZnI_2 and $ZnEt_2$.

Zinc propyl $ZnPr_2$. (148°) (S.); (146°) (Gladstone a. Tribe, *B.* 6, 1136); (150°) (Pape, *B.* 14, 1873). Formed by heating propyl iodide with zinc and a small quantity of an alloy of zinc and sodium (Stcherbakoff, *Bl.* [2] 37, 345). Heavy liquid, with disagreeable odour. Reacts with aldehydes, forming propylene and such compounds as $RCH_2.OZnPr$, which yield secondary alcohols on addition of water.

Zinc isopropyl $ZnPr_2$. (136°) with decomposition; (96° at 40 mm.). Got by heating PrI (170 g.) with ether (100 g.), zinc (100 g.), and zinc-sodium (3 g.) at 100° (Ragozin, *J. R.* 24, 549). Fuming liquid. Yields crystalline $Zn(OPr)_2$ on exposure to air. Split up at 132° into Zn and hydrocarbons (Gladstone a. Tribe, *C. J.* 39, 6).

Zinc isobutyl $Zn(C_4H_9)_2$. (166°) at 734 mm. (Garzarolli-Thurnlackh a. Popper, *A.* 223, 167). Formed from zinc and $Pr.CH_2I$. Got also from Zn and $Hg(C_4H_9)_2$ (Cahours, *Bl.* [2] 21, 357).

Zinc isoamyl $Zn(C_5H_{11})_2$. (220°). S.G. ^{0} 1·022. V.D. 6·95 (calc. 6·87). Prepared by heating zinc with $Hg(C_5H_{11})_2$ (Frankland, *A.* 85, 360; 130, 122). Liquid, fuming in the air but not taking fire. Takes fire in oxygen. When added to cooled aldehyde it yields, after addition of ice-cold water, methyl-isoamyl-carbinol, isopropyl-ethylene, and ethyl and isoamyl alcohols (Sokoloff, *C. C.* 1887, 988).

ZINCATES. Compounds derived from ZnO_2H_2 by replacing H by positive metals; *v.* ZINC HYDROXIDES, p. 888.

ZIRCONATES *v.* under ZIRCONIUM HYDROXIDE, p. 896.

ZIRCONIA; *oxide of zirconium* (*q. v.*, p. 896).

ZIRCONIUM. Zr. At. w. c. 90 (*v.* p. 894). Mol. w. not known. Melts above m.p. of Si (*i.e.* above c. 1300°) (Troost, *J.* 1865. 188). S.G. 4·15 (Troost, *l.c.*); 4·25 (Moissan, *C. R.* 116, 1222). S.H. (0°–100°) ·066 (Mixter a. Dana, A. 169, 388 [1873]).

Historical.—Klaproth in 1789 (*Beiträge*, 1, 203, 227) announced the discovery of a new earth, in combination with silica, in the rare mineral *zircon*. The same earth has been found in a few other rare minerals, such as *eudialyte*, *polymignite*, *fergusonite*, &c. Bright-coloured varieties of zircon are generally called *hyacinth*, the greyish or brown kinds are called *zirconite*, and a variety which is nearly colourless is known as *jargon*.

In 1845 Svanberg (*A.* 56, 223) stated that zirconia was a mixture of at least three oxides, but Berlin (*J. pr.* 58, 147), Marignac (*A. Ch.* [3] 60, 257), and Hermann (*J. pr.* 31, 75; 97, 331) failed to obtain any evidence of the composite character of zirconia. At a later time, Sorby (*B.* 2, 126, 193 [1869]), and also Forbes (*B.* 2, 337, 383), thought they had obtained spectroscopic indications of the presence of another earth in *zircon*; but it was shown that the abnormalities observed were due to traces of compounds of uranium (Sorby, *C. N.* 21, 73; Knop, *A.* 159, 44; *cf.* Hannay, *C. J.* 26, 703).

Occurrence.—Never uncombined. The principal naturally occurring compound of Zr is *zirconite*, which is more or less pure $ZrSiO_4$. This mineral is found in small quantities in the sand and alluvial deposits of certain rivers in Ceylon, and in the older rocks in many parts of the world; it has been found in the granites of Sweden, Switzerland, Tyrol, and North America (*v. J. M.* 1877. 97).

Formation.—1. By heating K_2ZrF_6 with K (Berzelius, *P.* 4, 117 [1825]).—2. By passing vapour of ZrF_4 over Na in a red-hot tube (Troost, *C. R.* 61, 109 [1865]).—3. By heating ZrO_2 with Mg (Phipson, *J. pr.* 96, 353 [1865]).—4. By melting ZrO_2 in a carbon crucible in an electric furnace; or by mixing ZrO_2 with carbon, melting in an electric furnace, then mixing the Zr carbides thus formed (*v. Carbides*, p. 894) with excess of ZrO_2 and again melting (Moissan, *C. R.* 116, 1222 [1893]).

Preparation.—1. Finely powdered *zirconite* ($ZrO_2.SiO_2$) is thoroughly mixed with an excess of finely powdered carbon, the mixture is compressed into small cylinders which are placed in a closed carbon crucible and heated in an electric furnace (with a current of 30 to 35 ampères and 70 volts), while a stream of CO_2 is sent through the crucible; the greater part of the SiO_2 is thus volatilised (Troost, *C. R.* 116, 1428). The carbides of Zr in the crucible are now mixed with excess of ZrO_2 and melted in the electric furnace (Moissan, *C. R.* 116, 1222).—2. Finely powdered and sifted *zirconite* is mixed with 2 to 3 times its weight of KHF_2, the mixture is heated to bright redness for c. 15 mins., and, after cooling, is boiled with water containing a little dilute HFAq; K_2SiF_6 is removed by filtration, the filtrate deposits K_2ZrF_6 on cooling. The K_2ZrF_6 is re-crystallised from water, then dried, mixed with K, and heated in a vessel of glass or iron; the product is washed with water, digested for a long time with conc. HClAq at 40°, then washed with water containing NH_4Cl, and finally with alcohol (Berzelius, *l.c.*; Troost, *A.* 136, 353). This method yields *amorphous zirconium*. According to Bailey (*Pr.* 46, 74 [1889]), the only method that gives nearly pure amorphous Zr is to heat ZrO_2 with Mg foil (not powder) and treat with HClAq.—3. *One part dry K_2ZrF_6 is mixed with 1½ pts. Al and the mixture is heated to the* melting-point of iron in a crucible made of gas coke; the product is digested with conc. HClAq diluted with twice its volume of water, when the crystalline leaflets of Zr, that have formed on the surface of the Al, separate from the mass of Al before the latter is wholly dissolved. When the whole of the Al has dissolved an alloy of Zr and Al remains, besides the crystalline leaflets of Zr; if the temperature of reduction is not sufficiently high, the main product is the Zr-Al alloy (Troost, *l.c.*; *cf.* Franz, *B.* 3, 58). This method yields *crystalline zirconium*.

Various methods have been used for decomposing *zirconite* and obtaining compounds of Zr. Franz (*B.* 3, 58) fuses the powdered mineral with $KHSO_4$, treats the fused material with boiling water containing a little H_2SO_4, washes the insoluble $3ZrO_2.SO_3$ thus formed, and adds it, in small portions at a time, to molten NaOH; he then lixiviates with cold water, dissolves the ZrO_2 that remains in hot conc. H_2SO_4, dilutes, ppts. by NH_3Aq, washes, dries, and decomposes the $ZrO_2.xH_2O$ by heat. The method of fusing with KHF_2 used by Marignac (*v. supra*, No. 2) yields pure K_2ZrF_6 very readily; $Zr(SO_4)_2$ may be obtained by heating the K_2ZrF_6 with conc. H_2SO_4 (*v.* Hiortdahl, *A.* 137, 34; *cf. J. pr.* 83, 201). For other methods *v.* Hermann (*J. pr.* 97, 330); Scheerer (*P.* 59, 48); Stromeyer (*A.* 113, 727); Chancel (*J. pr.* 74, 471); Berlin (*J. pr.* 58, 145); Henneberg (*J. pr.* 38, 508); Bailey (*Pr.* 46, 74 [1889]).

Properties.—Zirconium has been isolated as black amorphous powder, and also as a greyish crystalline solid.

Amorphous zirconium (*v. Preparation*, No. 2) is a black powder, which is extremely porous and resembles powdered charcoal; when pressed with a burnisher it agglomerates to graphite-like laminæ. After being heated strongly, and then cooled, *in vacuo*, it is said to glow and burn when exposed to air. The porous amorphous metal is said not to conduct electricity. Amorphous Zr is stated to be insoluble in ordinary acids, including *aqua regia*; but, according to Bailey (*Pr.* 46, 74 [1889]), it dissolves in cold conc. H_2SO_4; HFAq dissolves it readily, H being given off. It is oxidised by heating in the air, when it burns to ZrO_2 with a brilliant white light; oxidation is also effected by fusion with caustic or carbonated alkalis, or with KNO_3 or $KClO_3$.

Crystalline zirconium (*v. Preparation*, No. 3) is a very lustrous, greyish, brittle, solid, which resembles Sb in appearance; very hard, easily scratching glass and ruby (Moissan, *C. R.* 116, 1222). S.G. 4·15 (Troost, *J.* 1865. 183); 4·25 (Moissan, *l.c.*). S.H. (0° to 100°) ·066 (Mixter a. Dana, *A.* 169, 388 [1873]). Crystalline Zr burns in the O-H flame; it is not oxidised in O until heated to whiteness; it dissolves slowly in hot conc. HClAq, and is very slightly acted on by HNO_3Aq or H_2SO_4, even when warm; cold HFAq dissolves it readily. Molten $KClO_3$, or KNO_3, is said to be without action; molten KOH dissolves the metal as long as any moisture is present.

According to Troost (*J.* 1865. 188), Zr melts above the m.p. of Si (*i.e.* above c. 1800°). The emission-spectrum of Zr has been mapped by Thalén; the chief lines are 6127 in the red, and in the blue, 4815, 4771, 4738, 4709, and 4686.

The at. w. of Zr was determined, (1) by Berzelius (*P.* 4, 126; 8, 186 [1825]), by finding the ratio of ZrO_2 to SO_3 in the sulphate; (2) by Hermann (*J. pr.* 31, 77 [1844]) by analysing $ZrCl_4$: (3) by Marignac (*A. Ch.* [3] 60, 270 [1860]), by analysing K_2ZrF_6; (4) by Bailey (*Pr.* 46, 74 [1889]), by decomposing $Zr(SO_4)_2$ by heat and weighing the ZrO_2 produced; (5) by Mixter a. Dana (*A.* 169, 388 [1873]), by determining the S.H. of Zr; (6) by Deville a. Troost (*P.* 108, 636; 641 [1859]), by determining the V.D. of $ZrCl_4$. The results of Berzelius gave the at. w. of Zr as 89·2; those of Hermann, 88·5 to 90·7; those of Marignac, 90·3 to 90·6; and the results obtained by Bailey gave 90·4 as the at. w. of the metal.

Zirconium is the third member of the even-series family of Group IV. in the periodic classification of the elements. This group contains the following elements:—

Even Series	2	4	6	8	10	12
	C	Ti	Zr	Ce	—	Th
Odd Series	3	5	7	9	11	
	Si	Ge	Sn	—	Pb	

As is to be expected from its position in the classificatory system, Zr is a metal with some non-metallic properties; the oxide ZrO_2 forms corresponding salts, many of which are basic salts; the haloid compounds, ZrX_4, are probably all volatilisable without decomposition (the V.D. of $ZrCl_4$ only has been determined), but aqueous solutions yield oxyhalides on evaporation; hydrated ZrO_2 reacts as a weak acid towards strong bases, forming zirconates; salts are known derived from the acid H_2ZrF_6; there is an oxide higher than ZrO_2, probably ZrO_3. For a more detailed comparison of Zr with the other even-series elements of Group IV. *v.* TITANIUM GROUP OF ELEMENTS (this vol. p. 749), and *cf.* TIN GROUP OF ELEMENTS (this vol. p. 735). The atom of Zr is tetravalent in the gaseous molecule $ZrCl_4$.

Reactions and Combinations.—1. Heated in *air*, or *oxygen*, Zr burns to ZrO_2, giving out dazzlingly white light; amorphous Zr burns easily, crystalline only at a white heat, and then merely superficially.—2. Both amorphous and crystalline Zr dissolve readily in *hydrofluoric acid*, giving off H and forming ZrF_4.—3. According to Bailey (*Pr.* 46, 74), amorphous Zr dissolves in cold conc. *sulphuric acid.* Both forms dissolve in *aqua regia.*—4. Conc. *hydrochloric acid* reacts with Zr, when warm, forming $ZrCl_4$ solution. Crystalline Zr is said to interact with *gaseous hydrogen chloride*, at dull redness, forming $ZrCl_4$.—5. Amorphous Zr is oxidised by *molten potash* or *soda*, also by *molten nitre* or *potassium chlorate*; the crystalline form of Zr is said not to be acted on by molten KNO_3 or $KClO_3$, and by molten caustic alkalis only as long as there are traces of moisture present.—6. Zr combines directly with the *halogens*, to form ZrX_4, and probably with *sulphur* (*v. Sulphide*, p. 897).

Detection and Estimation.—Addition of hot conc. K_2SO_4Aq to solutions of salts of Zr ppts. white basic sulphate of Zr, which is insoluble in water and nearly insoluble in much HClAq. Turmeric paper becomes reddish-brown when immersed in a solution of a salt of Zr in HClAq; the reaction is completely masked by the presence of boric acid (*v.* Brush, *J. pr.* 62, 7). Bailey (*C. J.* 49, 481 [1886]) found that addition of H_2O_2Aq to a slightly acid solution containing salts of Zr, along with salts of Fe, Nb, and Ti, ppd. the whole of the Zr as ZrO_3 (or Zr_2O_5), but none of the other metals. Troost makes use of the comparatively small volatility of ZrO_2 at a very high temperature, to separate this oxide from SiO_2 (*v. C. R.* 116, 1428).

Zr is generally estimated as ZrO_2; salts of volatilisable acids are decomposed by heat; or solutions may be ppd. by NH_3Aq and the pp. washed, dried, and strongly heated.

Zirconium, alloys of. An alloy of Zr with *aluminium* is obtained in the preparation of Zr by reducing K_2ZrF_6 by Al (*v. Preparation of Zirconium*, No. 3). Mellis (*Z.* [2] 6, 296) obtained crystals having the composition $ZrAl_3$ (or perhaps Zr_2Al_6Si) by heating to whiteness a mixture of 1 pt. powdered *zirconite* with 5 pts. *cryolite* powder, 10 pts. mixed KCl and NaCl, and 1 pt. Al, treating with dilute HClAq, and separating the larger crystals of the alloy from the finer crystals of Si.

Zirconium, bromide of, $ZrBr_4$. Formula probably molecular, from analogy of $ZrCl_4$. Obtained by mixing finely powdered ZrO_2 with sugar charcoal, making into balls with starch paste, drying, and heating to bright redness in a current of *dry* CO_2 and *dry* Br (Mellis, *Z.* [2] 6, 296). $ZrBr_4$ is a white, microscopically crystalline, hygroscopic powder; it is easily volatilised; heated in H it is not reduced to a lower bromide. Contact with moist air or water produces the oxybromide $ZrOBr_2$; evaporation of an aqueous solution gives the heptahydrate of this compound $ZnOBr_2.7H_2O$ in large needle-shaped, transparent crystals (M., *l.c.*).

Zirconium, carbides of. By heating an intimate mixture of ZrO_2 and C in the electric arc, in an atmosphere of CO_2, Troost (*C. R.* 116, 1227 [1893]) obtained a very hard, steel-grey solid, approximating closely to the composition ZrC_2. By using less C, other carbides seem to be produced (*cf.* Moissan, *C. R.* 116, 1222), but analyses of other compounds are not given. ZrC_2 dissolves easily in dilute HFAq, but is not acted on by other acids. Moissan (*l.c.*) says that carbides of Zr containing more than 5 p.c. C (ZrC_2 contains c. 21 p.c. C) take fire fairly easily when exposed to the air; Troost says that carbides with a small proportion of C are only superficially oxidised by heating to redness, but that those with much C burn brilliantly at that temperature.

Zirconium, chloride of, $ZrCl_4$. Mol. w. c. 231·5. V.D. 117 at 440° (Deville a. Troost, *P.* 108, 636).

Formation.—1. By heating Zr in Cl.—2. By heating an intimate mixture of ZrO_2 and C in Cl.—3. By passing vapour of $SiCl_4$ over heated ZrO_2 (Troost a. Hautefeuille, *C. R.* 75, 1819).

Preparation.—A mixture of ZrO_2 with c. its own weight of lampblack is made into a paste with oil; little balls, c. the size of hazel-nuts are formed of this, and these are covered with powdered charcoal, and heated to full redness in a closed crucible until the oil is completely charred; the pellets are then heated to bright redness in a tube of hard glass, while a current of dry Cl is passed through the tube; the $ZrCl_4$ which forms on the cooler parts of the tube is sublimed, in a stream of dry Cl, into a tube drawn out into bulbs, which are sealed off when the operation is finished (*v.* Bailey, *Pr.* 46, 74).

Properties, Reactions, and Combinations.—A white solid; volatilises unchanged at c. 400°. Dissolves in *water*, with production of heat; the solution on evaporation gives *oxychlorides* (*q.v.*). Does not interact with *zinc ethide* at 180° (Hinsberg, *A.* 239, 253). Combines with *ammonia* to form $ZrCl_4.4NH_3$; with *sodium chloride* to form $ZrCl_4.2NaCl$ (Paykull, *B.* 6, 1467).

Zirconium, ferrocyanide of. According to Hornberger (*A.* 181, 232), the pp. formed by adding K_4FeCy_6Aq to a solution of a salt of Zr, when washed and dried, has the composition $Zr_3(FeCy_6)_2$(?); it is a blue powder with a greenish tinge, insoluble in water, decomposed by acids, giving off HCN.

Zirconium, fluoride of, ZrF_4. Formula probably molecular, from analogy of $ZrCl_4$.

Formation.—1. The *hydrated* compound $ZrF_4.3aq$ is formed by slowly evaporating a solution of ZrO_3H_2, or ZrF_4, in HFAq.—2. By heating ZrO_2 with twice its weight of $(NH_4)HF_2$ to dull redness, till all the ammonium salt is volatilised (Marignac, *A. Ch.* [3] 60, 263).

Preparation.—Deville (*A. Ch.* [3] 49, 84) obtained ZrF_4 by heating to whiteness a mixture of finely powdered *zirconite* and *fluorspar* in a stream of HCl (? $ZrSiO_4 + 2CaF_2 + 2HCl = ZrF_4 + CaCl_2 + CaSiO_3 + H_2O$).

Properties and Reactions.—Prepared as described, ZrF_4 is a colourless, transparent, crystalline (probably hexagonal) solid; volatilisable at white heat; insoluble in water and acids. ZrF_4 prepared by heating ZrO_2 with $(NH_4)HF_2$ is said to be soluble in water and in dilute HFAq. The crystals of $ZrF_4.3aq$ are partially decomposed on drying. Heated to full redness in air, ZrF_4 gives ZrO_2 and HF.

Combinations.—1. With *water* (*v. Formation*, No. 1) to form $ZrF_4.3aq$.—2. With various *metallic fluorides* to form compounds of the form $ZrF_4.xMF.yH_2O$. These salts are often called *zircono-fluorides*, or *fluo-zirconates*; they are better named *zirconi-fluorides*. The zirconi-fluorides have been examined chiefly by Marignac (*A. Ch.* [3] 60, 257); they are obtained either by gradual evaporation of solutions containing the constituent fluorides, or by adding hydroxides or carbonates of the various metals to solutions of ZrF_4 in HFAq, and evaporating.

Ammonium zirconi-fluorides. Two salts are described: (1) $2NH_4F.ZrF_4 = (NH_4)_2ZrF_6$, rhombic crystals, isomorphous with K_2ZrF_6; (2) $3NH_4F.ZrF_4$, small octahedra, showing simple refraction (Baker, *C. J.* 35, 762).

Cadmium zirconi-fluorides. Two salts seem to exist: (1) $2CdF_2.ZrF_4.6aq$, monoclinic crystals, isomorphous with the Mn salts; (2) $CdF_2.2ZrF_4.6aq$, laminar, fan-shaped groups of crystals.

Manganese zirconi-fluorides. (1) $MnF_2.ZrF_4.5aq$; and (2) $2MnF_2.ZrF_4.6aq$.

Nickel zirconi-fluorides. (1) $NiF_2.ZrF_4.6aq$, hexagonal prisms; S.G. 2·227 (Topsöe, *C. C.* 4, 76); and (2) $2NiF_2.ZrF_4.12aq$, monoclinic crystals. The first salt forms a *double salt* with K_2ZrF_6, viz. $NiZrF_6.K_2ZrF_6.8aq$.

Potassium zirconi-fluorides. (1) K_2ZrF_6; obtained by strongly heating *zirconite* with two or three times its weight of KHF_2, boiling with very dilute HFAq, filtering from K_2SiF_6, and allowing the filtrate to cool. Crystallises in rhombic crystals, terminated by six-sided pyramids; solubility = ·78 at 2°, 1·4 at 15°, 2·7 at 19°, and 25 at 100°. S.G. 3·582 (Topsöe, *l.c.*); (2) $KF.ZrF_4.aq$ ($= KZrF_5.aq$); obtained, in monoclinic crystals, by dissolving the preceding salt in water containing a large excess of ZrF_4. (3) $3KF.ZrF_4$ ($= K_3ZrF_7$); obtained by crystallising K_2ZrF_6 from a solution containing excess of KF; small, brilliant, regular octahedra, with simple refraction (*v.* Baker, *C. J.* 35, 762). Soluble in water; the hot conc. solution deposits K_2ZrF_6 on cooling.

Sodium zirconi-fluorides. The salt $5NaF.2ZrF_4$ is said to be always formed in whatever proportion the constituent fluorides are mixed. Small, monoclinic crystals; solubility at 18° = ·38, and at 100° = c. 1·6.

Zinc zirconi-fluorides. (1) $ZnZrF_6.6aq$, isomorphous with $ZnSiF_6.6aq$ and $ZnSnF_6.6aq$, crystallising in regular hexagonal prisms, easily soluble in water. S.G. 2·255 (Topsöe, *l.c.*). (2) $2ZnF_2.ZrF_4.12aq$; deposited from a solution containing excess of ZnF_2, in monoclinic crystals, isomorphous with $2NiF_2.ZrF_4.12aq$.

Zirconium, hydride of. By heating ZrO_2 and Mg powder, in the ratio ZrO_2:2Mg, in an atmosphere of H, Winkler (*B.* 24, 888; *cf. B.* 23, 2666) obtained a black powder which burnt in O, and contained c. ·73 p.c. H. On treating this with dilute HClAq, Mg and MgO dissolved, H being given off, and a black residue was left which W. regarded as ZrH_2. Supposing the reduction of the ZrO_2 had proceeded in accordance with the equation $ZrO_2 + 2Mg + 2H = 2MgO + 2ZrH_2$, the product would have contained 53·44 p.c. ZrH_2, and, therefore, would have given 1·15 p.c. H; as only ·73 p.c. H was found, W. concluded that c. $\frac{1}{3}$ of the ZrO_2 had been reduced.

Zirconium, hydroxide of, (?) ZrO_3H_2. Addition of NH_3Aq to a solution of a salt of Zr produces a white, bulky, gelatinous pp. of $ZrO_2.xH_2O$. According to Berzelius, the dry pp. has the composition $ZrO_2.H_2O = ZrO_3H_2$; Hermann (*J. pr.* 97, 318) gave the formula $ZrO_2.2H_2O = ZrO_4H_4$ to the pp. dried at 17·5°; Paykull (*B.* 12, 1719) said that after drying *in vacuo* the composition was $ZrO_2.3H_2O$. and after drying at 100° $ZrO_2.H_2O$. A detailed examination of the dehydration of the pp. formed by adding NH_3Aq to a cold solution of $Zr(SO_4)_2$ was made by Carnelley a. Walker (*C. J.* 53, 88, 82 [1888]). The loss of water by the air-dried pp. was fairly regular to c. 90°, when the pp. had approximately the composition $ZrO_2.2H_2O$; the loss was then less rapid, but very regular, up to c. 385°, whereat the composition was approximately $2ZrO_2.H_2O$; somewhere between 385° and 415° there was a sudden increase in the percentage loss of water for a rise of 10°, this increase being accompanied by a change of colour from grey to pure white; at 415° the composition was approximately $24ZrO_2.H_2O$; water was then given off very regularly, until at c. 550° dehydration was completed. C. a. W. conclude that probably no definite hydrate of ZrO_2, unchanged throughout a fair range of temperature, is formed by heating $ZrO_2.xH_2O$ ppd. from a salt of Zr; they think that the change of colour which accompanies the comparatively large percentage loss of water at c. 400° is an accompaniment of a condensation of molecules chiefly of the composition $n(2ZrO_2.H_2O)$ to molecules chiefly of the composition $n(24ZrO_2.H_2O)$. There is a distinct resemblance between the phenomena of the dehydration of $ZrO_2.xH_2O$ and those of the dehydration of $SiO_2.xH_2O$, $SnO_2.xH_2O$, and $TiO_2.xH_2O$.

Hydrated ZrO_2 ppd. cold, and washed with cold water, dissolves easily in the ordinary acids, including oxalic acid (Bailey, *C. J.* 49, 481), forming salts ZrX^I_4 and ZrX^{II}_2; when ppd. hot, or washed with hot water, the pp. is only slowly dissolved by the ordinary acids. According to Paykull (*B.* 12, 1719), moist $ZrO_2.xH_2O$ absorbs CO_2 from the air. Digestion with $Zr(SO_4)_2Aq$ produces basic sulphates $3ZrO_2.4SO_3.15aq$ and $6ZrO_2.7SO_3.19aq$ (*P.*, *l.c.*).

ZIRCONATES. $ZrO_2.xH_2O$ behaves as a weak acid towards the stronger bases. A few salts have been prepared which are most simply regarded as derived from $Zr(OH)_x$ by replacing H by alkali and alkaline earth metals; these zirconates are obtained by heating ZrO_2 with bases; they have been examined chiefly by Hiortdahl (*A.* 137, 34, 236 [1865]).

Sodium zirconates. (1) Na_2ZrO_3 ($=Na_2O.ZrO_2$); obtained by heating ZrO_2 with Na_2CO_3 in the ratio $ZrO_2:Na_2CO_3$; the crystalline mass thus formed is gradually decomposed by water with separation of amorphous ZrO_2. (2) Na_4ZrO_4 ($=2Na_2O.ZrO_2$); obtained by heating ZrO_2 with a considerable excess of Na_2CO_3 to whiteness for a considerable time; decomposed by water, with formation of (3)$Na_2O.8ZrO_2.12aq$, which forms hexagonal tablets.

Zirconates of calcium and *magnesium* were obtained by H (*l.c.*) by heating to redness mixtures of ZrO_2 with SiO_2 and $CaCl_2$ or $MgCl_2$. Ouvrard (*C. R.* 112, 1444 [1891]) describes *lithium zirconate*, Li_2ZrO_3, obtained by fusing ZrO_2 with LiCl, and cooling slowly; when Li_2CO_3 was used, and the fused mass was treated with boiling water containing a little acetic acid, pure ZrO_2 remained.

Zirconium, nitride of. In fusing amorphous Zr with Al, in a cracked lime crucible, Mallet (*Am. S.* [2] 28, 346 [1858]) obtained a dark-grey, porous solid, which gave yellowish lustrous microscopic cubes when treated with HClAq; the crystals were unchanged by *aqua regia* or alkali solutions; when fused with KOH they gave off NH_3. The yellow crystals were probably a nitride of Zr.

Zirconium, oxides of. Besides zirconia, ZrO_2, there exists a higher oxide, probably ZrO_3; and, possibly, also a lower oxide (?) ZrO.

ZIRCONIUM DIOXIDE ZrO_2. (*Zirconia. Zirconic anhydride.*) Mol. w. not known.

Preparation.—There are many methods for preparing ZrO_2 from *zirconite*. 1. The mineral is heated to redness and thrown into water, and the least-coloured pieces are finely powdered and levigated; the powder is very strongly heated with four times its weight of Na_2CO_3, in a Pt crucible, and the product is heated with excess of HClAq; the whole is evaporated to dryness; the residue is digested with water, filtered from SiO_2, and $ZrO_2.xH_2O$ is ppd. by NH_3Aq. The pp. is washed and dissolved in HClAq, and the solution is nearly saturated with Na_2CO_3, and boiled with $Na_2S_2O_3Aq$ as long as SO_2 is given off, whereby $ZrO_2.xH_2O$ is ppd. (Berzelius, *P.* 4, 124; 8, 186; Hermann, *J. pr.* 31, 77; Chancel, *A.* 108, 237; Stromeyer, *A.* 113, 127).—2. Very finely powdered *zirconite* is boiled with conc. HClAq, and the residue is washed with water and dried; 100 g. of the dried powder are added to 400 g. molten NaOH, with which 20 g. NaF have been mixed, and the whole is heated in a nickel crucible until the action ceases, when the molten mass is poured on to a sheet of nickel, and, after solidification, is plunged into water; the portion insoluble in water is dissolved in HClAq, the solution is evaporated to dryness, and treatment with HClAq and evaporation to dryness are repeated several times to remove SiO_2 and HF. The solution in HClAq is then ppd. by NH_3Aq; the $ZrO_2.xH_2O$ is thoroughly washed by decantation, dissolved in the smallest possible quantity of conc. HClAq, and the solution is evaporated to dryness; the residue is washed in a funnel with conc. HClAq mixed with 4 pts. of alcohol; the washed solid is then repeatedly crystallised from conc. HClAq. The white, lustrous crystals of $ZrOCl_2.xH_2O$ thus obtained are dissolved in water, and $ZrO_2.xH_2O$ is ppd. by NH_3Aq (Venable, *C. N.* 64, 315 [1891]; *cf.* Bailey, *Pr.* 46, 74 [1889]; *cf. Preparation* of ZIRCONIUM, p. 893). By heating ppd. $ZrO_2.xH_2O$ to c. 550°, ZrO_2 is obtained.

Crystalline zirconia is obtained from the amorphous form (1) by fusing with borax at a very high temperature, and washing with HClAq (Nordenskjöld, *P.* 114, 612; Knop, *A.* 157, 363); (2) by fusion with *microcosmic salt* (K., *l.c.*); (3) by heating to dull redness in dry HCl at a pressure of three atmospheres (Hautefeuille a. Perrey, *C. R.* 110, 1038); (4) by melting and volatilising in an electric furnace, using a current of 360 ampères and 70 volts (Moissan, *C. R.* 116, 1222 [1893]); (5) by heating, to dull redness, a salt of Zr with an acid that can be removed by heating, in a current of dry HCl (H. a. P., *l.c.*).

Properties.—Amorphous zirconia is a white, tasteless, inodorous powder; S.G. c. 5·5; insoluble in acids, except in conc. H_2SO_4 (*v. Reactions*, No. 7) or HFAq. Crystalline zirconia is a transparent, colourless solid; S.G. 5·1 (Moissan, *l.c.*), 5·42 (Knop, *l.c.*), 5·7 (Nordenskjöld, *l.c.*). The crystals are described by N. (*l.c.*) as quadratic prisms, isomorphous with SnO_2 (*tinstone*) and TiO_2 (*rutile*). The crystals are extremely hard; they scratch glass easily (Moissan, *l.c.*). It is generally said that when ZrO_2 is heated to incipient redness it glows brightly, and becomes denser; but the experiments of Carnelley a. Walker (*C. J.* 53, 82 [1888]) on the action of heat on $ZrO_2.xH_2O$

make it probable that the glowing is an accompaniment of the dehydration from approximately $2ZrO_2.H_2O$ to approximately $24ZrO_2.H_2O$. Zirconia reacts towards acids as a basic oxide, forming salts ZrX^{I}_4 and ZrX^{II}_2 (many of which are basic salts); it also decomposes alkali carbonates and some other alkali and alkaline earth salts, when fused therewith, forming zirconates $mZrO_2.nM_2O$ (*v. Zirconates*, p. 896).

Reactions.—1. When ZrO_2 is *heated* to a very high temperature it melts, boils, and volatilises, condensing in crystals; Moissan (*C. R.* 116, 1222 [1893]) effected the volatilisation in a crucible heated in the electric furnace, using a current of 300 ampères and 70 volts. 2. When very strongly *heated with excess of carbon*, carbides are formed (*v. Carbides*, p. 894). Heating in a carbon crucible in the electric furnace produces Zr (M., *l.c.*).—3. Heating with *magnesium* produces Zr, perhaps also an oxide lower than ZrO_2 (Winkler, *B.* 23, 2642; 24, 888; Phipson, *J. pr.* 96, 353; Bailey, *Pr.* 46, 74; *cf. Zirconium monoxide*). When *heated with magnesium in an atmosphere of hydrogen*, some ZrH_2 is perhaps produced (*v. Zirconium hydride*, p. 895).—4. $ZrCl_4$ is formed by heating ZrO_2 mixed with *carbon in a stream of chlorine*; using *bromine* produces $ZrBr_4$ (*v. Bromide* and *Chloride*, p. 894).—5. ZrF_4 is formed by heating ZrO_2 to dull redness with excess of *ammonium fluoride*.—6. K_2ZrF_6 is formed by slightly heating ZrO_2 with excess of *potassium hydrogen fluoride*, boiling with very dilute HFAq, and filtering.—7. $Zr(SO_4)_2$ is obtained by heating ZrO_2 with excess of a mixture of 2 pts. *conc. sulphuric acid* and 1 pt. water.

ZIRCONIUM PEROXIDE. By adding H_2O_2Aq and NH_3Aq to a solution of $Zr(SO_4)_2$, Clève (*Bl.* [2] 43, 53) obtained an oxide containing more O than ZrO_2; to this oxide he gave the formula ZrO_3. Bailey in 1886 (*C. J.* 49, 149, 481) examined the pp. obtained by adding H_2O_2Aq to solution of $Zr(SO_4)_2$; according to B., the moist pp. has the composition Zr_2O_5, and this composition is unchanged after keeping (moist) for some months. In Bailey's paper in 1889 (*Pr.* 46, 74) he gives the composition $ZrO_3.3H_2O$ to the oxide ppd. by H_2O_2Aq, either from an acid or an alkaline solution of $Zr(SO_4)_2$, after drying over P_2O_5; and the composition Zr_2O_5 after drying at 100°. The oxide $ZrO_3.xH_2O$ was obtained (*C. J.* 49, 485) by preparing a solution of $Zr(SO_4)_2$ by heating K_2ZrF_6 with H_2SO_4, and at once adding H_2O_2Aq. Zr peroxide is insol. in very dilute (1 p.c.) H_2SO_4Aq or $HC_2H_3O_2Aq$ (B., *l.c.*). Bailey (*l.c.*) employed the ppn. of $ZrO_2.xH_2O$ to separate Zr from Fe, Nb, and Ti.

ZIRCONIUM MONOXIDE (?)ZrO. By heating ZrO_2 and powdered Mg, in the ratio ZrO_2:Mg, in a stream of H, Winkler (*B.* 23, 2668 [1890]) obtained a black powder, which he allowed to cool in H, then kept for some time in CO_2, freed from Mg by treatment with dilute HClAq, washed with water containing HCl, then with alcohol, and finally with ether, and dried *in vacuo*. He thus obtained a deep-black powder, which was unacted on by HClAq, HNO_3Aq, or H_2SO_4Aq, even on warming, and which burnt to ZrO_2 when heated in air. W. supposed this black powder to be ZrO.

Zirconium, oxyacid of. Hydrated zirconia, $ZrO_2.xH_2O$, reacts as a weak acid towards strong bases (*v.* ZIRCONATES, p. 896).

Zirconium, oxybromide of, $ZrOBr_2.xH_2O$. $ZrBr_2$ dissolves in water; on evaporation, transparent needle-shaped crystals are formed, to which Mellis (*Z.* [2] 6, 296) gave the composition $ZrOBr_2.7H_2O$. By dissolving $ZrO_2.xH_2O$ in HBrAq and evaporating, Weibull (*B.* 20, 1394 [1887]) obtained lustrous needles of $ZrOBr_2.8H_2O$, isomorphous with $ZrOCl_2.8H_2O$.

Zirconium, oxychlorides of. Various oxychlorides have been described. (1) $ZrOCl_2.xH_2O$; prepared by dissolving $ZrO_2.xH_2O$ in HClAq and evaporating (for details as to the best conditions *v.* Weibull, *B.* 20, 1394). Hermann (*J. pr.* 81, 77) gave the formula as $ZrOCl_2.9H_2O$; Mellis (*Z.* [2] 6, 296) gave $2ZrOCl_2.9H_2O$; and Weibull (*l.c.*) $ZrOCl_2.8H_2O$ (*v.* also Paykull, *B.* 6, 1467; and Bailey, *Pr.* 46, 74). (2) Zr_2OCl_6; prepared by Troost a. Hautefeuille (*C. R.* 73, 563) by passing steam and vapour of $ZrCl_4$ through a red-hot tube. (3) $2Zr_2O_3Cl_2.15H_2O$; prepared by Endemann (*J. pr.* [2] 11, 219) by adding ether to a warm alcoholic solution of $ZrOCl_2.xH_2O$.

Zirconium, oxyiodides of. By adding the calculated weight of BaI_2, in solution, to $Zr(SO_4)_2$ dissolved in a slight excess of H_2SO_4Aq, filtering, evaporating over H_2SO_4, and removing free I from the residue by CS_2, Hinsberg (*A.* 239, 253 [1887]) obtained a white, amorphous powder, easily soluble in water, giving off I in moist air, to which he gave the formula $ZrIO_3H_3.xH_2O$ (x probably = 3).

Zirconium, oxysulphide of; *v.* ZIRCONIUM SULPHIDES (*infra*).

Zirconium, salts of. The salts formed by the replacement of H of acids by Zr belong to the forms ZrX_2^{II} and ZrX_4^{I}; many basic salts are known. The following are the chief salts of Zr derived from oxyacids: *Arsenates, borates, carbonates, nitrates, oxalates, phosphates, selenites, silicates, sulphates*, and *sulphites*.

Zirconium, silicofluoride of, (?)$ZrSiF_6$; probably obtained by Berzelius by evaporating a solution (? of $ZrO_2.xH_2O$ in H_2SiF_6Aq) (*v. Lehrbuch*, 3, 505 [5th ed.]).

Zirconium, sulphides of. According to Berzelius (*v. Lehrbuch*, 2, 189 [5th ed.]), a compound of Zr and S is formed by heating the elements together *in vacuo*, or with H. The compound, to which no formula is assigned, is described by B. as a dark-brown coloured powder; unacted on by H_2SO_4Aq, HNO_3Aq, or HClAq; slowly attacked by boiling *aqua regia*; dissolved easily by HFAq, giving off H_2S; insol. in KOHAq, and decomposed by fusion with KOH to K_2S and ZrO_2. By strongly heating ZrO_2 in vapour of CS_2, Fremy (*A. Ch.* [3] 38, 326 [1858]) obtained a graphite-like solid, which was rapidly acted on by HNO_3Aq, with separation of S; Fremy supposed that the substance might be an oxysulphide.

Zirconium, sulphocyanide of. By adding $Ba(SCN)_2$ to $Zr(SO_4)_2$ solution, Hornberger (*A.* 181, 232 [1876]) obtained a solution which, he said, contained $Zr(SCN)_4$; this solution quickly decomposed, depositing a yellow solid, while $Zr(SCN)_2$ remained in solution.

M. M. P. M.

ADDENDA

[DESCRIPTIVE INORGANIC CHEMISTRY ONLY.]

ALUMINIUM (vol. i. p. 141). *Preparation.*—By electrolysing a molten mixture of $AlF_3.3NaF$ with NaCl (Minet, *C. R.* 111, 603 [1890]). The best results are obtained by using the salts in the ratio $AlF_3.3NaF$:6NaCl; details of the quantities to be used, the strength of current, &c., are given by M.

Properties.—Minet (*C. R.* 111, 603 [1890]) gives m.p. of Al as 675°; and S.G. at 820° as 1·76. The S.H. of Al is given by Richards (*C. N.* 65, 97 [1892]) as ·221 at 20°, ·232 at 100°, and ·2845 at the m.p. = 625°; the S.H. of molten Al at 650° = ·308, according to Pionchon (*C. R.* 115, 162 [1892]). The molecule of Al in dilute solution in tin is perhaps diatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]).

Reactions.—Volatilises in electric furnace, with current of 250 ampères and 70 volts (Moissan, *C. R.* 116, 1429 [1893]). Not appreciably acted on by NO_2 at 500° (Sabatier a. Senderens, *C. R.* 115, 236 [1892]). An amalgam is formed by bringing Al into a solution of a mercuric salt (Klaudy, *C. C.* 1893 [1] 201; abstract in *C. J.* 64 [11] 376 [1893]). Heated with $NaPO_3$ in a current of H, from 28 to 31 p.c. of the P distils over; P is also obtained by heating Al with any phosphate of Ca or Mg (Rossel a. Frank, *B.* 27, 52 [1894]). According to Lunge (*C. N.* 65, 110 [1892]), vessels made of Al may be used for holding articles of food, at least at the ordinary temperature, without danger of the metal being dissolved; this result is confirmed by Balland (*C. R.* 114, 1536 [1892]).

Aluminium, alloys of (vol. i. p. 143). For an alloy with *gold*, Al_2Au, *v.* Heycock a. Neville (*C. J.* 65, 74 [1894]).

Aluminium, chloride of (vol. i. p. 144). Nilson a. Pettersson (*Z. P. C.* 4, 206 [1889]) made a number of determinations of the V.D. of $AlCl_3$; they find that the compound gradually dissociates above its b.p. until c. 800°, when its V.D. becomes constant and corresponds with the formula $AlCl_3$. $AlCl_3$ may be prepared by heating an alloy of Al and Cu nearly to redness in dry HCl; $AlCl_3$ distils over unmixed with any Cu compound (Mabery, *B.* 22, 2658 [1889]). Sabatier (*Bl.* [3] 1, 88 [1889]) says that crystals of the hydrated chloride after being *in vacuo* for three months at 20° over H_2SO_4 have the composition $AlCl_3.6H_2O$.

Aluminium, oxides of (vol. i. p. 146). By heating Al_2O_3 with Mg, in the ratio Al_2O_3:Mg, Winkler (*B.* 23, 780 [1890]) obtained a brownish-black powder which, he says, contained a considerable quantity of an oxide lower than Al_2O_3, probably AlO. By the incomplete combustion of Al, Pionchon obtained a dark-grey powder, said by P. to have the composition $Al_8O_7 = 2Al_2O_3.Al_2O$ (*C. R.* 117, 328; *abstract* in *C. J.* 64 [11] 572 [1893]). By heating amorphous Al_2O_3 to incipient redness in HCl gas at a pressure of three atmos., Hautefeuille a. Perrey (*C. R.* 110, 1038 [1890]) obtained crystals of *corundum*. According to Read (*C. J.* 65, 313 [1894]), Al_2O_3 is unchanged at c. 1750°.

Aluminium, phosphide of (vol. i. p. 146). A grey crystalline powder, Al_3P_5, was obtained by Rossel a. Frank (*B.* 27, 52 [1894]) by heating Al in vapour of P, and then heating the product till P ceased to come off.

AMMONIA (vol. i. p. 196). *Formation.*—According to Loew (*B.* 23, 1443 [1890]), traces of NH_3 are formed by shaking Pt black with very dilute NaOHAq in the air. NH_3 is also formed by the combined action of Pt black and dextrose on KNO_3Aq (L., *l.c.*, p. 675).

Properties.—Ludeking a. Starr (*Am. S.* [3] 45, 200 [1892]) give S.H. of liquid NH_3 as ·8857. For measurements of the wave-lengths of the lines in the emission spectrum of NH_3 *v.* Magnanini (*Z. P. C.* 4, 435 [1889]). Perkin (*C. J.* 55, 689, 728 [1889]) gives M. M. of NH_3 in aqueous and alcoholic solutions; also Mol. R. of various NH_4 salts in solution. Tables showing the solubility of NH_3 in alcohol of various concentrations, at 10°, 20°, and 30°, are given by Delépine (*J. Ph.* [5] 25, 496; *v. abstract* in *C. J.* 62, 1049 [1892]). For the freezing-points of aqueous solutions of NH_3 *v.* Pickering (*C. J.* 63, 181 [1893]).

Reactions.—*Dry* NH_3 does not combine with *dry* hydrogen chloride when these gases are mixed (Baker, *C. J.* 65, 611 [1894]). Nor do *dry* NH_3 and *dry* carbon dioxide combine (Hughes a. Soddy, *C. N.* 69, 138 [1894]). Michel a. Grandmougin (*B.* 26, 2565 [1893]) say that the products of passing NH_3 over heated peroxide of Ba, Pb, Mn, or Ni, are N with a little HNO_2 and HNO_3, and oxide or hydroxide of the metal. The reactions of liquid NH_3 with $CrCl_3$ and $FeCl_3$ are described by Christensen (*Zeit. f. anorg. Chemie*, 4, 227; *abstract* in *C. J.* 64 [11] 469 [1893]).

AMMONIUM COMPOUNDS (vol. i. p. 200).

Ammonium amalgam (vol. i. p. 201). From measurements of the polarisation given by this substance in a solution of NH_4Cl against zinc amalgam, and a comparison of these measurements with the polarisations given by metallic amalgams, Le Blanc concludes that ammonium amalgam really exists (*Z. P. C.* 5, 467; *abstract* in *C. J.* 58, 1204 [1890]).

Ammonium chloride (vol. i. p. 202). Baker (*C. J.* 65, 611 [1894]) asserts that the V.D. of the *dry* salt at 350° is 28·7, corresponding with that required by the formula NH_4Cl. B. also says that no reaction occurs when *dry* NH_4Cl and *dry* CaO are heated together.

ANTIMONY (vol. i. p. 282). *Reactions.*—Montemartini (*G.* 22, 384, 426) finds that no appreciable quantity of NH_3 is formed by the interaction of Sb and HNO_3Aq varying from 2 to 70·3 p.c. HNO_3; NO_2 is practically the only gaseous product of the reaction; when 70 p.c. HNO_3Aq is used, the residue probably has the composition $(SbO)NO_3$.

Antimonates (vol. i. p. 285). Several salts have been prepared, by double decomposition from the K salt, by Beilstein and O. v. Bläse (*C. C.* 1889. 803; *abstract* in *C. J.* 56, 1123). All the compounds are salts of $HSbO_3$; B. a. B. conclude that the only well-marked antimonates are derived from this acid. Ebel (*B.* 22, 3044 [1889]) describes several metantimonates.

Antimonites (vol. i. p. 285). For antimonites of K and Na *v.* Cormimbœuf (*C. R.* 115, 1305; *abstract* in *C. J.* 64 [11], 171 [1893]).

Antimony, bromide of (vol i. p. 286). The b.p. of $SbBr_3$ is given as 275° by Freyer a. V. Meyer (*Zeit. f. anorg. Chemie*, 2, 1 [1892]).

Antimony, trichloride of (vol. i. p. 286). Boils at 223° (Freyer a. V. Meyer, *l.c.*).

Antimony, pentachloride of (vol. i. p. 287). The V.D. at 218° and 58 mm. pressure was found to be 141·7 (corresponding with the formula $SbCl_5$) by Anschütz a. Evans (*A.* 253, 95 [1890]). *Double compounds* of $SbCl_5$ with RbCl and CsCl are described by Saunders (*Am.* 14, 152 [1892]), and by Wheeler (*Am. S.* [3] 46, 269 [1893]).

Antimony, fluoride of (vol. i. p. 287). The *double compound* $SbF_3.2AmF$ is described by H. von Helmholt (*Zeit. f. anorg. Chemie*, 3, 115 [1893]).

Antimony, hydride of (vol. i. p. 288). The temperature whereat decomposition of SbH_3 begins is given by Brunn (*B.* 22, 3202 [1889]) as c. 150°. For the reactions of SbH_3 with $AgNO_3Aq$ *v.* Vitali (*abstract* in *C. J.* 64 [11], 206 [1893]).

Antimonic oxide (vol. i. p. 290). When heated to dull redness Sb_2O_5 gives off O, forming Sb_2O_4, which at c. 1750° is further reduced to Sb_2O_3 (Read, *C. J.* 65, 313 [1894]).

Antimonious sulphide (vol. i. p. 291). Black Sb_2S_3 is formed, according to Mitchell (*C. N.* 67, 291 [1893]), by passing CO_2 into boiling water with ordinary Sb_2S_3 in suspension. Picton (*C. J.* 61, 142 [1892]) obtained a colloidal Sb_2S_3 in very fine suspension in water, by allowing solution of tartar emetic to flow into saturated H_2SAq.

Antimony, thio-chlorides and thio-iodides of (vol. i. pp. 292 3). Ouvrard (*C. R.* 116, 1516 [1893]) describes SbSCl and $Sb_4S_5Cl_2$, obtained by the action of H_2S on $SbCl_3$; and SbSI formed by heating SbI_3 to 150° in dry H_2S, and $Sb_2S_3I_6$ formed by heating Sb_2S_3 with I and crystallising from CS_2.

ARSENIC (vol. i. p. 301). A full account of the different forms of As obtained, along with As_2O_3, by subliming As in a tube is given by Retgers (*Z. P. C.* 4, 403; *abstract* in *C. J.* 64 [11], 570 [1893]). Petersen gives the following heats of oxidation, and atomic volumes, of the allotropic forms of As (*Z. P. C.* 8, 601 [1891]):—

	$[As^2,O^3]$	At. volume
Grey, rhombohedric	156,830	13·1
Grey-black, amorphous	154,840	15·94
Brown, amorphous	163,506	15·99

Arsenic, bromide of (vol. i. 309). $AsBr_3$ combines with NH_3 to form $AsBr_3.3NH_3$ (Besson, *C. R.* 110, 1258 [1890]).

Arsenates (vol. i. p. 307). For arsenates of Cd *v.* A. de Schulten (*Bl.* [3] 1, 473 [1889]); for arsenates of Cu, and of Cu and Na, *v.* Hirsch (*C. C.* 1891 [1]. 15; *abstract* in *C. J.* 60, 644); many double arsenates of K, and of Na, with Cd, Co, Mg, Mn, Ni, and Zn are described by Lefèvre (*C. R.* 110, 405 [1890]).

For *thio-arsenates* of Cu, Hg, Zn, and Zn and Na, *v.* Preis (*A.* 257, 178 [1890]).

Arsenites (vol. i. p. 306). For the preparation, by double decomposition from the salt $2K_2O.As_2O_3$, and properties of the arsenites of the following metals *v.* Reichard (*B.* 27, 1019 [1894]):—Al, Ba, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Pt, Ag, Sr, Sn, Ti, U, and Zn (references and criticisms of former investigations are given). Stavenhagen (*Zeit. f. angew. Chemie*, 1894, 165) obtained the *double salt* of K arsenite and sulphate, $K_3AsO_3.10K_2SO_4$, by evaporating solutions of the constituents after mixing.

Arsenic acid (vol. i. p. 307). For a detailed account of the reaction of H_2S with solutions of H_3AsO_4 *v.* Brauner a. Tomeetchek (*C. J.* 53, 145 [1888]).

Arsenious chloride (vol. i. p. 310). According to Besson (*C. R.* 109, 940 [1889]), $AsCl_3$ solidifies at −18°, forming white needles; at −30° $AsCl_3$ absorbs much Cl, forming a liquid which does not solidify at −60°, and which with water gives off much Cl and forms As_2O_3Aq. Besson (*C. R.* 110, 1258 [1890]) says that the compound formulated by Rose as $2AsCl_3.7NH_3$ is really $AsCl_3.4NH_3$.

Arsenious fluoride (vol. i. p. 310). Moissan (*A. Ch.* [6] 19, 280 [1891]) prepared AsF_3 by heating As_2O_3 with HF; he gives b.p. as 63° at 750 mm., and says that it solidifies to white crystals at −8·5°. Besson (*C. R.* 110, 1258 [1890]) describes the compound $2AsF_3.5NH_3$.

Arsenic, trihydride of (vol. i. p. 310). Brunn (*B.* 22, 3202 [1889]) finds that the first products of the action of air, or O, on AsH_3 are solid $nAsH$ and H_2O, and the next products are As and H_2O. AsH_3 and H_2S do not react in absence of air at the ordinary temperature either as gases or in solution (*B.*, *l.c.*). AsH_3 begins to decompose at c. 230° (*B.*, *l.c.*). For the reactions of AsH_3 with $AgNO_3Aq$ *v.* Vitali (*abstract* in *C. J.* 64 [11] 206 [1893]).

Arsenious iodide (vol. i. p. 311). Besson (*C. R.* 110, 1258 [1890]) describes the compounds $AsI_3.4NH_3$ and $AsI_3.12NH_3$.

Arsenious sulphide (vol. i. p. 315). Picton (*C. J.* 61, 140–144 [1892]) obtained an aqueous solution of colloidal As_2S_3, containing also some very finely divided sulphide in suspension, by allowing As_2O_3Aq to flow into saturated H_2SAq, into which H_2S was continually passing, and removing H_2S by a stream of H.

Arsenic pentasulphide (vol. i. p. 315) As_2S_5 is obtained, according to McCay (*Am.* 12, 547 [1891], by passing H_2S for a long time into a hot solution of an alkali dihydrogen arsenate, and then ppg. by a mineral acid.

Arsenic, thiochlorides and thio-iodides of (vol. i. p. 316). Ouvrard (*C. R.* 116, 1516 [1893]) obtained $As_4S_5Cl_2$ by passing H_2S into

$AsCl_3$, and washing the pp. with CS_2. By heating 1 pt. As_2S_3 with 10 pts. $AsCl_3$ to 150° he obtained AsSCl.

AZO-IMIDE (*v. Hydrazoic acid*, p. 919, *Addenda*).

BARIUM (vol. i. p. 440). Richards, in 1893, made an elaborate experimental revision of the at. w. of Ba (*P. Am. A.* 28, 1; 29, 55). As a mean result of the most trustworthy experiments, R. adopts 137·1 as the at. w. of Ba ($O = 15·96$). Limb (*C. R.* 112, 1434 [1891]) failed to obtain any Ba by electrolysing fused $BaCl_2$, or $BaCl_2$ mixed with NaCl.

Barium, carbide of. By heating a mixture of Ba amalgam and powdered charcoal in H, Maquenne (*C. R.* 114, 361 [1892]) obtained grey BaC_2; decomposed by water, giving BaO_2H_2Aq and C_2H_2; *v.* also Moissan, *C. R.* 118, 683 (*abstract* in *C. J.* 66 [1], 314 [1894]).

Barium, chloride of (vol. i. p. 441). By bringing $BaCl_2$ into contact with liquid NH_3, and allowing the gas to escape at 0° and 760 mm., Joannis obtained $BaCl_2.8NH_3$ (*C. R.* 112, 337 [1891]).

Barium, fluoride of (vol. i. p. 441). BaF_2 is obtained in microscopic crystals by adding $BaCl_2Aq$ (3·6 p.c.) to boiling KFAq (1 p.c.), boiling, washing, drying, and heating strongly (Moissan, *Bl.* [3] 5, 152 [1891]). Poulenc (*C. R.* 116, 987 [1893]) obtained BaF_2 in well-formed octahedra by fusing amorphous BaF_2 with KHF_2 and KCl.

Barium, nitrides of. Maquenne (*C. R.* 114, 220 [1892]) obtained a mixture, probably containing some Ba_3N_2, by heating Ba amalgam to redness in a current of N. Berthelot a. Matignon (*A. Ch.* (7) 2, 144 [1894]) say that BaN_6 is formed by heating AmN_3Aq with BaO_2H_2Aq.

Barium monoxide (vol. i. p. 442). BaO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]); it liquefies at c. 2,000°, but is not decomposed at c. 2,500° (Moissan, *C. R.* 115, 1034 [1892]).

Barium dioxide (vol. i. p. 443). BaO_2 is decomposed by salts of Al, Cr, Co, Fe, &c.; some salts—*e.g.* those of Ca, Li, K, Na—do not react with BaO_2 (*v.* Kwasnik, *B.* 25, 65). For decomposition of BaO_2 by heat *v.* Le Chatelier (*C. R.* 115, 654; *abstract* in *C. J.* 64 [11], 71 [1893]).

BERYLLIUM (vol. i. p. 504). Krüss a. Moraht (*B.* 23, 727 [1890]) obtained hexagonal crystals of Be, mixed with BeO, by heating $BeF_2.2KF$ to redness with Na. K. a. M. (*l.c.* p. 2552) obtained the value 9·03 for the at. w. of Be by converting BeO into $BeSO_4.4H_2O$, and this again to BeO. Gibson (*C. J.* 63, 909 [1893]) describes methods for preparing BeO from *beryl*.

Beryllium, fluoride of (vol. i. p. 506). Petersen (*Z. P. C.* 5, 263 [1890]) gives the thermal data H.F. $[BeO^2H^2, 2HFAq] = 19,$[illegible]83. The *double compound* $BeF_2.2AmF$ is described by H. von Helmholt (*Zeit. f. anorg. Chemie*, 3, 115 [1893]).

Beryllium, oxide of (vol. i. p. 506). By dissolving $BeO.x$aq in KOHAq, Krüss a. Moraht (*B.* 23, 727 [1890]) obtained *potassium beryllate* BeO_2K_2 (?), mixed with K_2CO_3, as a snow-white, silky solid.

BISMUTH (vol. i. p. 509). The at. w. of Bi was re-determined by Classen in 1890 (*B.* 23, 938 [1890]), by converting Bi into nitrate, and this into Bi_2O_3; the mean result was 208·80 ($O = 15·96$). Schneider (*J. pr.* [2] 42, 553; 44, 23 [1891]) criticises Classen's results, and maintains that Marignac's value (almost exactly 208) is as trustworthy as that obtained by C. The molecule of Bi in dilute solution in tin is perhaps diatomic (?) (Heycock a. Neville, *C. J.* 57, 376 [1890]).

Preparation.—Classen (*l.c.*) says that pure Bi is best prepared by electrolysing a solution of the metal in HNO_3Aq, using a cone of Pt as the negative electrode, then washing with alcohol, and fusing with KCy.

Properties.—Melts at 264°, according to Classen (*l.c.*); at 269·22°, according to Callendar a. Griffiths (*C. N.* 63, 1 [1891]). S.G. 9·7474 (C., *l.c.*; no temperature given); 9·787 at $\frac{0°}{4°}$, 9·673 solid at the m.p., 10·004 liquid at the m.p. (Vicentini, *Rend. Acad. Lincei*, 6 [11], 121, 147 [1891]). For S.G. of liquid Bi from 235° to 280° *v.* Cattaneo (*Rend. Acad. Lincei*, 7 [11], 88 [1892]). For electrical resistance *v.* E. v. Aubel (*C. R.* 108, 1102 [1889]).

Reactions.—According to Veley (*Pr.* 48, 458 [1891]), Bi does not dissolve in 30 p.c. HNO_3Aq at 30° if HNO_2 is absent; but Bi dissolves readily in 1 p.c. HNO_2Aq.

Bismuth, bromide of (vol. i. p. 511). $BiBr_3$ boils at 453° (V. Meyer, *A.* 264, 122 [1891]). Cavazzi a. Tivoli (*G.* 21 [11], 306 [1892]) describe a lustrous, black, hygroscopic solid, $PBrH(BiBr_2)_3$, obtained by allowing $BiBr_3$ to fall gradually into PH_3 (*abstract* in *C. J.* 62, 279).

Bismuth, chloride of (vol. i. p. 512). Boils at 435°–441° (uncor.) (V. Meyer, *l.c.*). The only *double chloride* of Bi and K of those hitherto described that exists is $BiCl_3.2KCl.2aq$, according to Brigham (*Am.* 14, 164 [1892]). B. has also prepared $BiCl_3.KCl.aq$.

Bismuth, fluoride of (vol. i. p. 512). H. von Helmholt describes the *double fluoride* $BiF_3.AmF$ (*Zeit. f. anorg. Chemie*, 3, 115 [1893]).

Bismuth, iodide of (vol. i. p. 513). Astre (*C. R.* 110, 525 [1890]) obtained the *double iodide* $2BiI_3.KI$ by keeping I, KCl, Bi, and water in contact for some weeks, and then crystallising from Et acetate.

Bismuthous oxide (vol. i. p. 513). Classen (*B.* 23, 938 [1890]) gives S.G. as 9·044. Read (*C. J.* 65, 313 [1894]) found Bi_2O_3 to be unchanged at c. 1750°.

Bismuth, oxysulphide of (vol. i. p. 516). By passing dry H_2S into boiling benzene containing Bi_2O_3 in suspension, P. v. Scherpenberg (*C. C.* 1889. [11] 643) obtained Bi_2O_2S.

Bismuth, selenide of (vol. i. p. 516). The *double compound* $Bi_2Se_3.K_2Se$ is described by P. v. S. (*l.c.*).

Bismuth, sulphide of (vol. i. p. 516). P. v. S. (*l.c.*) obtained the *double compound* $Bi_2S_3.K_2S$ by fusing Bi_2O_3 with K polysulphide.

BORON (vol. i. p. 524). The at. w. of B has been determined by Abrahall by the analysis of BBr_3 (*C. J.* 61, 650 [1892]); the value obtained was 10·67 ($O = 15·96$). Also by Ramsay a. Aston (*C. J.* 63, 207 [1893]) by finding the percentage of water in crystallised borax, and by distilling fused borax with HClAq and $CH_3.OH$ and weighing the residual NaCl; the values varied about 11, but showed considerable differences.

Rimbach (*B.* 26, 164 [1893]), by titrating solutions of borax with standard HClAq, using methyl orange as indicator, obtained the value 10·91 (O = 15·96). The following values for S.H. of amorphous B are given by Moissan a. Gautier (*C. R.* 116, 924 [1893]): 0° to 100° = ·3066, 0° to 192° = ·3407, 0° to 234° = ·3573. For atomic refraction of B *v.* Ghira (*G.* 23 [1], 452; *abstract* in *C. J.* 64 [11], 517 [1893]).

Preparation.—According to Moissan (*C. R.* 114, 319 [1892]), the methods employed to give *amorphous boron* yield substances containing from c. 45 to c. 72 p.c. of B. M. (*l.c.* p. 392) says that nearly pure amorphous B is obtained by heating to redness a mixture of one pt. powdered Mg with 3 pts. fused B_2O_3, washing with HClAq, KOH in alcohol, HFAq, and water (the process is tedious, details are given); by fusing this product with 50 pts. B_2O_3, and washing with HClAq &c., a brown powder is obtained containing c. 98·5 p.c. B, with traces of Mg and small quantities of other impurities.

Properties and Reactions.—The properties of *amorphous boron* are described by Moissan (*C. R.* 114, 617 [1892]). Brown powder; S.G. 2·45. Does not fuse in electric arc, but volatilises (M., *C. R.* 117, 423 [1893]); increases in density when heated to c. 1500° in H. Specific electrical resistance = 801 megohms. Burns in air at c. 700°. Combines directly with Br, Cl, (not I), N at c. 1200°, Se, S, (not Te); also with Al, Fe, Mg, Pt, and Ag. Reduces many oxyacids and oxides when heated therewith; $HClO_3$, HIO_3, HNO_3, and H_2SO_4 are readily reduced; As_2O_3 and As_2O_5, CO, N_2O, P_2O_5, SiO_2, steam, and SO_2 are also reduced; many metallic oxides are reduced to metals, often with explosive violence; molten KOH gives off H; metallic fluorides are generally decomposed, giving BF_3; many other metallic salts, both in solution and when heated as solids, are reduced by amorphous boron.

Boron, bromide of (vol. i. p. 525). BBr_3 boils at 90° (Freyer a. V. Meyer, *Zeit. f. anorg. Chemie*, 2, 1). Ghira (*Z. P. C.* 12, 768 [1893]) gives S.V. 94·72; and S.G. $\frac{0^\circ}{4^\circ}$ = 2·64985. According to Besson (*C. R.* 112, 1001 [1891]), when a mixture of gaseous HI and BBr_3 is passed through a glass tube at 300°-400° the products are BBr_2I, $BBrI_2$, and BI_3. BBr_2I and $BBrI_2$ are colourless liquids, distilling at c. 125° and 180°; they are rapidly decomposed by air and light. Tarible (*C. R.* 116, 1521 [1893]) says that BBr_3 combines with PBr_3 and PBr_5 to form compounds easily decomposed by water, Cl, or NH_3 in the cold. Besson (*C. R.* 114, 542 [1892]) describes $BBr_3.4NH_3$, obtained by passing dry NH_3 into BBr_3 in dry CCl_4 at 0°.

Boron, carbide of, B_6C. Moissan (*C. R.* 118, 556 [1894]) says that B and C combine when amorphous B is mixed with c. $\frac{1}{5}$ its weight of sugar charcoal, and the mixture is heated in the electric furnace for some minutes, using a current of 250-300 ampères and 70 volts. After treating the product with HNO_3Aq, and then with $KClO_3$ and HNO_3Aq, the carbide remains as a very hard, lustrous, black, crystalline powder; S. G. 2·51; burns very slowly in O at c. 1000°; acted on by Cl below 1000°, but not by Br, I, S, P, N, or mineral acids; reacts with molten KOH or $KNaCO_3$ (*abstract* in *C. J.* 66 [11], 279 [1894]).

Boron, chloride of (vol. i. p. 525). BCl_3 boiling at 17° (Freyer a. V. Meyer, *Zeit. f. anorg. Chemie*, 2, 1). Ghira (*Z. P. C.* 12, 768 [1893]) gives S.G. $\frac{0^\circ}{4^\circ}$ = 1·43386, and S.V. 81·94.

Boron, fluoride of (vol. i. p. 526). According to Besson (*C. R.* 110, 80 [1890]), BF_3 unites with PH_3 at c. −30° to form $2BF_3.PH_3$, decomposed by water giving off H and PH_3.

Ammonium borofluoride is described by Stolba (*C. C.* 1890. [1] 211; *abstract* in *C. J.* 58, 560).

Boron, hydride of (vol. i. p. 526). Sabatier (*C. R.* 112, 865 [1891]) says that the gas produced by adding HClAq to the brown powder formed by heating B_2O_3 with Mg in H has a very disagreeable odour, burns with a green flame, gives a brown pp. with $AgNO_3Aq$, deposits B when passed through a glass tube at a dull red heat (H coming off), and is decomposed by electric sparks, giving pure H. The gas contains a little B hydride, according to S. (*l.c.*); *cf.* Winkler (*B.* 23, 772 [1890]).

Boron, iodide of (vol. i. p. 527). BI_3. Prepared by Moissan (*C. R.* 112, 717 [1891]), (1) by heating I and B to 700°-800°; (2) by heating amorphous B (dried in H at 200°), in a stream of dry HI, in a tube of hard glass until the glass nearly softens; (3) by passing HI and BCl_3 vapours through a porcelain tube heated to redness. The product is dissolved in CS_2, shaken with Hg, and allowed to crystallise. Colourless crystals, very hygroscopic, rapidly become coloured in light. Melts at 43° and boils at 210°. Decomposed by water, giving HIAq and H_3BO_3Aq. (For other reactions *v. abstract* in *C. J.* 60, 979 [1891].) For compounds with NH_3 *v.* Besson (*C. R.* 114, 542 [1892]; *abstract* in *C. J.* 62, 771).

Boron, oxide of (vol. i. p. 527), B_2O_3. For reduction by Mg powder, giving Mg boride, *v.* Winkler (*B.* 23, 772 [1890]). The compound $B_2O_3.P_2O_5$ (= BPO_4) is obtained by evaporating H_3BO_3Aq mixed with H_3PO_4, heating to redness, and washing with hot water (G. Meyer, *B.* 22, 2919 [1889]).

Borates (vol. i. p. 529). For some new borates of Li, Rb, and Cs *v.* Reischle (*Zeit. f. anorg. Chemie*, 4, 166 [1893]). For remarks on the classification of alkali and alkaline earth borates *v.* Le Chatelier (*C. R.* 113, 1034 [1891]). For a full account of Mn borate, *v.* Hartley a. Ramage (*C. J.* 63, 129 [1893]). The compounds $6FeO.FeBr_2.8B_2O_3$ and $6ZnO.ZnBr_2.8B_2O_3$ are described by Rousseau a. Allaire (*C. R.* 116, 1445; *abstract* in *C. J.* 64 [11], 518 [1893]).

Boron, phosphide of. According to Besson (*C. R.* 113, 78 [1891]), a phosphide of B is obtained by passing PH_3 into BBr_3, and heating the product, $BBr_3.PH_3$, to 300°, when it gives HBr and B phosphide. The phosphide is said to be a brown powder, insoluble in water, reacting with boiling conc. alkali solutions to give PH_3; gives off P when heated to redness in N (for other reactions *v. abstract* in *C. J.* 60, 1418 [1891]).

Boron, selenide of. (?B_2Se_3). Obtained, as a yellowish grey powder, decomposed violently by water, giving H_2Se and some Se, by heating B to full redness in a current of H_2Se (Sabatier, *C. R.* 112, 1000 [1891]).

Boron, sulphides of (vol. i. p. 531). For heat of formation of B_2S_3 *v.* Sabatier (*C. R.* 112, 862; *abstract* in *C. J.* 60, 981 [1891]). Moissan (*C. R.* 115, 203 [1892]) gives details of various methods of preparing B_2S_3, and describes the reactions of this compound (*v. abstract* in *C. J.* 62, 1393 [1892]). According to M. (*l.c.* p. 271), *boron pentasulphide*, B_2S_5, is obtained by heating BI_3 with rather less than one equiv. of S in CS_2 solution at 60° for many hours. M. describes the compound, which was not obtained pure, as a light white crystalline powder. S.G. 1·85.

BROMHYDRIC ACID (vol. i. p. 532). The V.D. has been determined by Biltz at $-15°$ and $-28°$ (*Z. P. C.* 10, 354 [1892]); the results agree with the V.D. required by the formula HBr. The M. M.s of HBrAq from 15·47 to 65·59 p.c. HBr have been measured by Perkin (*C. J.* 55, 706 [1889]).

Preparation.—1. By the interaction of P, Br, and H_2O, *v.* Fileti a. Crosa (*G.* 21, 64 [1891]; *cf.* Gassman, *abstract* in *C. J.* 64 [11], 453 [1893]). 2. By passing H_2S into Br covered with water (Recoura, *C. R.* 110, 784 [1890]).—3. By adding H_2SO_4Aq S.G. 1·41 to KBr (Feit a. Kubierschky, *J. Ph.* [5] 24, 159; *abstract* in *C. J.* 60, 1320 [1891]; *v.* also Addyman, *C. J.* 61, 97 [1892]; *cf.* Léger, *abstract* in *C. J.* 64 [11], 114 [1893]).

Hydrates.—Pickering (*P. M.* [5] 36, 11 [1894]) has isolated $HBr.3H_2O$ and $HBr.4H_2O$; the former melting at $-48°$ and the latter at $-55·8°$.

Reactions.—For the decomposition of HBrAq by H_2SO_4Aq of different concentrations *v.* Addyman (*C. J.* 61, 98 [1892]).

BROMINE (vol. i. p. 534). Mol. w. in solution in water or acetic acid = 159·5 (Br_2) (Paterno a. Nasini, *B.* 21, 2153 [1888]). The V.D.s of Br from 15° to 280°, and at pressures from 75 to 760 mm., have been determined by Perman (*Pr.* 48, 45 [1891]); no indications of dissociation were obtained. For measurements of the absorption of light by Br *v.* Camichel (*C. R.* 117, 807; *abstract* in *C. J.* 64 [11], 561 [1893]).

Bromates (vol. i. p. 538). *Lithium bromate* $LiBrO_3$; prepared by the interaction of $Ba(BrO_3)_2Aq$ and Li_2SO_4Aq (Potilitzin, *J. R.* 22, 392; *abstract* in *C. J.* 62, 1275 [1892]). *Potassium bromate* $KBrO_3$. The decomposition of this salt by heat has been studied by Cook (*C. J.* 65, 802 [1894]); decrepitation occurs at c. 180°, with evolution of Br; the salt fuses at a higher temperature, and O is evolved, without any Br, until KBr remains; no oxy- compounds are formed.

Strontium bromate begins to decompose at c. 240°; the principal change is to $SrBr_2$ and O, but SrO is also formed (Potilitzin, *J. R.* 22, 454; *abstract*, with summary of *quantitative results*, in *C. J.* 64 [11], 11 [1893]).

CADMIUM (vol. i. p. 354) Determinations of the at. w. have been made by Partridge (*Am. S.* [3] 40, 377 [1891]), and by Morse a. Jones (*Am.* 14, 261 [1892]). P. converted CdC_2O_4 into CdO by heating, $CdSO_4$ into CdS by heating in H_2S, and CdC_2O_4 into CdS by heating in H_2S. M. a. J. converted Cd into $Cd(NO_3)_2$, and this into CdO by heating. The results all lie about 112 (*v. abstract* in *C. J.* 60, 399; *cf.* Clarke, *ibid.* 390 [1891], and 62, 1397 [1892]). Lorimer a. Smith (*Zeit. f. anorg. Chemie*, 1, 364 [1892]) obtained values varying from 112·182 to 111·908 (O = 16). The molecule of Cd in dilute solution in tin may be diatomic (*v.* Heycock a. Neville, *C. J.* 57, 376 [1890]). Cd melts at 320·68°, according to Callendar a. Griffiths (determined by Pt thermometer, *C. N.* 63, 1 [1891]). For the line-spectrum of Cd *v.* Ames (*P. M.* [5] 30, 33 [1890]). According to Williams (*Am.* 14, 273 [1892]), Cd crystallises in hexagonal and polyhedral forms; axial ratio $a:c = 1:1·6554$. Cd is superficially oxidised at a dull-red heat by *nitric oxide* (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]). Montemartini (*G.* 22 [1] 250; *v. abstract* in *C. J.* 62, 1278 [1892]) has analysed the gases produced by the interaction of Cd and nitric acid; with excess of HNO_3Aq (27·5 p.c.) at 8°, N, NO, N_2O and NH_3 are produced.

Cadmium, alloys of (vol. i. p. 655). For an alloy with *gold*, CdAu, *v.* Heycock a. Neville (*C. J.* 61, 914 [1892]; *cf. ibid.* 65, 65 [1894]). For alloys with *copper*, *gold*, and *silver*, prepared by immersing Cd in solutions of salts of the other metals, *v.* Mylius a. Fromm (*B.* 27, 630 [1894]).

Cadmium, bromide of (vol. i. p. 655). For the *double compounds* $CdBr_2.xCsBr$, $x = 1, 2$, and 3, *v.* Wells a. Walden (*Zeit. f. anorg. Chemie*, 5, 266 [1893]).

Cadmium, chloride of (vol. i. p. 655). Kwasnik (*Ar. Ph.* 229, 569; *abstract* in *C. J.* 62, 566 [1892]) describes $CdCl_2.2NH_3$ and $CdCl_2.NH_3$. For the *double compounds* $CdCl_2.CsCl$ and $CdCl_2.2CsCl$, *v.* Wells a. Walden (*l.c.*). *Double compounds* with HCl, NH_4Cl, LiCl, and KCl, of the form $CdCl_2.MCl.xaq$, are described by Chassevant (*A. Ch.* [6] 30, 5; *v. abstract* in *C. J.* 66 [11], 18 [1894]).

Cadmium, fluoride of (vol. i. p. 655). CdF_2 is obtained by (1) the interaction of HF and Cd at a red heat; (2) the interaction of HF and fused $CdCl_2$, or CdO at a red heat; it is a colourless, transparent solid; S.G. 6·64; somewhat soluble water, insoluble alcohol of 95° (Poulenc, *C. R.* 116, 581 [1893]).

Cadmium, iodide of (vol. i. p. 656). For the *double compounds* $CdI_2.xCsI$, when $x = 1, 2$, and 3, *v.* Wells a. Walden (*l.c.*).

Cadmium, oxides of (vol. i. p. 656). CdO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]).

According to Kouriloff (*J. R.* 22, 171; *abstract* in *C. J.* 62, 1278 [1892]), the compound $CdO_2.CdO_2H_2$ is obtained by heating CdO_2H_2 with H_2O_2Aq. Morse a. Jones (*Am.* 12, 488; *abstract* in *C. J.* 58, 1376 [1890]) obtained small crystals, which they say were cadmous oxide Cd_2O, by gently heating CdOH; the hydroxide was obtained by heating $CdCl_2$, $CdBr_2$, or CdI_2, with excess of Cd, to the melting-point, in N, or *in vacuo*, and treating with water, when $CdCl_2$, $CdBr_2$, or CdI_2 dissolved, a little CdO_2H_2 separated, and CdOH remained as a white amorphous powder.

Cadmium, salts of (vol. i. p. 656). For the electrical conductivities of very dilute solutions of $CdBr_2$, $CdCl_2$, CdI_2, K_2CdI_4, $Cd(NO_3)_2$, and $CdSO_4$, *v.* Wershoven (*Z. P. C.* 5, 481 [1890]).

Cadmium, sulphide of (vol. i. p. 657). Two forms (and perhaps more) of CdS seem to exist, one lemon-yellow and the other red; they differ slightly in S.G., and in crystalline form; the yellow is said to change to the red by friction (*v.* Buchner, *Chem. Zeit.* 11, 1087, 1107; 15, 778; von Klobukoff, *J. pr.* [2] 39, 412; *abstracts* in *C. J.* 54, 224 [1888]; 56, 946 [1889]; 62, 778 [1892]). A solution of colloidal CdS was obtained by Prost (*C. C.* 1888. 32; *abstract* in *C. J.* 54, 653 [1888]) by completely ppg. an ammoniacal solution of $CdSO_4$ by H_2S, washing well, suspending the pp. in water and passing in H_2S. A solution with 4 grms. CdS per litre remained clear for many days; one with 11 grms. coagulated in 24 hours.

CÆSIUM (vol. i. p. 657). According to Beketoff (*v. abstract* in *C. J.* 62, 274 [1892]), Cs is obtained by heating CsOH with c. ¼ its weight of Al.

Cæsium, haloid compounds of (vol. i. p. 658). A series of compounds of the form CsX_3, where $X_3 = Br_3$, I_3, or Br and I, Cl, Br and I, &c., is described by Wells a. Penfield (*Am. S.* [3] 43, 17; *abstract* in *C. J.* 62, 773 [1892]). *Double compounds* of Cs haloids with haloid compounds of Cd, Cu, Mg, Hg, Pb, and Zn are described by Wells (and others) (*Am. S.* [3] 44, 221; *Zeit. f. anorg. Chemie*, 3, 195; 5, 266, 273, 300, 304, 306; *abstracts* in *C. J.* 64 [11], 67, 322 [1893]; 66 [11], 45, 47 [1894]).

Cæsium, hydroxide of (vol. i. p. 658). S.G. $\frac{0°}{4°}$ 4·0178; [CsOH,Aq] = 15,876; [CsOHAq,HClAq] = 13,790 (Beketoff, *C. C.* 1891. [11] 451).

Cæsium, oxide of (vol. i. p. 658). According to Beketoff (*J. R.* 25, 433; *abstract* in *C. J.* 66 [11], 234 [1894]), Cs_2O reacts with slightly moist H to give Cs and CsOH.

CALCIUM (vol. i. p. 663). The molecule in dilute solution in tin may be diatomic (*v.* Heycock a. Neville, *C. J.* 57, 376 [1890]).

Calcium, carbide of. By heating 120 g. $CaCO_3$ with 70 g. sugar charcoal in the electric furnace with a current of 350 ampères and 70 volts, Moissan (*C. R.* 118, 501 [1894]) obtained lustrous, yellow crystals of CaC_2; S.G. 2·22 at 18°; insoluble in most solvents; reacts with Cl, Br, and I at 250°–350°; burnt to $CaCO_3$ by O at a red heat; interacts violently with water, giving off pure acetylene, and with steam giving $CaCO_3$, C, H, and C_2H_2 (*abstract* in *C. J.* 66 [1], 313 [1894]).

Calcium, oxide of (vol. i. p. 666). CaO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]). According to Veley (*C. J.* 63, 821 [1893]; 65, 1 [1894]), *dry* CaO does not appreciably combine with *dry* CO_2, SO_2, or Cl below 300°. Baker (*C. J.* 65, 611 [1894]) says that *dry* CaO does not react with *dry* SO_3, nor with *dry* NH_4Cl. Moissan (*C. R.* 115, 1034 [1892]) obtained crystals of CaO by heating ordinary lime in the electric furnace.

Calcium, oxychloride of (vol. i. p. 666). Prepared by boiling CaO with conc. $CaCl_2Aq$; crystallises in thin, lustrous needles; decomposed by water, alcohol, &c.; dissolves in glycerin. Composition is probably $3CaO.CaCl_2.15aq$ (Zahorsky, *Zeit. f. anorg. Chemie*, 3, 34 [1893]).

Calcium, oxyiodide of. By heating CaO with CaI_2Aq in a sealed tube at 150° for 6 hours, Tassilly (*Bl.* [3] 9, 629 [1893]) obtained needles of $CaI_2.3CaO.16aq$.

CARBON (vol. i. p. 684).

Diamond. Moissan (*C. R.* 116, 218; 118, 320; *abstracts* in *C. J.* 64 [11], 275; 66 [11], 189 [1893 and 1894]) obtained grey-black *carbonado* by dissolving C in iron, heating to 2000°–3000°, and rapidly cooling the exterior by water or by plunging into a bath of melted lead; the liquid interior expands as it cools and produces a very high pressure. Diamond blackens, swells, and changes to graphite in the electric furnace (M., *C. R.* 117, 423 [1893]). For various reactions of diamond, *v.* Moissan (*C. R.* 116, 460; *abstract* in *C. J.* 64 [11], 319 [1893]).

Graphite. For accounts of graphites prepared in different ways, the compositions of the graphitic oxides obtained, and the H.F.s of these oxides, *v.* Berthelot a. Petit (*C. R.* 110, 101, 106; *abstract* in *C. J.* 58, 448 [1890]). For the action of conc. HNO_3 on various graphites, *v.* Luzi (*B.* 24, 4085; 26, 1412 [1892 and 1893]).

Amorphous carbon. Mixter (*Am. S.* [3] 45, 363; *abstract* in *C. J.* 64 [11], 571 [1893]) describes the interactions of charcoal and N, S, O, and the halogens. According to Ernst (*J. pr.* [2] 48, 31; *abstract* in *C. J.* 64 [11], 461 [1893]), the composition of the products of combustion of coke (CO and CO_2) depends almost wholly on the temperature; the maximum formation of CO_2 is at c. 700°, at 1,000° CO is the only product.

Allotropy of carbon. The following heats of combustion, and atomic volumes, are given by Petersen (*Z. P. C.* 8, 601 [1891]):—

	$[C,O^2]$.	At. volume.
Amorphous .	96,530 to 96,980	6·7 to 8
Graphite . . .	93,360	5·3
Diamond . . .	93,240 to 94,550	3·4

For the reactions of various forms of C with $K_2Cr_2O_7$ and H_2SO_4 *v.* Wiesner (*M.* 13, 871; *abstract* in *C. J.* 62, 1273 [1892]); and with HNO_3 and $KClO_3$ *v.* Schutzenberger (*C. R.* 111, 774; *abstract* in *C. J.* 60, 265 [1891]).

Carbon, tetrabromide of (vol. i. p. 688). Collie (*C. J.* 65, 262 [1894]) finds that very many compounds of carbon give CBr_4 when heated with NaOHAq and Br.

Carbon, bromochorides of (vol. i. p. 688). The three compounds $CBrCl_3$, CBr_2Cl_2, and $CBrCl_3$ are formed by heating $CHCl_3$ and Br to 225° in a sealed tube (Besson, *C. R.* 114, 222 [1892].)

Carbon, tetrafluoride of, CF_4. Mol. w. 88·37. V.D. 44·6. Prepared by the direct union of C (purified lampblack) and F at the ordinary temperature; by the reaction of F with CCl_4 slightly heated, or with $CHCl_3$ at 100°, or with CH_4 (Moissan, *C. R.* 110, 296, 951; *abstracts* in *C. J.* 58, 557, 944 [1890]); also by heating AgF with CCl_4 to 220° in a sealed tube (Chabrié, *C. R.* 110, 279 [1890]). M. recommends to pass vapour of CCl_4 over AgF at 195°–200°, to let the vapours pass through a serpentine tube kept at −23°, and to collect the gas over Hg; the gas is kept in contact with fragments of caoutchouc (to remove CCl_4), then shaken with absolute alcohol, in which it dissolves, and then expelled by heat, collected and shaken with H_2SO_4 (to remove alcohol vapour); metal vessels must be used. CF_4 is a colourless gas, liquefying at −15° and 760 mm. pressure, or at 20° under a pressure of 4 atmos. Other fluorides seem to be formed along with CF_4; Chabrié (*l.c.*) says that AgF and C_2Cl_4 yield C_2F_4.

Carbon, tetra-iodide of (vol. i. p. 689). Moissan (*C. R.* 113, 19; *abstract* in *C. J.* 60, 1420 [1891]) prepares CI_4 by heating CCl_4 (free from $CHCl_3$) with excess of BI_3 to 90° in a sealed tube, washing the crystals with $NaHSO_3Aq$, drying, and slowly subliming *in vacuo*. CI_4 reacts with Cl to form CCl_4 and chlorides of I; reduced to CHI_3 by H at 140° (for other reactions *v.* M., *l.c.*).

Carbon monoxide (vol. i. p. 689). For some experiments on the sparking of CO, with the formation of brown solids, *v.* Berthelot (*C. R.* 110, 609) and Schützenberger (*C. R* 110, 560; *abstracts* in *C. J.* 58, 691 [1890]). Winkler (*B.* 24, 873 [1891]) finds that CO is reduced to C, at a full red heat, by Mg; carbides of Mg are probably formed (*cf.* W., *B.* 23, 2642 [1890]).

Carbon dioxide (vol. i. p. 691). For S.H. of CO_2 *v.* Kurnakoff (*J. R.* 22, 493; *abstract* in *C. J.* 64 [11], 5 [1893]). CO_2 is reduced by heating to redness with Mg, amorphous C and some CO being formed (Winkler, *B.* 23, 2642; 24, 873 [1890-91]). *Dry* CO_2 is said not to combine with *dry* NH_3 (Hughes a. Soddy, *C. N.* 69, 138).

Carbon, oxychloride of (vol. i. p. 692). $COCl_2$ becomes viscid, but remains clear, at −75° (Haase, *B.* 26, 1052 [1893]).

Carbon disulphide (vol. i. p. 693). The contractions observed when mixtures of CS_2 and air are exploded show that the reaction is more complicated than is shown by the equation $CS_2 + 3O_2 = CO_2 + 2SO_2$; the volume of CO_2 found is, practically, in accordance with the equation, but the volume of SO_2 is smaller; some of the N of the air is oxidised (*v.* Pedler, *C. J.* 57, 625 [1890]). By heating CS_2 with excess of *aqua regia*, Schlagdenhauffen a. Bloch (*J. Ph.* [5] 28, 241 [1893]) obtained $SO(OCCl_3)Cl$. Decomposition of CS_2, heated in dry N, begins at 216°, and explosion with O at a higher temperature (Baker, *C. J.* 65, 611 [1894]).

Tricarbon disulphide C_3S_2. B. von Lengyel (*B.* 26, 2960 [1893]) obtained this compound by keeping the vapours of CS_2 in an electric arc between C poles for some hours, filtering off the black substance formed, allowing the red filtrate to stand over Cu for 6 to 8 days, and evaporating in a current of dry air. C_3S_2 is a deep-red liquid, S.G. 1·27389; the vapour, even in minute quantities, causes violent catarrh; can be distilled, with partial change to a black solid, at 60°–70° and reduced pressure; insoluble water, but dissolved by EtOH, Et_2O, CS_2, $CHCl_3$, or C_6H_6. A conc. solution in CS_2 deposits a black solid; the same solid is formed by gently heating the liquid, if heating to 100°–120° is rapid the change is explosive. The black solid is probably a polymeride. A solution of C_3S_2 in CS_2 reacts with Br to form $C_3S_2Br_6$. (For other reactions, *v. abstract* in *C. J.* 66 [11], 91 [1894].)

Carbon, thiobromide of, $C_3S_2Br_6$; formed by the action of Br on a solution of C_3S_2 in CS_2 (*v. supra*).

Carbon, thiochloride of (vol. i. p. 695). The polymeride of thio-carbonyl chloride has the molecular formula $(CSCl_2)_2$, according to the cryoscopic determinations of Carrara (*G.* 23 [ii.] 12; *abstract* in *C. J.* 66 [11], 15 [1894]).

CERIUM (vol. i. p. 723). For details regarding the preparation of Ce compounds free from compounds of Di and La, *v.* Schottländer (*B.* 25, 378 [1892]); also Bricout (*C. R.* 118, 145 [1894]).

Cerium, hydride of. According to Winkler (*B.* 24, 873 [1891]), a compound of Ce and H, probably CeH_2, is formed by reducing CeO_2 by Mg in presence of H.

Cerium dioxide (vol. i. p. 725). CeO_2 is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]).

CHLORHYDRIC ACID (vol. ii. p. 5). Biltz (*Z. P. C.* 10, 354 [1892]) finds that the V.D. at −77° agrees with the formula HCl. Perkin (*C. J.* 55, 703, 705 [1889] has determined M. M. of HClAq and HCl in iso-amyl oxide; the values obtained for HCl in Aq are c. double those for HCl in iso-amyl oxide. For measurements of the E.C. of HCl in different solvents, *v.* Kablukoff (*Z. P. C.* 4, 429 [1889]). For revised tables giving S.G. of HClAq, *v.* Lunge a. Marchlewski (*Zeit. f. anorg. Chemie*, 1891. 133).

For the relations between the number of molecules of HCl required to ppt. one mol. of different chlorides, and the reduction of the freezing-points of solutions of the chlorides and of HCl, *v.* Engel (*C. R.* 117, 845; *abstract* in *C. J.* 66, 40 [1894]).

Bailey a. Fowler (*C. J.* 53, 755 [1888]) find that when HCl stands over P_2O_5 the gas is absorbed, with production of $POCl_3$ and HPO_3; and that when HCl and O stand over Hg an oxychloride, probably $Hg_2OCl_2.H_2O$, is formed. Baker (*C. J.* 65, 611 [1894]) states that *dry* HCl does not combine with *dry* NH_3 when the gases are mixed.

CHLORINE (vol. ii. p. 10). For the S.G. of *liquid chlorine* from −80° to 77°, and the vapour pressures from −88° to 146°, *v.* Knietsch (*A.* 259, 100 [1890]). For the preparation of Cl for use in the laboratory, *v.* Klason (*B.* 23, 330; *abstract* in *C. J.* 58, 445 [1890]). Shenstone (*C. J.* 61, 445 [1892]) finds that Cl obtained by heating $PtCl_4$ always contains some HCl and O, with water, and perhaps a trace of N. Cl expands when brought into sunlight. Richardson (*P. M.* [5] 32, 277 [1891]) has constructed an instrument wherein the expansion is used to measure the intensity of light. Baker (*C. J.* 65, 611 [1894]) found that no explosion occurred when a mixture of equal vols. of *dry* Cl and *dry* H was exposed to bright sunlight; and that after exposure to bright sunshine for two days, and to diffused light for two days, more than a quarter of the mixture remained unchanged.

Pedler (*C. J.* 57, 613 [1890]) has examined the interaction of Cl and water in tropical sunlight; he finds that there is very little action, unless there is an extremely large excess of water. With very much water and little Cl, exposed to the full light of the sun in the hot season in India, the main reaction is $2H_2O + 2Cl_2 + Aq = 4HClAq + O_2$; with diffused sunlight HClAq and HClOAq are formed at first, and finally HClAq, $HClO_3Aq$, and O. Harker (*Z. P. C.* 9, 673 [1892]), from an extended investigation of the explosion of mixtures of Cl, H, and O, concluded that when there is insufficient H to combines with all the Cl and all the O, a division of the H between the Cl and O occurs; and that the product of the numbers of molecules of HCl and O, divided by the product of the numbers of molecules of H_2O and Cl_2 is a constant, or, in other words, that the law of Guldberg a. Waage holds good. According to Gautier a. Charpy (*C. R.* 113, 597 [1891]), there is no reaction between Mg or Zn and liquid Cl at the ordinary temperature, very little reaction with Fe or Ag, and rather more with Cu.

Chlorates (vol. i. p. 18). Spring a. Prost (*Bl.* [3] 1, 340 [1893]) have determined the quantities of Cl obtained by decomposing by heat chlorates of Al, Ba, Cu, Pb, Hg, K, Ag, Na, and Zn; the amount of Cl varied from ·02 p.c. from $KClO_3$ to 14·45 p.c. from $Zn(ClO_3)_2$.

Calcium chlorate. Dry $Ca(ClO_3)_2$ melts between 300°-350°, having previously given off from 3 to 5 p.c. of its weight of O; the rate of evolution of O increases, at 330°, until c. 60 p.c. of the total O is given off, after which the rate decreases. For the quantities of O evolved, of $Ca(ClO_3)_2$ decomposed, and of $CaCl_2$ and $Ca(ClO_4)_2$ formed, *v. abstract* in *C. J.* 62, 1275 [1892].

Potassium chlorate. McLeod (*C. J.* 55, 184 [1889]) concluded from his experiments that when $KClO_3$ is heated with MnO_2 some $KMnO_4$ is formed and again decomposed (*v.* MANGANESE PEROXIDE, vol. iii. p. 183), and that Cl is always given off in this reaction. In 1893 (*B.* 26, 1790) Brunck stated that Cl is not given off when $KClO_3$ and MnO_2 are heated together, but that ozone is produced. McLeod (*C. J.* 65, 202 [1894]) has proved that Cl is produced in the reaction. Fowler a. Grant (*C. J.* 57, 272 [1890]) have studied the influence of various oxides on the decomposition of $KClO_3$ (references are given to older memoirs); they support McLeod's view of the reaction with MnO_2, and think that the oxides of Fe, Co, Cu, and Ni react similarly to MnO_2; acidic oxides, such as V_2O_5, U_3O_8, and WO_3 cause evolution of O accompanied by much Cl, a vanadate, uranate, or tungstate being also formed; powdered glass or sand also assists the reaction, but only when very finely divided (*v.* summary of conclusions, *C. J.* 57, 281-2). According to Thorpe a. Perry (*C. J.* 61, 925 [1892]), the main reaction which occurs when an intimate mixture of $KClO_3$ and iodine is heated is $2KClO_3 + I_2 = 2KIO_3 + Cl_2$, and some of the Cl reacts with unchanged I to form ICl and ICl_3. Basset (*C. J.* 57, 760 [1890]) examined the reactions between $KClO_3$, water, and iodine; he concluded that the main reaction, at 80°, in the presence of a very small quantity of HNO_3Aq, is as shown by the equation $6I_2 + 10KClO_3 + 6H_2O + Aq = 6KHI_2O_6Aq + 4KClAq + 6HClAq$; in evaporating the solution to dryness Cl was given off, and the results of several experiments led to the representation of the change produced by evaporation to dryness as $12KHI_2O_6 + 8KCl + 12HCl = 11KHI_2O_6 + 9KCl + 6H_2O + ICl + ICl.HCl + 4Cl_2$. For determinations of the quantities of oxidising gases (Cl and oxides of Cl) removed by passing air through $KClO_3Aq$ mixed with HClAq, *v.* Pendlebury a. McKillop (*C. S. Proc.* 1893-4. [No. 129] 211).

Strontium chlorate. For experiments on the decomposition of this salt by heat, giving $SrCl_2$, $Sr(ClO_4)_2$, and O, *v.* Potilitzin (*J. R.* 21, 451; *abstract* in *C. J.* 58, 696 [1890]).

CHROMIUM (vol. ii. p. 152). S.H. of pure Cr (0° to 98°) = ·12162 (Jäger a. Krüss, *B.* 22, 2028 [1889]). The at. w. of Cr was re-determined by Rawson in 1889 (*C. J.* 55, 213) by strongly heating $(NH_4)_2Cr_2O_7$, measuring the N given off, and weighing the Cr_2O_3 that remained; also by reducing $(NH_4)_2Cr_2O_7Aq$ to $CrCl_3Aq$ by HClAq and alcohol, ppg. by NH_3Aq, and weighing Cr_2O_3 produced; the mean value thus obtained was 52·06, or 51·98 reduced to 0° and a vacuum (O = 15·96). Meineke in 1891 (*A.* 261, 339; *abstract* in *C. J.* 60, 882 [1891]) re-determined the at. w. of Cr by estimating (1) Ag and Cr, and also O, in Ag_2CrO_4 and in $Ag_2CrO_4.NH_3$, (2) O in $K_2Cr_2O_7$; (3) O and Cr in $(NH_4)_2Cr_2O_7$; the extreme values, from thirty-six experiments, were 52·12 and 51·83; twenty-eight of the experiments gave values between 51·9 and 52. According to Prinz (*C. R.* 116, 392 [1893]), Cr crystallises in minute cubes with pyramidal faces. For the absorption spectra of salts of Cr, *v.* Lapraik (*J. pr.* [2] 47, 305 [1893]).

Preparation.—Glatzel (*B.* 23, 3127 [1890]) says that almost perfectly pure Cr can be obtained by reducing $CrCl_3.KCl$ by Mg powder (for details *v. abstract* in *C. J.* 60, 152 [1891]). Placet (*C. R.* 115, 945 [1892]) prepares Cr by electrolysing a solution of Cr alum, containing an alkali sulphate and H_2SO_4. Moissan (*C. R.* 116, 349 [1893]) says that Cr can be obtained by reducing a mixture of Cr_2O_3 and C in the electric furnace, using a current of 50 volts and 100 ampères, and then breaking up the product, which contains from 8·6 to 12·9 p.c. C, and heating it, mixed with more Cr_2O_3, again in the electric furnace in a carbon crucible.

Chromic acid (vol. ii. p. 154). Miss Field (*C. J.* 61, 405 [1892]) has found that only CrO_3 is obtained by working according to Moissan's directions for preparing H_2CrO_4. Determinations of the increase in the b.p. of water caused by solution of CrO_3 led to the conclusion that an aqueous solution of CrO_3 contains some H_2CrO_4, and probably also $H_2Cr_2O_7$.

Chromic bromide $CrBr_3$ (vol. ii. p. 161). Recoura (*C. R.* 110, 1029, 1193) obtained green $CrBr_3.6H_2O$ by boiling saturated CrO_3Aq with a large excess of HBrAq and concentrating; deliquescent crystals, soluble alcohol, insoluble ether. Unchanged when kept solid, but solution soon becomes blue and then violet, with rise of temperature. By boiling a green solution, then saturating with HBr while cold, filtering, and drying the pp. thus formed on porous plates, crystals of the blue variety, $CrBr_3.6H_2O$, were obtained; very soluble water, insol. alcohol. Heat of solution of blue crystals = 28,700; and of green = 1,860. The blue solid is changed to the green at 100°. (For more details *v. abstract* in *C. J.* 58, 1063 [1890].)

Chromic chloride $CrCl_3$ (vol. ii. p. 161). Marchetti (*G.* 22 [11], 375 [1892]) finds that th molecular lowering of the freezing-point of wate by the violet form of $CrCl_3$ is considerably greate than that caused by the green form.

Chromic fluoride CrF_3 (vol. ii. p. 162) Fabris (*G.* 20, 582 [1890]) obtained $CrF_3.9H_2$ as a green crystalline pp., by adding excess

NH_4FAq gradually to a cold solution of violet $Cr_2(SO_4)_3$. Slightly sol. water; insoluble NH_4FAq or alcohol; heating in air leaves Cr_2O_3. Poulenc (*C. R.* 116, 253 [1893]) obtained CrF_3 in green crystals by heating $CrCl_3$, Cr_2O_3, or $CrF_3.xH_2O$ in HF.

Chromous fluoride. According to Poulenc (*l.c.*), CrF_2 is formed by heating Cr to redness in HF, or by the interaction of $CrCl_2$ and HF at the ordinary temperature. CrF_2, after fusion, is described as a transparent, green, crystalline mass; S.G. 4·11; slightly sol. water, insol. alcohol. Heated in air it gives Cr_2O_3. (For more details *v. abstract* in *C. J.* 64 [11], 281 [1893].)

Chromic oxide Cr_2O_3 (vol. ii. p. 164). Moissan (*C. R.* 115, 1034 [1892]) found that Cr_2O_3 melted to a black mass, dotted with black crystals, in an electric furnace, using a current of 55 volts and 30 ampères.

Chromium trioxide CrO_3 (vol. ii. p. 164). For action of water *v.* CHROMIC ACID, p. 905. Reduced to Cr_2O_3 by NO at the ordinary temperature (Senderens a. Sabatier, *C. R.* 114, 1476 [1892]). For the reaction of CrO_3Aq with O and BaO_2H_2Aq—said to give a pp. approximately $BaCrO_5$—*v.* Péchard, *C. R.* 113, 39 (*abstract* in *C. J.* 60, 1431 [1891]).

Chromium salts (vol. ii. p. 167). According to Recoura (*C. R.* 112, 1439; *abstract* in *C. J.* 60, 1430 [1891]), the green solutions obtained by heating solutions of the normal violet chromic salts contain free acid and a soluble basic salt; in the case of the sulphate this soluble basic salt is said to be $2Cr_2O_3.5SO_3$. For preparation of green soluble normal sulphates *v.* Recoura, *C. R.* 115, 857 (*abstract* in *C. J.* 62, 411 [1892]).

CHROM-AMMONIUM COMPOUNDS (vol. ii. p. 158). Petersen (*Z. P. C.* 10, 580 [1892]) finds, by cryoscopic determinations, that the formulæ usually assigned to the chief salts of this class are probably molecular. For a discussion of the constitution of these salts *v.* Jörgensen (*J. pr.* [2] 42, 206; 45, 274).

CHROMATES; *and derivatives* (vol. ii. p. 154).

Ammonium chromates. According to Jäger a. Krüss (*B.* 22, 2028 [1889]), *normal ammonium chromate* has not hitherto been obtained pure; they prepare the pure salt by adding excess of NH_3Aq S.G. ·9 to CrO_3Aq free from H_2SO_4Aq, warming until the solid that separates dissolves, and placing in a freezing mixture. $(NH_4)_2CrO_4$ crystallises in long, monosymmetric, golden needles, $a:b:c = 1·9603:1:2·4452$; S.G. 1·886 at 11°.

Ammonium trichromate $(NH_4)_2Cr_3O_{10}$ is prepared by J. a. K. (*l.c.*) by dissolving $(NH_4)_2Cr_2O_7$ in hot conc. CrO_3Aq, concentrating, and drying at 100° the red crystals that separate on cooling; S.G. 2·342 at 13°; explodes at 190°, giving off NO_2, and leaving Cr_2O_3.

Ammonium tetrachromate $(NH_4)_2Cr_4O_{13}$ is formed by dissolving the trichromate in warm HNO_3Aq S.G. 1·09, and letting cool slowly; S.G. 2·343 at 10°; melts at 170°, and suddenly decomposes at 175°, giving off NO and leaving Cr_2O_3. J. a. K. (*l.c.*) failed to obtain *hexachromate*; they say that no nitro-chromates are obtained by treating ammonium chromates with HNO_3Aq. (For more details *v. abstract* in *C. J.* 56, 1117 [1889].) Various *double compounds* of $(NH_4)_2Cr_2O_7$ with $HgCl_2$ are described by J. a. K. (*l.c.*).

Ceric dichromate $CeO_2.2CrO_3.2H_2O$. Prepared by passing a current of 2·5 to 3 volts through a slightly acid solution formed by dissolving $Ce_2(CO_3)_3$ in CrO_3Aq; insoluble water; boiling water forms yellow $Ce(CrO_4)_2$ and then $CeO_2.xH_2O$ (Bricout, *C. R.* 118, 145 [1894]).

Lead chromates. For *double compounds* of $PbCrO_4$ with Li_2CrO_4, K_2CrO_4, and Na_2CrO_4, *v.* Lachaud a. Lepierre, *C. R.* 110, 1035 (*abstract* in *C. J.* 58, 1065 [1890]).

Mercury chromates. For *basic mercuric chromates* and a *double compound* of $HgCrO_4$ with NH_2HgCl *v.* Jäger a. Krüss, *B.* 22, 2028 (*abstract* in *C. J.* 56, 1120 [1889]).

Potassium chromates. Jäger a. Krüss (*l.c.*) prepare *potassium trichromate* $K_2Cr_3O_{10}$ by treating $K_2Cr_2O_7$ with HNO_3Aq S.G. 1·19, pouring off from KNO_3 that separates, and crystallising; S.G. 2·648 at 11°. $K_2Cr_3O_{10}$ is quickly decomposed by water to CrO_3Aq and $K_2Cr_2O_7Aq$; melts at 250°. *Potassium tetrachromate* $K_2Cr_4O_{13}$ is prepared by J. a. K. (*l.c.*) by dissolving $K_2Cr_2O_7$ in hot conc. HNO_3Aq S.G. 1·41; S.G. 2·649 at 11°; not deliquescent; decomposed by water; crystallises unchanged from HNO_3Aq S.G. 1·41. Schmidt (*B.* 25, 2917 [1893]) says that no nitrochromate is obtained by the action of HNO_3Aq on $K_2Cr_2O_7$; the substances obtained by Darmstädter (*v.* vol. ii. p. 158) were mixtures of KNO_3 and $K_2Cr_4O_{13}$.

Silver chromates. Pure *silver chromate* Ag_2CrO_4 is prepared by J. a. K. (*l.c.*) by repeatedly boiling $Ag_2Cr_2O_7$ with water as long as anything dissolves; it is a deep-green solid, insol. water.

Sodium perchromate. Häussermann (*J. pr.* [2] 48, 70; *abstract* in *C. J.* 64 [11], 471) describes a salt $Na_6Cr_2O_{15}.28aq$, prepared by adding Na_2O_2 to a thin paste of CrO_3H_3 and water, kept at 10°–20°.

Thallium chromates. For preparation of Tl_2CrO_4 and the *double compound* $Tl_2CrO_4.K_2CrO_4$ *v.* Lachaud a. Lepierre, *Bl.* [3] 6, 232 (*abstract* in *C. J.* 62, 567 [1892]).

Uranium chromates. For *double uranyl chromates* *v.* Formánek, *A.* 257, 102 (*abstract* in *C. J.* 58, 852 [1890]).

IODOCHROMATES (vol. ii. p. 157). A series of salts of the forms $IO_2.O.CrO_2.OM^I$ and $(IO_2.O.CrO_2.O)_2M^{II}$ has been obtained by Berg (*C. R.* 104, 1514 [1887]; 111, 42 [1890]); $M^I = NH_4$, Li, K, Ag, and Na; $M^{II} =$ Co, Cu, Mg, and Ni. Most of the alkali salts were formed by dissolving the alkali iodate in excess of CrO_3Aq and crystallising; the other salts were usually prepared by dissolving the oxide or carbonate of the metal in excess of CrO_3Aq and adding HIO_3Aq. (For details *v. abstracts* in *C. J.* 52, 776 [1887]; 58, 1378 [1890].)

PHOSPHOCHROMATES. By adding conc. $H_3PO_4Aq + CrO_3Aq$ to K_2CO_3Aq, Blondel (*C. R.* 118, 194; *abstract* in *C. J.* 66 [11], 193 [1894]) obtained compounds of the form $mK_2O.P_2O_5.nCrO_3.xaq$, m being 2 and 3, n 4 and 8, and x being 0 or 1.

SULPHOCHROMATES. In 1882 Cross a. Higgin described a compound of Cr_2O_3, SO_3, and H_2O (*C. J.* 41, 113), and also compounds of Cr_2O_3, SO_3, K_2O and H_2O. Recoura (*C. R.* 114, 477

[1892]; 116, 1367; 117, 37, 101 [1893]) has made a more complete examination of these and allied compounds. By evaporating, at 100°, solutions containing violet $Cr_2(SO_4)_3$ and H_2SO_4, in the molecular ratio 1:1, 1:2, and 1:3, R. obtained *chromosulphuric acid* $H_2Cr_2(SO_4)_4$, *chromodisulphuric acid* $H_4Cr_2(SO_4)_5$, and *chromotrisulphuric acid* $H_6Cr_2(SO_4)_6$; by using various sulphates in place of H_2SO_4 he obtained *chromosulphates*, *chromodisulphates*, and *chromotrisulphates*. The acids are green powders, easily sol. water; they gradually decompose in solution; dilute $BaCl_2Aq$ ppts. Ba chromosulphates, but conc. $BaCl_2Aq$ gives $BaSO_4$. R. obtained *chromopyrosulphuric acid* $Cr_2(OH)_2(S_2O_7H)_4$, by evaporating a solution of $Cr_2(SO_4)_3$ and H_2SO_4, in the molecular ratio 1:5, at 100°, and heating the dark-green syrupy liquid so obtained to 110°-115° for some days. The acid forms brittle, transparent, pale-green laminæ. Salts of the form $Cr_2(S_2O_7)_2(OM)_2$ are obtained by adding alkalis to the acid in solution; these salts R. calls *pyrosulphochromites*. By adding conc. HClAq or H_2SO_4 to a solution of chromopyrosulphuric acid, R. obtained a compound $Cr_2(OH)_2(S_2O_7)_2$, *pyrosulphochromic hydroxide*, isomeric with chromosulphuric acid $Cr_2(SO_4)_4H_2$. (For more details *v. abstracts* in *C. J.* 62, 783 [1892]; 64 [11], 470, 528 [1893].)

COBALT (vol. ii. p. 217). Winkler has redetermined at. w. of Co, (1) by dissolving electrolytically deposited Co in HClAq, evaporating to dryness, and determining Cl in the $CoCl_2$ obtained (*Zeit. f. anorg. Chemie*, 4, 10 [1893]); (2) by finding the quantity of Ag deposited from solution of Ag_2SO_4 by electrolytically deposited Co (*l.c.* p. 462). The values obtained were all about 59·6 (Ag = 107·66).

Alleged decomposition of cobalt. Krüss a. Schmidt (*B.* 22, 11, 2026 [1889]) supposed they had separated Ni into two constituents (*v.* vol. iii. p. 500); and they thought that Co also was probably not a homogeneous substance. Remmler, in 1893, obtained a number of specimens of Co_2O_3, by ppg. $CoCl_2Aq$ by KOHAq and Br water, treating the pp. with NH_3Aq, which gradually dissolves it, decanting off the ammoniacal solution at intervals during 9 months, evaporating each and heating in CO_2; the different specimens of Co_2O_3 were heated in H, and the quantity of Co obtained in each case was determined. The values thus obtained for the at. w. of Co varied from 59·53 to 58·3. R. concluded that Co purified by the ordinary methods is not a homogeneous substance. Winkler's determinations of the at. w. (*v. supra*), however, gave very constant values.

Reactions.—Heated in NO to 150°, CoO is formed (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]); finely divided Co burns in NO_2 at the ordinary temperature, giving Co_4O_5; but if the NO_2 is largely diluted with N, a black compound is formed, Co_2NO_2, called by S. a. S. (*C. R.* 115, 236 [1892]) *nitro-cobalt*. This compound reacts rapidly with H_2O, giving off NO, and forming a solution containing $Co(NO_3)_2$ with a very little $Co(NO_2)_2$, Co remaining insoluble, and sometimes also a basic nitrite; when heated in N, oxides of N are given off and then rapid decomposition occurs with formation of Co and oxides of Co; when mixed with combustible substances Co_2NO_2 explodes (S. a. [illegible] *Bl.* [3], [illegible] [1893]). Montemartini (*G.* 22 [1], 250) finds that the gases produced by the interaction of Co and excess of HNO_3Aq (27·5 p.c.) are NH_3, N_2O, and N (*v. abstract* in *C. J.* 62, 1278 [1892]).

Cobalt, chloride of (vol. ii. p. 219). For the solubility of $CoCl_2$ in water, and the changes of colour produced by diluting the solution, with a discussion of the hydrations and dehydrations that accompany these changes, *v.* Étard, *C. R.* 113, 699 (*abstract* in *C. J.* 62, 278 [1892]); Engel, *Bl.* [3] 6, 239 (*abstract* in *C. J.* 62, 569 [1892]); and Potilitzin, *Bl.* [3] 6, 264 (*abstract* in *C. J.*, *l.c.* p. 571). The *double compounds* $CoCl_2.HCl.3aq$, $CoCl_2.LiCl.3aq$, and $CoCl_2.NH_4Cl.6aq$ are described by Chassevant (*A. Ch.* [6] 30, 5 [1893]).

Cobalt, fluoride of (vol. ii. p. 220). Poulenc (*C. R.* 114, 1426; *v. abstract* in *C. J.* 62, 1159 [1892]) prepares CoF_2 by heating $CoCl_2$ with excess of NH_4F for 15 minutes, and repeatedly washing the double fluoride $CoF_2.2NH_4F$ thus obtained with boiling alcohol. By heating CoF_2 to 1200°-1300° in HF, the salt is obtained in small, rose-red prisms; S.G. 4·43. The *double compound* $CoF_2.2KF$ is formed by heating $CoCl_2$ with KHF_2 (*P.*, *l.c.* p. 746; *abstract*, *l.c.* p. 781).

Cobalt, iodide of (vol. ii. p. 220). For solubility in water of CoI_2, and the formation of various hydrates attending solution, *v.* Étard, *C. R.* 113, 699 (*abstract in C. J.* 62, 278 [1892]).

Cobaltous oxide CoO (vol. ii. p. 220). This oxide melts in the electric furnace, and forms rose-coloured crystals (Moissan, *C. R.* 115, 1034 [1892]).

Cobaltous hydroxide CoO_2H_2 (vol. ii. p. 220). A. de Schulten (*C. R.* 109, 266 [1889]) obtained this compound in microscopic, brownish-red, four-sided prisms, S.G. 3·597 at 15°, by heating 10 g. $CoCl_2.6aq$ in 60 c.c. water with 250 g. KOH, in a flask filled with coal-gas, letting stand for 24 hours, and washing away the lighter amorphous products of the reaction.

Cobalto-cobaltic oxides (vol. ii. p. 221). Regarding Co_3O_4 and oxides intermediate between this and Co_2O_3, *v.* Schröder, *C. C.* 1890. [1] 931 (*abstract* in *C. J.* 58, 1213 [1890]). Co_3O_4 heated to c. 1750° loses all its O, and leaves Co (Read, *C. J.* 65, 313 [1894]).

Cobalt, dioxide of. By the reaction of IAq and NaOHAq on $CoSO_4Aq$, filtering, and acidifying with acetic acid, Vortmann (*B.* 24, 2744; *abstract* in *C. J.* 60, 1429 [1891]) obtained a greenish-black pp. nearly agreeing with the formula CoO_2. For compounds of CoO_2 with BaO *v.* Rousseau, *C. R.* 10[illegible], 64 (*abstract* in *C. J.* 56, 1115 [1889]).

Cobalt, salts of (vol. ii. p. 221). Marshall (*C. J.* 59, 760 [1891]) has prepared the salts $Co_2(SO_4)_3.18aq$ and $Co_2(C_2O_4)_3.3(NH_4)_2C_2O_4.6aq$ by electrolysing a solution of $CoSO_4$ in H_2SO_4Aq, and of CoC_2O_4Aq containing $(NH_4)_2C_2O_4$.

COBALTAMMINES (vol. ii. p. 222). By cryoscopic determinations, Petersen (*Z. P. C.* 10, 580 [1892]) concludes that the formulæ generally given to the chief cobaltammines are molecular. For a discussion of the constitution of these compounds, *v.* Jörgensen (*J. pr.* [2] 41, 429, 440 [1890]; 42, 206; 45, 274 [1891-92]). For various *octammines*, *v.* Vortmann a. Blasberg (*B.* 22, 2648), and V. a. Magdeburg (*B.* 22, 2630; *abstracts* in *C. J.* 58, 14 [1890]). V. a. Morgulis (*B.* 22, 2644; *abstract* in *C. J.* 58, 13 [1890]), describe several *mercuricobaltammines*. A number of *croceo-*, *luteo-*, and *xantho- salts*, and also several *flavo- salts* isomeric with the croceo-salts, are described by Jörgensen in *Zeit. f. anorg. Chemie*, 5, 147 (*abstract* in *C. J.* 65 [11], 50 [1894]).

COPPER (vol. ii. p. 251). An elaborate investigation of the at. w. of Cu has been made by Richards, *P. Am. A.* 26, 240 [1891] (*v.* *C. N.* 65, 236, &c.; *abstract* in *C. J.* 64 [11], 12 [1893]). $CuSO_4.5H_2O$ was analysed and synthesised, and CuO was analysed; the final value obtained by R. is 63·604 (O = 16), or 63·44 (O = 15·96). The molecule of Cu in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). For the absorption spectra of solutions of $CuCl_2$, $CuSO_4$, and $Cu(NO_3)_2$, *v.* Evan, *P. M.* [5] 33, 317 (*abstract* in *C. J.* 64 [11], 149 [1893]).

Preparation.—For the preparation by electrolysis of pure copper *v.* Richards (*P. Am. A.* 25, 199, 206 [1890]).

Reactions.—Heated in the electric furnace, using a current of 70 volts and 350 ampères, Cu rapidly volatilises, and the vapour forms CuO in the air (Moissan, *C. R.* 116, 1429 [1893]). According to Neumann (*M.* 13, 40 [1893]), the H occluded in Cu prepared by reducing CuO by H, cannot be wholly expelled by heating in a stream of CO_2; some of the CO_2 is also absorbed by the Cu. N. also says that Cu reduced by vapour of MeOH or EtOH, or by coal gas, retains very small traces of C and H after being heated to 220°. Montemartini (*G.* 22, 384, 397, 426 [1892]) says that the reaction between Cu and HNO_3Aq of less than 30 p.c. produces $Cu(NO_3)_2$ and HNO_2, the HNO_2 then decomposing to HNO_3, NO, and H_2O; with acid more conc. than 30 p.c. HNO_3 some NO_2 is produced with a little N_2O_3, and with 70 p.c. acid only NO_2 is given off; no appreciable quantity of NH_3 is produced with acid from 3 to 27·5 p.c. HNO_3. According to Freer a. Higley (*Am.* 15, 71 [1893]), the only gaseous products of the reaction of Cu with excess of HNO_3Aq S.G. 1·4 (c. 65 p.c. HNO_3) are NO_2 and N_2O_3, c. 90 p.c. NO_2 and 10 p.c. N_2O_3. Cu is superficially oxidised in NO at a dull red heat (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]). Reduced Cu absorbs NO_2 at the ordinary temperature, forming a brownish powder Cu_2NO_2 (S. a. S., *C. R.* 115, 236 [1892]). For the reactions of this *nitro-copper* *v.* S. a. S., *C. R.* 116, 756 (*abstract* in *C. J.* 64 [11], 374 [1893]).

Copper, alloys of (vol. i. p. 253). For a description of alloys of Cu with Cd, Sn, and Zn, prepared by immersing plates of Cd, Sn, or Zn, in solutions of salts of Cu, *v.* Mylius a. Fromm, *B.* 27, 630 (*abstract* in *C. J.* 66 [11], 235 1894]).

Cupric bromide (vol. ii. p. 254). According to Sabatier (*C. R.* 118, 980 [1894]), the green crystals that separate from $CuBr_2Aq$ are $CuBr_2.4aq$. A solution of $CuBr_2$ in conc. HBrAq has an intense purple colour which becomes less marked on dilution, but even with ·0015 mgm. Cu in solution the colour can be detected (S., *l.c.*) The *double salts* $CuBr_2.CsBr$ and $CuBr_2.2CsBr$ are described by Wells a. Walden (*Zeit. f. anorg. Chemie*, 5, 304; *abstract* in *C. J.* 66 [11], 47 [1894]).

Cupric chloride (vol. ii. p. 255). Tzuchanoff (*J. R.* 25, 151; *abstract* in *C. J.* 66 [11], 47 [1894]) finds that the E.C. of dilute blue-coloured $CuCl_2Aq$ increases with increase of concentration to a maximum, after which it decreases while the colour changes to yellowish-brown. For heats of solution and dilution of $CuCl_2.2aq$, *v.* Reicher a. Deventer (*Z. P. C.* 5, 559 [1890]).

Double salts.—$CuCl_2.HCl.3aq$, $CuCl_2.LiCl.xaq$, $CuCl_2.NH_4Cl$, $CuCl_2.2NH_4Cl.2aq$, $CuCl_2.KCl$, and $CuCl_2.2KCl.2aq$ (Chassevant, *A. Ch.* [6] 30, 5 [1893]); $CuCl_2.CsCl$, $CuCl_2.2CsCl.xaq$ ($x = 0$ and 2), and $2CuCl_2.3CsCl$ (Wells a. Dupree, *Zeit. f. anorg. Chemie*, 5, 300 [1893]).

Cuprous chloride (vol. ii. p. 255). Wells (*l.c.*, p. 306) describes the *double salts* $2CuCl.CsCl$, $2CuCl.3CsCl$, and $CuCl.3CsCl.aq$.

Cupric fluoride (vol. ii. p. 256). Pouleno (*C. R.* 116, 1446; *abstract* in *C. J.* 64 [11], 525 [1893]) prepares CuF_2, as a white amorphous powder, by heating NH_4F with $CuF_2.2aq$; by heating in HF at 500° (not above) the CuF_2 becomes crystalline. Crystalline CuF_2 is also obtained by heating CuO, or $CuF_2.2aq$, in HF at 400° (P., *l.c.*). Heated to 300° in air CuO is formed; heating in steam gives CuO and HF; H_2S forms CuS and HF; HCl forms $CuCl_2$. CuF_2 absorbs water from the air, and becomes blue. H. von Helmholt (*Zeit. f. anorg. Chemie*, 3, 115 [1892]) describes the *double salts* $CuF_2.KF$, $CuF_2.RbF$, $CuF_2.AmF.xaq$, and $CuF_2.2AmF.2aq$.

Cuprous fluoride (vol. ii. p. 256). According to Mauro (*Real. Acad. Lincei*, 1892 [1]. 194; *abstract* in *C. J.* 64 [11], 124 [1893]), Cu_2F_2 does not exist, and the substance obtained by Berzelius was almost certainly merely impure copper. Pouleno, however (*C. R.* 116, 1446; *abstract* in *C. J.* 64 [11], 525 [1893]), says that Cu_2F_2 is formed by heating Cu_2Cl_2 to dull redness in HF (the action is not complete until 1100°–1200°); also by heating CuF_2 in HF at c. 600°, raising the temperature to 1100°–1200° towards the end of the reaction. P. describes Cu_2F_2 that has been fused as a ruby-red, transparent solid, with a crystalline fracture; exposed to moist air it changes to $CuF_2.xaq$; it is easily reduced by H at a red heat.

Cuprous iodide (vol. ii. p. 256). Brun (*C. R.* 114, 667; *abstract* in *C. J.* 62, 1157 [1893]) describes *double compounds* with $(NH_4)_2S_2O_3$ and NH_4I, and also with $(NH_4)_2S_2O_3$ and $Cu_2S_2O_3$.

Cuprous oxide (vol. ii. p. 258). Russell (*C. N.* 68, 308 [1893]) prepares Cu_2O by completely reducing $CuSO_4Aq$ mixed with excess of NaCl by SO_2, heating till excess of SO_2 is removed, and then ppg. by Na_2CO_3, added solid to the hot solution. With HFAq, CuF_2Aq and Cu are formed (Pouleno, *C. R.* 116, 1446 [1893]).

Cupric oxide (vol. ii. p. 258). Moissan (*C. R.* 115, 1034 [1892]) says that CuO is entirely decomposed in the electric furnace at c. 2500°, yielding Cu and a crystalline compound of CuO and CaO (the reaction was effected in a block of CaO). By heating CuO to whiteness, in a Fletcher injector-furnace, in an oxidising atmosphere, Bailey a. Hopkins (*C. J.* 57, 269 [1890]) obtained a very hard, yellowish-red solid agreeing with the formula Cu_2O. Richards (*P. Am. A.* 26, 281 [1891]) found that CuO occludes gas, chiefly N; when prepared by heating $Cu(NO_3)_2$ the oxide retained c. ·08 p.c. of its weight of N, which could not be removed by heating. For experiments on the dehydration of $CuO.xH_2O$ *v.* Spring a. Lucion (*Zeit. f. anorg. Chemie*, 2, 195; *abstract* in *C. J.* 64 [11], 210 [1893]). For colloidal, jelly-like $CuO.xH_2O$ *v.* J. van Bemmelen (*Zeit. f. anorg. Chemie*, 5, 466; *abstract* in *C. J.* 66 [11], 191 [1894]).

Copper, oxybromides of (vol. ii. p. 260). Dupont a. Jansen (*Bl.* [3] 9, 193; *abstract* in *C. J.* 64 [11], 463 [1893]) obtained the salt $3CuO.CuBr_2.3aq$ by heating Cu_2Br_2Aq with CuO in a sealed tube at 200°, or, better, by heating neutral dilute Cu_2Br_2Aq at 225°; the compound crystallised in green rhombohedral plates, S.G. 4·39.

Copper, oxychlorides of (vol. ii. p. 260), *v.* Rousseau, *C. R.* 110, 1261 (*abstract* in *C. J.* 58, 1058 [1890]).

Copper, oxysulphides of (vol. ii. p. 260), *v.* Cliche, *Ar. Ph.* 228, 374 (*abstract* in *C. J.* 58, 1211 [1890]).

Copper, phosphides of (vol. ii. p. 260). For descriptions of Cu_5P_2 and Cu_3P, prepared by heating Cu in vapour of P, *v.* Granger, *C. R.* 113, 1401; and for Cu_2P_2, prepared by heating red P with excess of Cu phosphite and water, *v.* G., *C. R.* 117, 231 (*abstracts* in *C. J.* 62, 410 [1892]; and 64 [11], 526 [1893]).

Cupric sulphide. From experiments on the interaction of H_2S and $CuSO_4Aq$, and $CuSO_4Aq$ in presence of acetic acid, Linder a. Picton (*C. J.* 61, 120 [1892]) conclude that a compound $7CuS.H_2S$ is formed, and that then such compounds as $9CuS.H_2S$ and $22CuS.H_2S$ are produced, and finally $(CuS)_n$ is formed.

COPPER-AMMONIUM COMPOUNDS (vol. ii. p. 262). Several derivatives of *cupriammonium bromide* are described by Richards a. Shaw (*P. Am. A.* 28, 247 [1893]).

FERRICYANIDES.

Barium ferricyanide (vol. ii. p. 337); *v.* Rammelsberg, *J. pr.* [2] 39, 455 (*abstract* in *C. J.* 56, 950 [1889]).

Lead ferricyanide (vol. ii. p. 339); *v.* Rammelsberg (*l.c.*).

Potassium ferricyanide (vol. ii. p. 339); *v.* Kassner, *Chem. Zeit.* 13, 1701 (*abstract* in *C. J.* 58, 352 [1890]).

DIDYMIUM (vol. ii. p. 382). For an investigation into the separation of Di and Er, *v.* Krüss, *A.* 265, 1 (*abstract* in *C. J.* 60, 1424 [1891]). For the emission spectra of oxides of neodymium and praseodymium, *v.* Haitinger, *M.* 12, 362 (*abstract* in *C. J.* 62, 2 [1892]). Read (*C. J.* 65, 313 [1894]) says that Di_2O_3 is unchanged at c. 1750°.

ERBIUM (vol. ii. p. 456). For the separation of compounds of Er and Di, *v.* Krüss, *A.* 265, 1 (*abstract* in *C. J.* 60, 1424 [1891]).

FERRITES (vol. ii. p. 547). J. van Bemmelen a. Klobbie (*J. pr.* [2] 46, 497 [1892]) say that $Fe_2O_3.K_2O$ and $Fe_2O_3.Na_2O$ are obtained, in crystals, by continued heating Fe_2O_3 with conc. KOHAq and NaOHAq respectively; these ferrites are decomposed by water, giving $Fe_2O_3.H_2O$.

FLAME (vol. ii. p. 549). Reference should be made to Smithells a. Ingle on 'The Structure and Chemistry of Flames' in *C. J.* 61, 204 [1892], and to Lewes on 'The Luminosity of Coal-gas Flames' in *ibid.* p. 322.

FLUORHYDRIC ACID (vol. ii. p. 558). Berthelot a. Moissan (*C. R.* 109, 209 [1889]) give the thermal data [H,F] = 37,600; [H,F,Aq] = 49,400. For the description of an apparatus for purifying HFAq, *v.* Hamilton (*C. N.* 60, 252 [1889]).

FLUORINE (vol. ii. p. 560). Moissan (*C. R.* 111, 570 [1890]) determined the at. w. (1) by converting Na_2CO_3 into NaF, and this into Na_2SO_4; (2) by converting CaF_2 into $CaSO_4$, and (3) by converting BaF_2 into $BaSO_4$; the mean of the results regarded by M. as the most trustworthy was 19·05. V.D. at the ordinary temperature, 18·3 (Moissan, *C. R.* 109, 861; *v. abstract* in *C. J.* 58, 208 [1890]). A column of F one metre long shows no definite absorption bands (M., *l.c.* p. 937); for the emission spectrum *v.* M. (*l.c.*; *abstract* in *C. J.* 58, 329 [1890]). F does not liquefy at −95° at the ordinary pressure (M., *A. Ch.* [6] 25, 125 [1893]). Gladstone (*P. M.* [5] 31, 1 [1891]) has determined the atomic refraction of F in C_6H_5F to be as follows for the different lines of the solar spectrum, at 22·8°:—

	A	C	D	F	G	H
at. refraction	·63	·63	·53	·48	·44	·35

The values are much smaller than those for Cl, Br, or I, which are 10·0, 15·23, and 25·2 for the line A.

Formation.—According to Brauner (*C. J.* 65, 393 [1894]), F is given off when $3KF.PbF_4.HF$ (*v.* LEAD TETRAFLUORIDE, p. [illegible]) is heated to dull redness.

Reactions.—F combines with the more porous forms of carbon at the ordinary temperature, with incandescence, forming CF_4; the denser forms of C combine with incandescence at from 50° to 100° (Moissan, *C. R.* 110, 276; *abstract* in *C. J.* 58, 557 [1890]). For a discussion of the chemical relations of F, *v.* Moissan, *Bl.* [3] 5, 880 [1891].

GALLIUM (vol. ii. p. 597). Lecoq de Boisbaudran (*C. R.* 114, 815; *abstract* in *C. J.* 62, 930 [1892]) gives measurements of the chief lines in the spark emission spectrum of Ga; the spectrum varies much according to the conditions under which the spark is applied.

GERMANIUM (vol. ii. p. 610). A new mineral from Bolivia, *canfieldite*, Ag_8GeS_6, identical in composition with *argyrodite* from Freiberg, but crystallising in isometric forms (the form of *argyrodite* is monoclinic), is described by Penfield in *Am. S.* [3] 46, 107 (*abstract* in *C. J.* 66 [11], 12 [1894]).

GOLD (vol. ii. p. 647). Mallet (*Pr.* 46, 71; *abstract* in *C. J.* 58, 708 [1890]) has re-determined the at. w. of gold by various methods; the mean value obtained is 196·9, but the value 196·88 M. thinks is more trustworthy. The molecule of gold in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Gold volatilises considerably in the electric furnace with a current of 70 volts and 360 ampères (Moissan, *C. R.* 116, 1429 [1893]).

Concerning the volatilisation of gold *v.* Rose (*C. J.* 63, 714 [1893]). Neumann (*M.* 13, 40 [1892]) says that gold absorbs from 33 to 48·5 times its volume of O at c. 450°. According to Petersen (*Z. P. C.* 8, 601 [1891]), the heats of formation of $Au_2O_3.3H_2O$ from gold (1) reduced from $AuCl_3$, (2) from $AuHBr_4$, and (3) from AuBr, differ very markedly. From the results of many experiments on the reaction between gold and KCNAq, Maclaurin (*C. J.* 63, 724 [1893]) concludes that O must be present to accomplish solution, and that the equation $4Au + 8KCNAq + O_2 + 2H_2O =$ $4(AuCN.KCN)Aq + 4KOHAq$ (Elsner, *J. pr.* 37, 333 [1846]) expresses the proportion between K and Au in the solution.

Gold, alloys of (vol. ii. p. 648). For an alloy with Cd, AuCd, *v.* Heycock a. Neville (*C. J.* 61, 914 [1892]). For alloys with Cd and Sn, *v.* H. a. N. (*C. J.* 59, 936 [1891]). For alloys with Al and Sn, Cd and Bi, Cd and Pb, and Cd and Tl, *v.* H. a. N. (*C. J.* 65, 65 [1894]). For alloys with Cd and with Zn, prepared by immersing plates of Cd and Zn in solution of a salt of gold, *v.* Mylius a. Fromm (*B.* 27, 630; *abstract* in *C. J.* 66 [11], 235 [1894]).

Gold, bromides of (vol. ii. p. 648). Petersen (*J. pr.* [2] 46, 328) upholds the existence of Au_2Br_4 against the statements of Krüss a. Schmidt (*B.* 20, 2634); in a later paper (*J. pr.* [2] 47, 301) K. a. S. still maintain that $AuBr_3$ is the ultimate product of the reaction of Br with gold (*v. abstracts* in *C. J.* 64 [11], 126, 284). For the *double salts* $AuBr_3.CsBr$ and $AuBr_3.RbBr$, *v.* Wells a. Wheeler (*Am. S.* [3] 44, 157 [1892]).

Gold, chlorides of (vol. ii. p. 649). Petersen (*J. pr.* [2] 46, 328; 48, 88) maintains that Au_2Cl_4 is a definite compound; Krüss a. Schmidt (*J. pr.* [2] 47, 301; *Zeit. f. anorg. Chemie*, 3 421) say this substance is a mixture (*v. abstracts* in *C. J.* 64 [11], 126, 284, 474 [1893]).

Double salts of $AuCl_3$ with CsCl and RbCl are described by Wells a. Wheeler (*l.c.*); for a double salt $AuCl_3.AgCl$, *v.* Hermann (*B.* 27, 596; *abstract* in *C. J.* 66 [11], 234 [1894]).

Gold, sulphides of (vol. ii. p. 651). Concerning the conditions of formation of Au_2S_3, *v.* Antony a. Lucchesi (*G.* 19, 545; *abstract* in *C. J.* 58, 1216 [1890]).

Auric sulphide Au_2S_3. This compound is formed, according to A. a. L. (*G.* 20, 601; 21 [11], 209; *abstracts* in *C. J.* 60, 526; 62, 480 [1892]), by passing H_2S into a solution of $AuCl_3.LiCl$ kept at −10°, extracting LiCl by absolute alcohol, and drying in N at 70°. Au_2S_3 is a black, amorphous solid; decomposed by heat at 200°–205° to Au and S (for other reactions *v. abstracts, l.c.*).

Schneider (*U. S. Geol. Survey Bull.* No. 90, 56 [1892]) obtained aqueous solutions of colloidal Au_2S and Au_2S_3.

HYDRAZOIC ACID (*v.* p. 919, *Addenda*).

HYDROGEN (vol. ii. p. 719). The ratio between the densities of H and O is 1:15·882; the weight in grams of 1 litre of H is ·08991 (Rayleigh, *Pr.* 53, 134 [1893]). For solubility in water, and in alcohol, *v.* Timofeeff (*Z. P. C.* 6, 141); Winkler (*B.* 24, 89); Henrich (*Z. P. C.* 9, 435); (*abstracts* in *C. J.* 60, 15, 384 [1891]; 62, 1043 [1892]). For the line spectrum of H, *v.* Ames (*P. M.* [5] 30, 48 [1890]); and *cf.* Grünwald (*M.* 13, 111; *abstract* in *C. J.* 62, 1381 [1892]).

Wilm (*B.* 25, 217; *abstract* in *C. J.* 62, 563 [1892]) describes a lecture experiment to show the occlusion of H by Pd. Regarding the occlusion of H by other metals *v.* Streintz (*M.* 12, 642; *abstract* in *C. J.* 62, 567 [1892]).

Baker (*C. J.* 65, 611 [1894]) found that a mixture of equal volumes of *dry* H and *dry* Cl did not explode in bright sunlight, and that more than a quarter of the mixed gases remained uncombined after exposure for two days to diffused light and two days to bright sunshine.

Reactions.—Neumann (*Z. P. C.* 14, 193 [1894]) has examined the reducing action of H occluded by Pt on solutions of salts of Al, Sb, As, Bi, Cd, Cu, Co, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Ag, Sn, Tl, and Zn. Regarding the rate of combination of H and O, *v.* WATER (p. 860). Regarding the explosion of mixtures of H with O and Cl, *v.* CHLORINE (*Addenda*, pp. 904, 905).

Hydrogen dioxide (vol. ii. p. 722). Schöne (*B.* 26, 3011; 27, 1233 [1893-4]) affirms the occurrence of H_2O_2 in the atmosphere against the contention of Ilosva (*B.* 27, 920).

Formation.—Regarding the formation from ether *v.* Dunstan a. Dymond (*C. J.* 57, 574, 988 [1890]). H_2O_2Aq is formed by the action of light on $H_2C_2O_4Aq$, excess of O being present (Richardson, *C. J.* 65, 450 [1894]). Richardson (*C. J.* 63, 1110 [1893]) has examined the formation of H_2O_2 in urine exposed to sunlight.

Preparation.—By making commercial 3 p.c. H_2O_2Aq distinctly alkaline by Na_2CO_3, filtering, shaking with 10–12 vols. of ether, separating the ethereal solution, evaporating this to ·01–·0025 of its original volume on a water-bath, and removing the rest of the ether by standing in a bell-jar over solid paraffin, Shiloff (*J. R.* 25, 293; *abstract* in *C. J.* 66 [11], 186 [1894]) obtained a thick, transparent, slightly acid liquid, S.G. 1·2475, containing 79·6 g. H_2O_2 in 100 c.c. For preparation of conc. H_2O_2Aq *v.* Talbot a. Moody (*abstract* in *C. J.* 64 [11], 369 [1893]).

Molecular weight. Tammann in 1889 (*Z. P. C.* 4, 441) by cryoscopic measurements determined mol. formula to be H_4O_4; but T.'s results were called in question by Carrara in 1893 (*G.* 22 [1], 341), who found mol. w. 33·92 (H_2O_2) from cryoscopic measurements, and this result was confirmed by Orndorff a. White (*Am.* 15, 347 [1893]), and also by Tammann himself (*Z. P. C.* 12, 431 [1893]).

Reactions.—Regarding the reaction between H_2O_2Aq and $KMnO_4Aq$, *v.* Engel (*Bl.* [3] 6, 17; *abstract* in *C. J.* 62, 277 [1892]).

Hydrogen sulphide (vol. ii. p. 725). Henrich (*Z. P. C.* 9, 435 [1892]) gives the absorption coefficient of H_2S by water as $4·4015 - ·089117t + ·00061954t^2$. Hughes (*P. M.* [5] 33, 471 [1892]) says that H_2S dried by $CaCl_2$ and P_2O_5 does not redden dry litmus paper, and does not react with BaO or Fe_2O_3, nor with salts of Sb, As, Bi, Cd, Co, Cu, Pb, Hg, Ag, or Sn. According to Pedler (*C. J.* 57, 625 [1890]), the equation $2H_2S + 3O_2 = 2SO_2 + 2H_2O$ correctly represents the explosion of H_2S and air or O.

HYDROXYLAMINE (vol. ii. p. 734). NH_2OH has been isolated, as a solid, by

(R. T. C. 10, 100; 11, 18; abstracts in C. J. 62, 402, 1891 [1892]). $NH_2OH.HCl$ dissolved in MeOH is treated with CH_3ONa solution, and most of the MeOH is distilled off at 100 mm. pressure; the residue is distilled in small portions at 40 mm. pressure (for details v. C. J., l.c.). For the preparation from $2NH_2OH.ZnCl_2$ v. Crismer, *Bl.* [3] 6, 793 (*abstract* in C. J. 62, 771 [1892]). For details of suitable apparatus for the fractionation of NH_2OH *in vacuo*, v. Brühl (*B.* 26, 2508 [1893]; *cf.* L. de B., *B.* 27, 967; and reply by B., *ibid.* 1347 [1894]). For thermal data of NH_2OH, v. Berthelot a. André (*C. R.* 110, 830; *abstract* in *C. J.* 58, 934 [1890]). Hydroxylamine is a white inodorous solid, melting at c. 33°, and remaining superfused at 0°; boils at 58° under 22 mm. pressure; decomposes at 90°-100°, and detonates at a higher temperature. S.G. 1·35; S.G. when liquid, 1·23. A drop heated in a test tube explodes very violently (v. Brühl, *l.c.*). B., *l.c.*, discusses the molecular refraction of NH_2OH. NH_2OH is fairly stable up to 15°, then gradual decomposition occurs, giving NH_3, HNO_2, and $H_2N_2O_2$, which react with unchanged NH_2OH producing $_2$O and N (L. de B., *B.* 27, 967; *abstract* in C. *J.* 66 [11], 278 [1894]). For a full account of the reactions of NH_2OH v. Lobry de Bruyn (*l.c.*; *abstract* in *C. J.* 62, 1391 [1892]). $NH_2OH.HCl$ in water and $NaNO_2Aq$ react to form $Na_2N_2O_2Aq$ (*v.* Tanatar, *J. R.* 25, 342; *abstract* in *C. J.* 66 [11], 136 [1894]; *cf.* Vislicenus, *B.* 26, 771; *abstract* in *C. J.* 64, 618 [1892]). For the reactions of $2NH_2OH.H_2SO_4$ with NaOHAq v. Kolotoff (*J. R.* 25, 295; *abstract* in *C. J.* 66 [11], 187 [1894]). For compounds of NH_2OH with metallic salts, *v.* Crismer (*Bl.* [3] 8, 114); Goldschmidt a. Syngros (*Zeit. f. anorg. Chemie*, 5, 129); and Feldt (*B.* 27, 401) (*abstracts* in *C. J.* 58, 558 [1890]; 66 [11], 45, 187 [1894]). Kolotoff discusses the constitution of NH_2OH in *J. R.* 23, 3 (*abstract* in *C. J.* 64 [11], 114 [1893]). Kjellin (*B.* 26, 2377) describes NHEt.OH and NHMe.OH (*abstract* in *C. J.* 66 [11], 9 [1894]).

INDIUM (vol. iii. p. 1). The molecule of indium in dilute solution in tin is perhaps diatomic (*v.* Heycock a. Neville, *C. J.* 57, 376 [1890]). Linder a. Picton (*C. J.* 61, 134 [1892]) failed to isolate *indium hydrosulphide*, but they think that it is formed by passing H_2S into water with $In_2O_3.xH_2O$ in suspension; the continued passage of H_2S produces In_2S_3. Read (*C. J.* 65, 313 [1894]) found that *indium sesquioxide*, In_2O_3, is unchanged at c. 1750°.

IODHYDRIC ACID (vol. iii. p. 11). For the Mol. R. of HIAq from 20·77 to 67·02 p.c., *v.* Perkin (*C. J.* 55, 708 [1889]). For a research on the dissociation of HI, *v.* Bodenstein (*Z. P. C.* 13, 56 [1894]; *abstracts* in *C. J.* 64 [11], 369; 66 [11], 12 [1893-4]). Pickering (*B.* 26, 2307) has isolated three *hydrates* of HI: $HI.2H_2O$, melting at c. −43°; $HI.3H_2O$, melting at c. −48°; and $HI.4H_2O$, melting at c. −36·5°.

IODINE (vol. iii. p. 14). The mol. w. of iodine dissolved in Et_2O or CS_2 was found by Beckmann (*Z. P. C.* 5, 76 [1890]) to be 254, from determinations of the boiling-points; whose results were confirmed by Sakurai (*C. J.* 61, 994 [1892]). By determining the lowering of the f.p. of naphthalene by solution therein of I, Hertz (*Z. P. C.* 6, 358 [1890]) found the value 254 for the mol. w. of iodine.

According to Meineke (*Chem. Zeitung*, 16, 1219, 1230), very pure I is prepared by covering ordinary I with a solution of $CaCl_2$ S.G. 1·35, mixed with a little conc. KIAq and a few drops of HClAq, heating until the I fuses, letting cool, washing the I, drying and subliming it twice, the first time with addition of a little BaO.

For the reactions of I with $KClO_3$, and with $KClO_3$ and water, *v.* POTASSIUM CHLORATE (*Addenda*, p. 905).

Iodine monochloride (vol. iii. p. 17). For thermal data bearing on the two forms of ICl, *v.* Stortenbeker (*Z. P. C.* 10, 183; *abstract* in *C. J.* 62, 1387 [1892]). Tanatar (*J. R.* 25, 97; *abstract* in *C. J.* 64 [11], 514) gives details of the methods for preparing the two forms of ICl.

Iodates (vol. iii. p. 21). For *iodates of cæsium* and *rubidium*, *v.* Wheeler, *Am. S.* [3] 44, 123 (*abstract* in *C. J.* 64 [11], 68 [1894]). Pure *potassium iodate* is prepared, according to Gröger (*Zeit. angew. Chemie*, 1891. 13), by heating to 100° for 20-30 minutes 20 g. KI in as little water as possible mixed with 40 g. pure $KMnO_4$ in 1,000 c.c. water, reducing excess of $KMnO_4$ by cautious addition of alcohol, filtering, adding acetic acid till acid, evaporating to c. 50 c.c., washing the crystals of KIO_3 with conc. alcohol, and drying. By heating KIO_3 till it fuses, O and some I are given off, and KI finally remains; no other oxy- compounds are formed (Cook, *C. J.* 65, 802 [1894]).

IRIDIUM (vol. iii. p. 46). From analyses of the salts $ICl_3.3KCl.aq$ and $ICl_3.3NH_4Cl.aq$, Joly deduced the value 192·75 for the at. w. of Ir (*C. R.* 110, 1131 [1890]). According to Prinz (*C. R.* 116, 392 [1893]), Ir crystallises in regular octahedra and in forms derived therefrom. Mylius a. Foerster (*B.* 25, 665 [1892]) stated that Ir is slightly volatilised when heated in a current of CO and Cl to c. 238°; Antony, however (*G.* 23 [11], 547 [1893]), asserts that no trace of any volatile compound of Ir is formed under these conditions.

Irid-ammonium salts (vol. iii. p. 47). Palmaer (*B.* 22, 15; 23, 3810 [1889-90]) describes a number of *irido-ammonium compounds*. He calls them *iridiumpentammine salts*, and formulates them as $Ir(NH_3)_5X^I_3$: compounds are described where $X_3 = Cl_3$, $ClBr_2$, ClI_2, $ClSO_4$, $Cl(NO_3)$, $Cl(NO_2)_2$, ClC_2O_4, $ClPtCl_6$; also where $X_3 = Br_3$, $BrSO_4$, and $Br(NO_3)_2$. One-third of the Cl in the salt when $X_3 = Cl_3$ is not removed by the action of cold H_2SO_4Aq or cold $AgNO_3Aq$; the reactions of the salts are similar to those of the purpureo-cobaltammines (*v.* vol. ii. p. 227) (*abstracts* in *C. J.* 56, 252 [1889]; 60, 402 [1891]). In *B.* 21, 2090 (*v. abstract* in *C. J.* 60, 11 [1891]) P. describes compounds analogous with the roseo-cobaltic salts $Co_2(NH_3)_{10}(H_2O)_2X^{II}_2.xAq$; as the Ir salts are almost colourless, P. thinks the prefix *roseo-* is unsuitable; he calls them *iridium aquopentammines*, and formulates them as $Ir(NH_3)_5(H_2O)X^I_3$. Salts are described in which $X_3 = Br_3$, Cl_3, and $(NO_3)_3$. The *chloride* $Ir(NH_3)_5(H_2O)Cl_3$ is formed by boiling, for five hours, 5 g. $Ir(NH_3)_5Cl_3$ with 1½ times the calculated weight of KOH in 50 c.c. water, filtering, partially freezing the filtrate, adding 30 c.c. fuming HClAq, washing the pp. thus formed with 22 p.c. cold HClAq and then with alcohol, dissolving in water, and again ppg. by conc. HClAq (for details *v. abstract* in *C. J.* 60, 1166 [1891]).

Iridium tribromide (vol. iii. p. 48). Compounds of this bromide with PBr_3 are described by Geisenheimer (*C. R.* 111, 40; *abstract* in *C. J.* 58, 1383 [1890]). By heating $IrO_2.xH_2O$ with $IrBr_3$ and PBr_3, red needles of $IrBr_3.3PBr_3$ are formed; by heating this with PBr_3, black crystals of $IrBr_3.2PBr_3$ are produced.

Iridium tetrabromide (vol. iii. p. 48). Geisenheimer (*l.c.*) describes the compound $IrBr_4.2PCl_3$, obtained by heating $IrBr_3.3PBr_3$ with PCl_3.

Iridium trichloride (vol. iii. p. 48). The following compounds with PCl_3 are described by Geisenheimer (*C. R.* 110, 1004; *abstract* in *C. J.* 58, 1068 [1890]). $IrCl_3.3PCl_3$; $IrCl_3.2PCl_3$; $IrCl_3.PCl_5.2PCl_3$; $IrCl_3.PCl_3.PCl_5$. Various compounds of $IrCl_3$ with H_3PO_3 and H_3PO_4, and salts of these, are also described. G. (*C. R.* 110, 1336; *abstract* in *C. J.* 58, 1069 [1890]) also describes the complex compounds $2IrP_2Cl_{13}.5AsCl_3$ and $IrCl_3.2PCl_3.2AsCl_3$. For the salts $IrCl_3.3KCl.$ aq and $IrCl_3.3NH_4Cl.$ aq, *v.* Joly (*C. R.* 110, 1131; *abstract* in *C. J.* 58, 1067 [1890]). For a description of $IrCl_3.3LiCl.xaq$, *v.* Antony (*G.* 23 [1], 190; *abstract* in *C. J.* 64 [11], 380 [1893]). According to A. (*G.* 23 [1], 184; *abstract* in *C. J.* 64 [11], 379 [1890]), the passage of H_2S through a 2 p.c. solution of $IrCl_3.3KCl$ produces pps. which are mixtures of Ir_2S_3 and IrS_2.

Iridium dioxide (vol. iii. p. 50). For methods of preparing IrO_2, *v.* Geisenheimer (*C. R.* 110, 855; *abstract* in *C. J.* 58, 948 [1890]).

Iridium disulphide (vol. iii. p. 50). IrS_2 is obtained by passing H_2S over $IrCl_3.3LiCl$ at 4° to 7°, washing with absolute alcohol, and drying at 90° to 100° in a current of CO_2 (Antony, *G.* 23 [1], 190; *abstract* in *C. J.* 64 [11], 380 [1893]).

IRON (vol. iii. p. 51). Lockyer (*Pr.* 54, 359 [1893]) gives the emission spectrum obtained by using very fine electrolytically deposited iron as the poles of an electric lamp.

Properties and Reactions.—Iron volatilises in the electric furnace, using a current of 850 ampères and 50 volts (Moissan, *C. R.* 116, 1429 [1893]). Iron is superficially oxidised by heating to dull redness in NO (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]); heated in NO_2 to c. 350°, reduced iron is oxidised with incandescence to Fe_2O_3 (S. a. S., *C. R.* 115, 236 [1892]; *cf. abstract* in *C. J.* 66 [11], 95 [1894]). Montemartini (*G.* 22 [1], 350) says that NH_3, N_2O, and N are formed by the solution of iron in excess of 27·5 p.c. HNO_3Aq (for quantities, *v. abstract* in *C. J.* 62, 1278 [1892]). For quantities of iron dissolved by HNO_3Aq of different concentrations, *v.* Gautier a. Charpy (*C. R.* 112, 1451; *abstract* in *C. J.* 60, 1426 [1891]).

Passivity of iron. Concerning the passivities of steel and wrought iron to HNO_3Aq, *v.* Andrews (*Pr.* 48, 116; 49, 481; *abstracts* in *C. J.* 60, 250, and 64 [11], 16 [1891 and 1893]).

Iron, bromochloride of. The compound $FeBrCl_2$ was obtained by Lenormand (*C. R.* 116, 820; *abstract* in *C. J.* 64 [11], 377) by heating $FeCl_2$ with excess of Br in a sealed tube at c. 100°. The compound is opaque in thin sections, and green by reflected light; very deliquescent; crystallises probably in hexagonal plates; easily sol. alcohol and ether, CS_2, &c.; can be sublimed by heating in a tube containing a little Br.

Iron carbide. Arnold a. Read (*C. J.* 65, 788 [1894]) confirm the existence of Fe_3C in steel (*v.* Abel, *Proc. Inst. Mechan. Engineers*, 1885. 80; also Müller, *Stahl und Eisen*, No. 3); A. a. R. say that two forms of Fe_3C are found in steel.

Iron carbonyls. In 1891 Mond a. Quincke (*C. J.* 59, 604) obtained a compound of Fe with CO; further investigation of the reaction by Mond a. Langer (*C. J.* 59, 1090 [1891]) led to the isolation of two compounds.

Ferropentacarbonyl $Fe(CO)_5$. Mol. w. 195·55. V.D. at 142° = 93·2, S.G. $\frac{18°}{18°} = 1·4664$; distils completely, without decomposition, at 102·8° under 749 mm. pressure; solidifies at −21°.

Preparation.—FeC_2O_4, ppd. by adding a slight excess of $K_2C_2O_4Aq$ to hot $FeSO_4Aq$, is well washed, and dried at 120°; it is then heated in a slow stream of H, temperature being raised until the substance in the tube is black, and then kept constant until gas ceases to come off, when the current of H is stopped; the product is allowed to cool in H, placed in water without coming into the air, and treated with successive quantities of boiling water until sulphate is removed; it is then quickly dried on plates of gypsum, placed in the combustion tube, heated to c. 300° in H till quite dry, and allowed to cool in H. The tube is then connected with a gas-holder containing CO, and the H is completely displaced by CO; one end of the tube is then sealed, and the open end is kept in connection with the supply of CO. After 24 hours the tube is heated to c. 120°, while a slow current of CO is passed through it, and the issuing gases are passed through a tube kept at −20°. When iron carbonyl ceases to come over, the tube is let cool, and is then again put in connection with the CO supply. These processes are repeated many times; the daily yield of the carbonyl is not more than c. 1 g. from 100 g. iron.

Properties.—A pale-yellow, somewhat viscous liquid; unchanged in the dark, but in sunlight gives solid $Fe_2(CO)_7$ (*v. infra*); slowly decomposed on exposure to air, giving chiefly $Fe_2O_3.xH_2O$; completely decomposed at 180° to Fe and CO; soluble in EtOH, Et_2O, C_6H_6, mineral oils, &c. (For S.G., V.D., &c., *v. supra.*) $Fe(CO)_5$ is not acted on by dilute H_2SO_4Aq, HClAq, or HNO_3Aq at the ordinary temperature; but is rapidly decomposed—to $Fe(NO_3)_3Aq$, $FeCl_3Aq$, or $FeBr_3Aq$—by conc. HNO_3Aq, ClAq, and BrAq.

Diferroheptacarbonyl $Fe_2(CO)_7$. Obtained by exposing $Fe(CO)_5$ in a sealed tube to sunlight for some hours, collecting the solid that forms, washing with ether, and drying over H_2SO_4 for a short time. Yellow, lustrous flakes; gradually decomposed by exposure to air, turning brown. Not acted on by H_2SO_4Aq or HClAq at the ordinary temperature; decomposed by HNO_3Aq, Cl or Br.

Iron carbonyls seem to be present in waters; also sometimes in compressed coal-gas (v. Roscoe a. Scudder, *C. J. Proc.* 1891. No. 101).

Ferrous chloride (vol. iii. p. 53). Chassevant (*A. Ch.* [6] 30, 5 [1893]) describes the *double salts* $FeCl_2.2AmCl$, $FeCl_2.LiCl.3aq$, and $FeCl_2.2KCl$.

Ferric chloride (vol. iii. p. 54). By determining the rise of b.p. of alcohol and ether when $FeCl_3$ is dissolved in these solvents, Müller (*C. R.* 118, 644; *abstract* in *C. J.* 66 [11], 282 [1894]) finds that the molecular formula of the chloride in these solutions is $FeCl_3$. $FeCl_3Aq$ reacts with many metallic sulphides, when heated therewith in sealed tubes; $FeCl_2Aq$, S, and a chloride of the metal of the sulphide are generally formed (Cammerer, *C. C.* 1891 [11]. 370; *abstract* in *C. J.* 62, 18 [1892]). Seubert a. Dorrer (*Zeit. f. anorg. Chemie*, 5, 339, 411; *v. abstracts* in *C. J.* 66 [11], 140, 190 [1894]) have made a full investigation of the interaction of $FeCl_3Aq$ and KIAq; their results are in keeping with the hypothesis that the direct reaction $FeCl_3Aq + KIAq = FeCl_2Aq + KClAq + IAq$ is counterbalanced by the reverse reaction $FeCl_2Aq + KClAq + IAq = FeCl_3Aq + KIAq$. S. a. D. think that the first stage of the reaction is to produce an iodochloride; thus $FeCl_3Aq + KIAq = FeICl_2Aq + KClAq$; that this then decomposes, more or less completely (according to conditions of concentration, time, temperature, and mass), into $FeCl_2Aq$ and IAq; and that $FeICl_2Aq$, and probably $FeCl_3Aq$, are re-formed until equilibrium is established. S. a. D. do not agree with the explanation of the mechanism of the reaction given by Carnegie (*v.* vol. iii. p. 55). Roozeboom (*Z. P. C.* 10, 477 [1892]) has investigated the conditions of equilibrium in aqueous solution of the *hydrates* of $FeCl_3$; he has isolated hydrates $2FeCl_3.xH_2O$ where $x = 4, 5, 7$, and 12. (For details, *v. abstract* in *C. J.* 64 [11], 119 [1893]). For a study of the interaction of $FeCl_3Aq$ and oxalic acid, *v.* Lemoine, *C. R.* 116, 981 (*abstract* in *C. J.* 64 [11], 405 [1893]). A compound of $FeCl_3$ with *nitrosyl chloride*, $FeCl_3.NOCl$, was obtained by Sudborough (*C. J.* 59, 660 [1891]), by immersing iron in liquid NOCl, and letting the liquid stand over H_2SO_4; the compound forms small golden-brown, deliquescent crystals (*cf.* vol. iii. p. 56; *Combinations*, No. 7).

Ferrous fluoride (vol. iii. p. 56). FeF_2 was obtained by Poulenc (*C. R.* 115, 941; *abstract* in *C. J.* 64 [11], 122 [1893]) by passing air-free HF over red-hot iron or dry $FeCl_2$; small, white, rhombic prisms; S.G. 4·09; decomposed by heating with H_2SO_4, Na_2CO_3, steam, air, HCl, or H.

Ferric fluoride (vol. iii. p. 56). Poulenc (*l.c.*) obtained FeF_3, in small, very refractive, greenish crystals, S.G. 3·87, by passing HF over red-hot iron, Fe_2O_3, $FeF_3.xaq$, or $FeCl_3$; also by dropping $FeF_3.xaq$ into fused AmCl and heating in a current of an inert gas. FeF_3 does not fuse at 1000°; but is decomposed by heating in air, also by fusion with Na_2CO_3, by heating in steam, or with HCl or H_2SO_4. According to Speransky (*J. R.* 24, 304; *abstract* in *C. J.* 64 [11], 314 [1893]), FeF_3Aq shows a very small electrical conductivity; there is, therefore, no appreciable electrolytic dissociation; as the solution scarcely effects any inversion of cane sugar, S. concludes that there is practically no hydrolytic dissociation. Cryoscopic determinations showed that the molecules in a dilute aqueous solution are chiefly FeF_3, but indicated the existence of Fe_2F_6 in more conc. solutions.

Iron, nitrides of (vol. iii. p. 59). Fowler (*C. N.* 68, 152 [1893]) obtained Fe_2N by heating reduced iron in a rapid stream of NH_3. (For details *v. abstract* in *C. J.* 66 [11], 50 [1894].)

Ferric oxide (vol. iii. p. 61; also p. 57 for *hydrates*). At c. 1750° Fe_2O_3 is completely changed to Fe_3O_4 (Read, *C. J.* 65, 313 [1894]); in the electric furnace Fe_3O_4 is formed, partly melted and partly crystallised (Moissan, *C. R.* 115, 1034 [1892]). According to J. van Bemmelen a. Klobbie (*J. pr.* [2] 46, 497 [1893]), crystallised $Fe_2O_3.H_2O$ is obtained by treating with water the hexagonal crystals of $Fe_2O_3.Na_2O$ formed by heating Fe_2O_3 for some time with conc. NaOHAq; the crystalline $Fe_2O_3.H_2O$ is not hygroscopic; H_2O is given off below 100°.

Iron, oxychlorides of (vol. iii. p. 62). Rousseau (*C. R.* 110, 1032; 113, 643; 116, 392; *abstracts* in *C. J.* 58, 1083 [1890]; 62, 119 [1892]; 64 [11] 280 [1893]) describes compounds $xFeCl_3.yFe_2O_3$, some crystalline and some amorphous, formed by heating $FeCl_3Aq$ at different temperatures, and also by the interaction of $FeCl_3$ and steam.

LANTHANUM (vol. iii. p. 116). Bettendorff (*A.* 256, 159 [1890]) obtained the value 138·28 for the at. w.; and Brauner (*B.* 24, 1328 [1891]) the value 138·21 (O = 16).

Winkler (*B.* 24, 873 [1891]) obtained results, by heating La_2O_3 with Mg in H, which pointed to the existence of a *hydride* of La (*cf.* Brauner, *l.c.*).

LEAD (vol. iii. p. 122). The molecule in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). The m.p. of lead was found by Griffiths a. Calendar (using a Pt thermometer) to be 327·69° (*C. N.* 63, 1 [1891]). Lehmann (*Z. K.* 17, 274 [1890]) says that lead separated electrolytically, by a weak current, crystallises in leaflets that are probably monosymmetric, but that the crystals are regular octahedra when separated by a strong current. Veley (*S. C. I.* 10, 206; summary of conclusions in *C. J.* 62, 410 [1892]) has examined the interaction of lead and nitric acid: an acid of intermediate concentration acts most rapidly; when HNO_2 is present the action increases. Montemartini (*G.* 22, 384, 397, 426 [1892]) found that a little NH_3 was produced, especially with dilute HNO_3Aq. Lead rapidly oxidises to PbO when heated in NO; oxidation occurs at c. 200° in NO_2, with formation of a basic nitrate (Sabatier a. Senderens, *C. R.* 114, 1429; 115, 236 [1892]).

Lead, bromide of (vol. iii. p. 125). Several *double compounds* of $PbBr_2$ with alkali bromides have been described. For $PbBr_2.2AmBr.aq$ and $2PbBr_2.AmBr$, *v.* Wells a. Johnston, *Am. S.* [3] 46, 25 (*abstract* in *C. J.* 64 [11], 523 [1893]); for $PbBr_2.KBr.xaq$ and $PbBr_2.2KBr.aq$, *v.* Herty, *Am.* 15, 357 (*abstract* in *C. J.* 66 [11], 465 [1894]); for $2PbBr_2.RbBr$ and $2(PbBr_2.2RbBr).aq$ *v.* Wells, *Am. S.* [3] 46, 34 (*abstract* in *C. J.* 66 [11], 324 [1893]); and for $K_2Pb_2Br_6.4aq$ and $K_2Pb_2(BrI)_3.4aq$, *v.* Wells, *l.c.* p. 190 (*abstract*, *l.c.* p. 524).

Lead, chlorides of (vol. iii. p. 125). The statement, on p. 125 (vol. iii.), that only one chloride has been isolated is no longer true; $PbCl_4$ was prepared by Friedrich in 1893.

Lead tetrachloride (vol. iii. p. 126). $PbCl_4$ has been obtained by Friedrich (*B.* 26, 1434; *abstract* in *C. J.* 64 [11], 415 [1893]; *cf. M.* 14, 505; *abstract* in *C. J.* 66 [11], 16 [1894]), by passing Cl into HClAq containing $PbCl_2$ in suspension, adding NH_4Cl to the solution thus obtained, separating and drying the compound $PbCl_4.2NH_4Cl$ thus formed, adding it to conc. cooled H_2SO_4, allowing the oily drops that formed to collect at the bottom of the vessel, and shaking these drops repeatedly (and quickly) with conc. H_2SO_4. $PbCl_4$ is a transparent, yellow, very refractive liquid, fuming in moist air with formation of $PbCl_2$ and Cl; it is unchanged in contact with cold conc. H_2SO_4, but when heated with the acid it decomposes explosively to $PbCl_2$ and Cl; when heated with conc. H_2SO_4 in a current of Cl, some $PbCl_4$ passes over, but at c. 105° explosion occurs. $PbCl_4$ has S.G. 3·18 at 0°; at c. −15° it solidifies to a yellowish, crystalline mass. A *hydrate* is formed with a little water; but addition of more water produces HClAq and PbO_2. By adding $PbCl_4$ to a little cooled conc. HClAq, a crystalline compound, probably $PbCl_4.2HCl$, is formed.

Several *double salts* of $PbCl_4$ with alkali chlorides have been isolated. Classen a. Zahorski (*Zeit. f. anorg. Chemie*, 4, 100) give the formula $2PbCl_4.5AmCl$ to the salt formed by digesting $PbCl_2$ with liquid Cl and fuming HClAq, and adding AmCl; but Friedrich (*l.c.*) says the compound is $PbCl_4.2NH_4Cl$. For compounds $PbCl_4.2MCl$, when $M = NH_4$, Cs, K, and Rb, *v.* Wells (*Am. S.* [3] 46, 180; *abstract* in *C. J.* 64 [11], 523 [1893]); C. a. Z. (*l.c.*) describe compounds of $PbCl_4$ with the hydrochlorides of pyridine and quinoline (*abstract* in *C. J.* 64 [11], 462 [1893]).

Lead dichloride (vol. iii. p. 125). Several *double compounds* with alkali chlorides are described by Randall (*Am.* 15, 494 [1893]); Wells a. Johnston (*Am. S.* [3] 46, 25 [1893]); and Wells (*l.c.* p. 34). The compounds are of the forms $PbCl_2.2MCl$, $PbCl_2.3MCl.xaq$, and $2PbCl_2.MCl$ (*v. abstracts* in *C. J.* 64 [11], 523, 524 [1893]).

Lead, fluorides of (vol. iii. p. 127). Brauner (*C. J.* 65, 393 [1894]) has prepared the compound $PbF_4.3KF.HF$ in various ways; the simplest process being to dissolve $Pb(C_2H_3O_2)_4$ (*v.* RED OXIDE OF LEAD, *Addenda, infra*) in conc. HFAq and add KF. By acting on this salt with conc. H_2SO_4, B. obtained evidence of the formation of *lead tetrafluoride*, PbF_4, but he did not succeed in isolating the compound.

Lead, iodide of (vol. iii. p. 127). Several *double compounds* of PbI_2 with alkali iodides have been isolated by Wells, W. a. Johnston, and Herty (*v. References* under LEAD BROMIDE, p. 914). For the compound $PbI_2.2MgI_2.16aq$, *v.* Otto a. Drewes (*Ar. Ph.* 229, 179; *abstract* in *C. J.* 64 [11], 984 [1893]).

Lead iodobromides and iodochlorides (vol. iii. p. 128). Miss Field (*C. J.* 63, 540 [1893]) has described the compounds $2PbBr_2.PbI_2$, $2PbCl_2.PbI_2$, and $5PbCl_2.PbI_2$.

Lead protoxide (vol. iii. p. 128). PbO is unchanged at c. 1750° (Read, *C. J.* 65, 318 [1894]). The hydrate $2PbO.H_2O$ (vol. iii. p. 12 is obtained in large crystals by allowing a solution of PbO in KOHAq to cool in the air; CO is absorbed, and the hydrate is deposited i colourless, tetragonal crystals, *a:b:c* = 1:·82 (Luedeking, *Am.* 13, 120 [1891]).

Red oxide of lead (vol. iii. p. 130). Hutchinson a. Pollard (*C. J.* 63, 1136 [1893]) have examined the reaction of Pb_3O_4 with glacial acetic acid, and have isolated *lead tetracetate* $Pb(C_2H_3O_2)_4$, melting at c. 175°, and decomposing a little above that temperature.

Note.—The formula $PbO(OC_2H_3O)_2$ said to be assigned by Jacquelain to the salt obtained by him (vol. iii. p. 130, col. 2, line 28 from top; and p. 131, col. 2, line 24 from bottom) should have been given as $PbO_2(C_4H_3O_3)_2$ *old notation.*

Plumbates (vol. iii. p. 132). Kassner (*Ar. Ph.* [3] 28, 109; *abstract* in *C. J.* 58, 561 [1890]) describes plumbates of Ba, Ca, and Sr. Regarding the dissociation of Ca plumbate, *v.* Le Chatelier (*C. R.* 117, 109; *abstract* in *C. J.* 64 [11], 524 [1893]).

Lead oxyiodides (vol. iii. p. 132). Gröger (*M.* 13, 510; *abstract* in *C. J.* 62. 1892) describes the compound $PbO.PbI_2$.

Lead, salts of (vol. iii. p. 132). The salt $Pb(C_2H_3O_2)_4$ (*v. supra*, *Red oxide of lead*) belongs to the type PbX^{I}_4, to which form $PbCl_4$ also belongs.

Lead, sulphide of (vol. iii. p. 133). According to Hannay (*C. J. Proc.*, Nos. 139 and 141 [1894]), when air is passed into molten PbS, one half of the lead remains as lead, and one half is volatilised, and deposited as PbS; H. accounts for this change by supposing the reaction to be $2PbS + O_2 = Pb + PbS.SO_2$, the volatile $PbS.SO_2$ being decomposed in the colder part of the apparatus to PbS and SO_2.

Lead sulphobromide and sulphochloride (vol. iii. p. 133). Parmentier (*C. R.* 114, 298; *abstract* in *C. J.* 62, 685 [1892]) obtained the compounds $PbS.PbBr_2$ and $PbS.PbCl_2$, by dissolving the halides in their acids and shaking the liquids while H_2S was passed over the surfaces of the solutions.

LITHIUM (vol. iii. p. 147). Guntz (*C. R.* 117, 732 [1893]) recommends to use a mixture of equal weights of LiCl and KCl, for the electrolytic preparation of the metal; the mixture melts at 450° and the m.p. decreases as electrolysis proceeds. (For details as to size of electrodes, strength of current, &c., *v. abstract* in *C. J.* 66 [11], 91 [1894].) Holt a. Sims, *C. J.* 65, 443 [1894], find that traces of a peroxide are formed, along with Li_2O, by burning Li in O.

Lithium, amide of, $LiNH_2$. Formed by gently heating clean Li in a stream of NH_3 until violent action ceases, and then heating to c. 400° until the reaction is finished. A white, crystalline, transparent solid; melts between 380° and 400°; decomposes in cold water slowly, giving LiOHAq and NH_3; decomposed by heating in air, but without taking fire (Titherley, *C. J.* 65; 504 [1894]; *q. v.* for further reactions).

Lithium, bromide of (vol. iii. p. 150). The hydrates $LiBr.xaq$, where x = 1 and 2, are described by Bogorodsky (*J. R.* 25, [illegible] [1893]).

Lithium, chloride of (vol. iii. p. 150). For $LiCl.aq$ and $LiCl.2aq$ *v.* Bogorodsky (*l.c.*). For the *double compounds* $LiCl.MCl_2.xaq$, where

M = Cu, Cd, Fe, Mn, or Ni; v. Chassevant (C. R. 114, 646; 115, 113; *abstracts* in C. J. 62, 118, 1373 [1892]).

Lithium, fluoride of (vol. iii. p. 150). Poulenc (*Bl.* [3] 11, 15 [1894]) obtained LiF in regular octahedra by heating the amorphous fluoride with KHF_2 and KCl, and washing with water; sl. sol. water, insol. 95 p.c. alcohol; melts at c. 1000° in H, and partially volatilises at 1100°–1200°.

Lithium, hydroxide of (vol. iii. p. 150). For the freezing-points of aqueous solutions of LiOH v. Pickering (*C. J.* 63, 899 [1893]).

Lithium, nitride of. Ouvrard (*C. R.* 114, 120 [1892]) obtained a black solid, probably Li_3N, by heating commercial Li to dull redness in N.

Lithium, oxides of (vol. iii. p. 151). Almost the only product of heating Li in O is Li_2O; only traces of a peroxide are formed (Holt a. Sims, *C. J.* 65, 443 [1894]).

MAGNESIUM (vol. iii. p. 157). Burton a. Vorce (*Am.* 12, 219 [1890]) obtained the value 24·22 (O = 15·96) for at. w., by converting pure Mg into $Mg(NO_3)_2$ and this to MgO. The molecule of Mg in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Mg crystallises in holohedral hexagonal forms, $a:c = 1:1·6202$, isomorphous with Zn and Be (B. a. V., *l.c.*).

According to Montemartini (*G.* 22, 384, 397, 426 [1892]), a considerable quantity of H is given off when Mg interacts with HNO_3Aq (c. 13 p.c.); the quantity of NH_3 formed increases with concentration of the acid up to 40 p.c. HNO_3, after which it decreases. Mg burns in NO at a dull red heat (Sabatier a. Senderens, *C. R.* 115, 236 [1892]). Giorgis (*G.* 21, 510 [1891]) says that Mg dissolves in water saturated with CO_2; that H is given off, and crystals of $MgCO_3.3aq$ are deposited. For the interactions of Mg and chlorides v. Seubert a. Schmidt (*A.* 267, 218; *abstract* in *C. J.* 62, 776 [1892]). Winkler has made an extended examination of the interactions of Mg and oxides (*B.* 23, 44, 120, 772, 2642; 24, 873, 1966; *abstracts* in *C. J.* 58, 331, 451, 693, 1372 [1890]; 60, 801, 1155 [1891]).

Magnesium, bromide of (vol. iii. p. 159). Beketoff (v. *abstract* in *C. J.* 62, 762 [1892]) gives H.F. $[Mg,Br^2] = 121,700$. The *double salt* $2MgBr_2.PbBr_2.16aq$ is described by Otto a. Drewes (*Ar. Ph.* 229, 585; *abstract* in *C. J.* 62, 566 [1892]).

Magnesium, chloride of (vol. iii. p. 159). Skinner (*C. J.* 61, 341 [1892]) gives the boiling-points of solutions of $MgCl_2$ in water and alcohol, from c. 4·5 to c. 14·5 p.c. $MgCl_2$.

Magnesium, iodide of (vol. iii. p. 161). Beketoff (*l.c.*) gives H.F. $[Mg,I^2] = 84,800$.

Magnesium, nitride of (vol. iii. p. 161). For description of an experiment to demonstrate the formation of Mg_3N_2 v. Merz (*B.* 24, 3,940; *abstract* in *C. J.* 62, 409 [1892]).

Magnesium, oxide of (vol. iii. p. 161). MgO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]); heated in the electric furnace, it melts with a current of 70 volts and 350 ampères (Moissan, *C. R.* 115, 1034; *cf. C. R.* 116, 1429 [1892–3]). Richards a. Rogers (*P. Am. A.* 28, 200 [1893]) found that MgO, prepared by evaporating $MgCO_3$ or Mg, with HNO_3Aq and heating very strongly, retained c. 10 times its volume of gas, chiefly O and N.

Magnesium, silicides of (vol. iii. p. 162). Regarding the formation of compounds by heating together Mg and Si, v. Winkler (*B.* 23, 2642; *abstract* in *C. J.* 58, 1373 [1890]).

MANGANESE (vol. iii. p. 177). Moissan (*C. R.* 116, 349 [1893]) obtained Mn containing 4 to 5 p.c. C, by fusing MnO with charcoal (keeping MnO in excess) by means of a current of 60 volts and 300 ampères. Prelinger (*M.* 14, 353; *abstract* in *C. J.* 66 [ii], 49 [1894]) prepared pure Mn by heating Mn amalgam (formed by electrolysing $MnCl_2Aq$ using a cathode of Hg) in pure H.

Mn is described by P (*l.c.*) as a grey porous metal; unchanged in dry air; reacts slowly with cold, rapidly with warm, water; dissolves in NH_4ClAq giving off NH_3 and H; S.G. 7·4212 referred to water at 4°. Moissan (*C. R.* 116, 1429 [1893]) found that Mn volatilises readily in the electric furnace, using a current of 80 volts and 380 ampères. Montemartini (*G.* 22, 384, 397, 426 [1892]) says that the gaseous products of the interaction of Mn and HNO_3Aq are H, NH_3, N, and N_2O. Finely divided Mn reacts with CO at c. 400°, producing MnO and C (Guntz, *C. R.* 114, 115 [1892]).

Manganese, alloys of. The presence of 0·5 p.c. Mn in iron or steel scarcely affects the properties, except by slightly increasing the tenacity and malleability; a very hard tool-steel is formed with c. 1½ p.c. Mn. Alloys with iron containing from 7 to 30 p.c. Mn are extremely hard and tough.

Manganese, amalgams of (vol. iii. p. 179). Prelinger (*M.* 14, 353; *abstract* in *C. J.* 66 [ii], 49 [1894]) prepared Mn_2Hg_5 by passing a current from a kathode of Hg through saturated $MnCl_2Aq$ to an anode of C, or Pt-Ir, in a porous vessel, washing in running water, squeezing out excess of Hg, and drying in H over $CaCl_2$. By heating gently in a stream of pure, dry H, pure Mn was obtained.

Manganous chloride (vol. iii. p. 179). Chassevant (*A. Ch.* [6] 30, 5 [1893]) describes several *double salts* of $MnCl_2$; viz. $MnCl_2.AmCl.2aq$, $MnCl_2.2AmCl.aq$, and $MnCl_2.LiCl.3aq$. For the *double salts* $M.KCl.2aq$, $M.CsCl.2aq$; $M.2XCl.2aq$, $X = NH_4$, Cs, Rb; $2M.MgCl_2.12aq$ ($M = MnCl_2$), v. Saunders (*Am.* 14, 127; *abstract* in *C. J.* 62, 780 [1892]).

Manganic chlorides (vol. iii. p. 180). Regarding the composition of the chloride in the solution obtained by dissolving MnO_2 in HClAq, v. Vernon (*P. M.* [5] 31, 469), and Pickering (*P. M.* [5] 33, 284) (*abstracts* in *C. J.* 62, 19, 687 [1892]).

Manganese peroxide (vol. iii. p. 183). Regarding the compositions of the hydrated oxides, approximately $MnO_2.xaq$, prepared by different methods, v. Gorgeu (*Bl.* [3] 4, 16 [1891]). G. (*C. R.* 110, 857; *abstract* in *C. J.* 58, 946 [1890]) gives some details regarding the interaction of $MnO_2.xaq$ and H_2O_2Aq. Heated in the electric furnace, MnO_2 melts, gives off O, and leaves MnO (Moissan, *C. R.* 115, 1034 [1892]). Mn_2O_3 is said to be formed by heating MnO_2 to c. 400° in NO (Sabatier a. Senderens, *C. R.* 114, 1476 [1892]). McLeod (*C. J.* 65, 202 [1894]) has confirmed his former observation that Cl is given off when MnO_2 and $KClO_3$ are heated together. Regarding compounds of MnO_2 with basic oxides, *v.* Rousseau (*C. R.* 112, 525; 114, 72; 116, 1060; *abstracts* in *C. J.* 60, 645 [1891]; 62, 569 [1892]; 64 [11], 416 [1893]).

Permanganates (vol. iii. p. 186). Regarding the interaction of permanganates with H_2O_2Aq, *v.* Gorgeu (*C. R.* 110, 958; *abstract* in *C. J.* 58, 1062 [1890]). Klobb (*Bl.* [3] 3, 508; *abstract* in *C. J.* 58, 947 [1890]) describes compounds of NH_3 with permanganates of Cd, Cu, Ni, and Zn.

Barium permanganate $BaMn_2O_8$ (the formula is wrongly printed $BaMnO_4$ in vol. iii. p. 186). For the preparation of this salt from $KMnO_4Aq$ and $Ba(NO_3)_2Aq$ *v.* Muthmann (*B.* 26, 1016; *abstract* in *C. J.* 64 [11], 324 [1893]).

Calcium permanganate. The formula given on p. 186 of vol. iii. is wrong; it should be $CaMn_2O_8.5H_2O$.

Potassium permanganate (vol. iii. p. 186). Tivoli (*G.* 19, 630 [1890]) gives the following as the reactions that occur when pure AsH_3 is passed into dilute $KMnO_4Aq$: (1) $2KMnO_4Aq + AsH_3 = K_2HAsO_4Aq + Mn_2O_3 + H_2O$; (2) $2KMnO_4Aq + AsH_3 = K_2HAsO_3Aq + 2MnO_2 + H_2O$.

Silver permanganate (vol. iii. p. 187). $AgMnO_4$ decomposes slowly at the ordinary temperature, rapidly at 100°, and very rapidly at 125° (Gorgeu, *C. R.* 114, 912; *abstract* in *C. J.* 62, 942 [1892]).

Manganous sulphide (vol. iii. p. 188). The pp. produced by adding $(NH_4)HSAq$ to an ammoniacal solution of a Mn salt, after washing in an atmosphere of H_2S and drying in CO_2 at 70°, is MnS; S.G. $\frac{17°}{17°} = 3{\cdot}55$. By heating to 300°–320°, or by leaving in contact with $(NH_4)HSAq$ for some days, the reddish MnS becomes green without changing its composition; the green form of MnS is crystalline, S.G. $\frac{17°}{17°} = 3{\cdot}63$ (Antony a. Donnini, *G.* 23 [1], 560 [1892]).

MASRIUM. In 1892 (*C. J.* 61, 491) Richmond a. Husseinoff obtained indications of the existence of an element before unknown in specimens of Egyptian fibrous alums. The supposed new element gave reactions indicating analogies with Be, Ca, and Zn; the results obtained by decomposing the oxalate by heat led to the at. w. of c. 228. The authors suggested the name *masrium*, from the Arabic name for Egypt.

MERCURAMMONIUM COMPOUNDS (vol. iii. p. 206).

Mercuro-ammonium salts $NH_{4-x}Hg_xX$ (vol. iii. p. 207). Barfoed's conclusion that these supposed compounds are really mixtures of mercuri-compounds and Hg is confirmed by Pesci (*G.* 21 [11], 569 [1891]). The product of the interaction of HgCl and NH_3Aq, described as *dimercuro-ammonium chloride* $NH_2Hg_2.Cl$ in vol. iii. (p. 208), leaves metallic Hg when treated with ammoniacal $(NH_4)_2SO_4Aq$, according to P. When the reaction of HgCl with NH_3Aq proceeds out of the light, P. says that the change is $2Hg_2Cl_2 + 4NH_3Aq = (NHg_2)Cl.NH_4Cl + 2NH_4ClAq + 2Hg$. Similarly the reaction of NH_3Aq with Hg_2SO_4 produces a double compound of dimercuro-ammonium sulphate $((NHg_2)_2SO_4.(NH_4)_2SO_4)$ and Hg; and $(NHg_2)NO_3.NH_4NO_3$ and Hg are formed, according to P., when $HgNO_3Aq$ is treated with NH_3Aq.

Mercuri-ammonium salts $NH_2Hg.X$. Regarding the conditions of formation of compounds of mercuri-ammonium chloride $NH_2Hg.Cl$ (vol. iii. p. 208) with $HgCl_2$ and $NH_4(Hg_2O)Cl$, *v.* Balestra (*G.* 21 [11], 294; *abstract* in *C. J.* 62, 276 [1892]).

Dimercuri-ammonium salts NHg_2X (vol. iii. p. 209). Pesci (*G.* 20, 485 [1890]) has examined the conditions of formation of various salts of this class, especially the *nitrate* $NHg_2.NO_3$ and compounds of this with NH_4NO_3. The *sulphate* $(NHg_2)_2SO_4.2aq$ was formed by saturating conc. NH_3Aq with $HgSO_4$, allowing the solution to evaporate in an atmosphere of NH_3 over CaO, and collecting the first crop of crystals; various compounds of $(NHg_2)_2SO_4$ with $(NH_4)_2SO_4$ are also described (*v. abstract* in *C. J.* 60, 268 [1891]).

MERCURY (vol. iii. p. 212). Heycock a. Neville's results (*C. J.* 57, 376 [1890]) show that some condensation from monatomic molecules perhaps occurs in dilute solutions of Hg in tin. For corrected tables of the vapour pressures of Hg for each 10° from 180° to 480°, and each 1° from 330° to 360°, *v.* Young (*C. J.* 59, 629 [1891]).

Jäger (*W.* 48, 209 [1893]) recommends to prepare pure Hg by converting Hg that has been distilled *in vacuo* into $HgNO_3$ and electrolysing a solution of the salt, using Pt as cathode and distilled Hg as anode. Shenstone (*C. J.* 61, 452 [1892]) noticed that Hg adheres to glass when brought into contact with Cl, Br, or I. Montemartini (*G.* 22, 384, 397, 426 [1891]) finds that the amount of NO produced by the interaction of Hg and HNO_3Aq decreases as concentration of the acid increases; that NO_2 is produced with acid more conc. than 27·5 p.c. HNO_3, $HgNO_3$ is formed with 25 p.c. acid, but $Hg(NO_3)_2$ with 50 to 70 p.c. acid; no NH_3 is formed with 27 and 50 p.c. acid.

Mercuric bromide (vol. iii. p. 215). $HgBr_2$ boils at 325°, according to Freyer a. V. Meyer (*Zeit. f. anorg. Chemie*, 2, 1 [1892]).

Mercurous chloride (vol. iii. p. 215). Harris a. V. Meyer have re-determined the V.D. of calomel at 448° and 518°; the value obtained was 117·5. H. a. M. obtained considerable quantities of Hg and $HgCl_2$ by allowing the vapours obtained by heating calomel to c. 465° to diffuse along a glass tube; also by heating calomel at 420° for half an hour in a distillation flask at 33 mm. pressure. By heating calomel to 240°–260°, and bringing a piece of KOH, which had been heated to c. 250°, into the vapour, they noticed that the surface of the KOH at once became covered with yellow HgO; they also found that a piece of gold leaf held for a moment in the vapour was amalgamated (if kept for some time in the hot vapour the yellow colour was restored). H. a. M. think their results leave no doubt that the vapour obtained by heating calomel is $Hg + HgCl_2$, and that the molecular formula of calomel is Hg_2Cl_2.

The reaction of Hg_2Cl_2 with NH_3Aq gives $(NHg_2)Cl.NH_4Cl$ and Hg, according to Pesci (*v. supra.* MERCURO-AMMONIUM SALTS).

Mercuric chloride (vol. iii. p. 217). $HgCl_2$ boils at 307° (Freyer a. V. Meyer, *Zeit. f. anorg. Chemie*, 2, 1 [1892]). The white substance produced by the reaction of $HgCl_2$Aq with a silver photographic image, or with pulverulent Ag, is $HgAgCl_2$, according to Jones (*S. C. I.* 12, 983; *abstract* in *C. J.* 66 [11], 188 [1894]).

Mercuric cyanide; for an account of the conditions of formation and properties of the *double mercury-zinc cyanide*, v. Dunstan (*C. J.* 61, 666 [1892]).

Mercury, haloid compounds of (vol. iii. p. 219). Wells (*Am. S.* [3] 44, 221; *abstract* in *C. J.* 64 [11], 68 [1893]) describes a number of double compounds of mercury and cæsium halides; the compounds belong to the forms (1) Cs_3HgX_5, (2) Cs_2HgX_4, (3) $Cs_2Hg_3I_8$, (4) $CsHgX_3$, (5) $CsHg_2X_5$, (6) $CsHg_5X_{11}$; X = Cl, Br or I; in some cases the total X atoms comprise two different halogens.

Mercury hydrosulphide; for experimental attempts to prepare a definite compound, v. Linder a. Picton (*C. J.* 61, 123 [1892]).

Mercury phosphide (vol. iii. p. 223). By heating Hg and PI_2 in a sealed tube for many hours at 275°–300°, and removing HgI_2 by treatment with KIAq, Granger (*C. R.* 115, 229 [1892]) obtained Hg_3P_2 in lustrous, metal-like, hexagonal crystals, appearing red by transmitted light, and giving a brown powder. The compound gives Hg and P when heated; heated in air it burns; detonates when mixed with $KClO_3$ and struck; burns in Cl; dissolved by *aqua regia*.

Mercurous sulphide (vol. iii. p. 224). Antony a. Sestini (*G.* 24 [1], 193 [1894]) obtained a black powder by passing dry H_2S, diluted with CO_2, over dry Hg_2Cl_2 or $Hg(C_2H_3O_2)$, kept at −10°; when freshly prepared the black powder was scarcely changed in dry HCl at −18°, but at a somewhat higher temperature (below 0°) Hg_2Cl_2 was quickly formed. The substance dissolved in cold K_2SAq or Na_2SAq, but when temperature rose above 0° the solution became turbid and ppd. Hg. A. a. S. think their results show that Hg_2S exists at low temperatures (*abstract* in *C. J.* 66 [11], 318 [1894]).

Mercury sulphochloride (vol. iii. p. 225). The compound $2HgS.HgCl_2$ is formed, according to Colson (*C. R.* 115, 657 [1892]), by passing H_2S into a solution of $HgCl_2$ in dry benzene.

MOLYBDENUM (vol. iii. p. 421). Smith a. Maas (*A. C. J.* 15, 397 [1893]) obtained the mean value 95·85 (O = 15·96) for the at. w. of Mo, by heating Na_2MoO_4 in a current of dry HCl and weighing the NaCl that remained ($MoO_3.2HCl$ and H_2O were formed and removed). Smith a. Oberholtzer (*Zeit. f. anorg. Chemie*, 5, 63 [1893]) say that a mixture of $MoOCl_4$ and $Mo(CO)Cl_4$ is formed by heating Mo to 150°–200° in $COCl_2$; and that $Mo_3S_7Cl_4$ is produced by heating Mo to redness in S_2Cl_2. Mo is said to ppt. Ag from $AgNO_3$Aq, Au from $AuCl_3$Aq, HgCl and then Hg from $HgCl_2$Aq, and Cu from solutions of its salts (Smith, *Zeit. f. anorg. Chemie*, 1, 360 [1891]). Montemartini (*G.* 22, 384, 397, 426 [1891]) finds that no NH_3 is formed in the interaction of Mo and HNO_3Aq with from 3 to 70 p.c. HNO_3; the most vigorous action occurs with acid c. 50 p.c., but the whole of the metal is not oxidised to MoO_3, a nitrate being probably formed; the gaseous products are NO and NO_2, the quantity of NO decreasing as the concentration of the acid increases.

Molybdenum, carbides of. By heating a mixture of MoO_2 and charcoal in the electric furnace, Moissan (*C. R.* 116, 1225 [1893]) obtained a very hard carbide, containing from 9·77 to 9·9 p.c. C; S.G. 8·6.

Molybdenum sesquioxide (vol. iii. p. 431). Heating Mo_2O_3 in NO produces MoO_2 (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]).

Molybdenum trioxide (vol. iii. p. 432). MoO_3 partially volatilises, and is partially reduced to one of the blue oxides, at c. 1750° (Read, *C. J.* 65, 313 [1894]). According to Smith a. Oberholtzer (*Zeit. f. anorg. Chemie*, 4, 236 [1893]), the products of heating MoO_3 in HBr are (1) $MoO_3.3HBr$, and (2) $Mo_2O_3Br_4$; when HI is used and the temperature kept at 105°–120°, a blue oxide $Mo_3O_8.x$aq is formed; HF at 300°–400° forms $Mo_2O_3F_4$ (*v. abstract* in *C. J.* 64 [11], 471 [1893]). Cammerer (*Chem. Zeit.* 15, 957; *abstract* in *C. J.* 62, 944 [1892]) says that $2MoO_3.H_2O_2.H_2O$ is formed by boiling MoO_3 with H_2O_2Aq.

Molybdenum, oxybromides of (vol. iii. p. 433). Smith a. Oberholtzer (*Zeit. f. anorg. Chemie*, 4, 236 [1893]) describe $Mo_2O_3Br_4$; square plates, colour of $KMnO_4$. Formed, along with $MoO_3.3HBr$, by heating MoO_3 in HBr.

Molybdenum, oxychlorides of (vol. iii. p. 433). For the products of the interaction of MoO_2Cl_2 and NH_3, v. Smith a. Lehner (*Zeit. f. anorg. Chemie*, 4, 374; *abstract* in *C. J.* 64 [11], 529 [1893]).

Molybdenum, oxycyanide of. By dissolving MoO_2 in KCyAq, and adding a strong acid, Péchard (*C. R.* 118, 804 [1894]) obtained MoO_2Cy_2. Easily decomposed by contact with acids; *double compounds* with KCy and AgCy are also described.

Molybdenum, oxyfluorides of (vol. iii. p. 433) For $Mo_2O_3F_4$, a white, crystalline, deliquescent solid, obtained by heating MoO_3 in HF at 300°–400°, v. Smith a. Oberholtzer (*l.c.*).

Molybdenum, thiochloride of. For $Mo_3S_7Cl_4$, v. S. a. O. (*l.c.* 5, 63).

Molybdates, and derivatives thereof (vol. iii. p. 423). For compounds of molybdates of NH_4 and K with SO_2 and SeO_2, v. Péchard (*C. R.* 116, 1441; 117, 104; *abstracts* in *C. J.* 64 [11], 530 [1893]).

Permolybdates. By the reaction of H_2O_2Aq with $K_2Mo_3O_{10}$Aq, Péchard (*C. R.* 112, 720; *abstract* in *C. J.* 60, 988 [1891]) obtained *potassium permolybdate* $K_2Mo_2O_8$. 4aq; the corresponding NH_4 salt was also formed.

Arseno-molybdates (vol. iii. p. 425). For salts of this class, v. Friedheim (*Zeit. f. anorg. Chemie*, 2, 314; 6, 11, 27; *abstracts* in *C. J.* 64 [11], 283; 66 [11], 238 [1893–4]).

Iodomolybdates. A great many salts of the form $xMoO_3.yI_2O_5.zMO$ are described by Blomstrand (*Zeit. f. anorg. Chemie*, 1, 10; *abstract* in *C. J.* 64 [11], 122 [1893]).

Phosphomolybdates (vol. iii. p. 426). Friedheim (*Zeit. f. anorg. Chemie*, 4, 275; 6, 11, 27; *abstracts* in *C. J.* 64 [11], 472; 66 [11], 238 [1893–4]) describes several salts of this class.

Fluomolybdates (vol. iii. p. 425), v. Piccini (*Real. Acad. Lincei*, 7 [1], 267; *abstract* in *C. J.* 62, 784 [1892]), and Mauro (*l.c.*, 1892 [1], 194; *abstract* in *C. J.* 64 [11], 124 [1893]).

NICKEL (vol. iii. p. 498). The at. w. has been re-determined (1) by Schützenberger, by reducing oxides of Ni in H (*C. R.* 114, 1149 [1892]); (2) by Winkler, by estimating Cl in $NiCl_2$ prepared from electrolytically deposited Ni (*Zeit. f. anorg. Chemie*, 4, 10 [1893]). Schützenberger's values varied from 58·52 to 59·8; Winkler's mean value from the gravimetric determinations was 58·903, and from the volumetric determinations 58·910 (Cl = 35·37, Ag = 107·66). Krüss a. Schmidt (*Zeit. f. anorg. Chemie*, 2, 235 [1892]) insist that the substance called nickel is not an element, but Winkler (*l.c.*) controverts this statement (*v. abstracts* in *C. J.* 64 [11], 212, 469 [1893]). The molecule of Ni in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Schützenberger (*C. R.* 113, 177 [1891]) says that a volatile compound is formed by passing dry HCl over finely divided Ni heated to dull redness. Montemartini (*G.* 22 [1], 250; *abstract* in *C. J.* 62, 1278 [1892]) gives the quantities of NH_3, N_2O, N, and HNO_2 (no NO) produced by the reaction of excess of HNO_3Aq (27·5 p.c.) with Ni. Heated to 200° in NO, the oxide NiO is formed without any Ni_2O_3 (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]). By passing NO_2, diluted with N, over reduced Ni, *nitro-nickel* (? Ni_2NO_2) is obtained; it resembles nitro-cobalt (*q. v.*, p. 908) (S. a. S., *Bl.* [3] 9, 669 [1893]).

Nickel carbonyl $Ni(CO)_4$. (*Nickel carbonoxide*, vol. iii. p. 501.) Mol. w. was confirmed by Mond a. Nasini (*Z. P. C.* 8, 150 [1891]), by finding the depression of the freezing-point of benzene. S.G. 1·35613 at 0°, 1·27132 at 36° (water at 4° = 1); S.G. at b.p. = 1·25406; molecular volume = 136·04; critical temp. = 151°. For some reactions *v.* Berthelot (*C. R.* 112, 1343; *abstract* in *C. J.* 60, 1427 [1890]).

Nickel, chloride of (vol. iii. p. 501). A volatile substance, decomposed by heating, is said to be formed by passing dry HCl over dry $NiCl_2$ at dull redness (Schützenberger, *C. R.* 113, 177; *v. abstract* in *C. J.* 60, 1429 [1890]). Chassevant (*A. Ch.* [6] 30, 5 [1893]) describes the *double compounds* $NiCl_2.AmCl.6aq$ and $NiCl_2.KCl.3aq$.

Nickel, fluoride of (vol. iii. p. 502). Poulenc (*C. R.* 114, 1426 [1892]) obtained amorphous NiF_2 by heating $NiCl_2$ with excess of NH_4F, and washing away NH_4Cl with boiling alcohol; by heating in HF to 1200°-1300°, the amorphous NiF_2 became crystalline, forming green prisms, S.G. 4·63, not acted on by warm HNO_3Aq, HClAq, or H_2SO_4Aq. Heated in air, NiF_2 gives NiO; heated with S it gives NiS; and with H it is reduced to Ni (for other reactions, *v. abstract* in *C. J.* 62, 1159 [1892]). The *double salt* $NiF_2.KF$ is formed by heating $NiCl_2$ with KHF_2, and washing away KCl by water (P., *C. R.* 114, 746 [1892]).

Nickel monoxide (vol. iii. p. 502). NiO melts and forms green crystals in the electric furnace (Moissan, *C. R.* 115, 1034 [1892]). NiO occludes small quantities of N and O (Richards a. Rogers, *P. Am. A.* 28, 200 [1893]).

Nickel sesquioxide (vol. iii. p. 502). Ni_2O_3 fuses, gives up all its O, and leaves Ni at c. 1750° (Read, *C. J.* 65, 313 [1894]).

Nickel peroxide (vol. iii. p. 503). Campbell a. Trowbridge (*J. Anal. and App. Chem.* 7. 301; *abstract* in *C. J.* 66 [11], 238 [1894]) conclude that an oxide with more O than Ni_2O_3 can be obtained by ppg. $NiSO_4Aq$ by Na_2CO_3Aq in presence of Br at different temperatures.

Nickel monosulphide (vol. iii. p. 508). Regarding the oxidation of this salt in air, to $NiSO_4.6NiO$, &c., *v.* P. de Clermont (*C. R.* 117, 229; *abstract* in *C. J.* 64 [11], 528 [1893]).

NIOBIUM (vol. iii. p. 505). Nb_2O_5 is not changed at c. 1750° (Read, *C. J.* 65, 313 [1894]). Piccini (*Zeit. f. anorg. Chemie*, 2, 21 [1892]) has prepared *potassium fluoxyperniobate* $NbO_2F_3.2KF.aq$.

NITRAMIDE $NO_2(NH_2)$. Thiele a. Lachman (*B.* 27, 1909 [1894]) obtained this compound by throwing $NO_2.NK.CO_2K$ (potassium nitro-carbamate) into a mixture of ice and excess of H_2SO_4, extracting with ether, and evaporating in a stream of air. Crystallises in clear prisms, which melt at 72° with decomposition; decomposed instantly to N_2O and H_2O by alkalis, alkali carbonates, borax, or Na acetate.

NITRATES (vol. iii. p. 509). Rousseau a. Tite (*C. R.* 115, 174 [1892]) find that many basic nitrates are completely decomposed by heating with water at 150°-200°. Regarding the formation of basic nitrates of Cd, Ca, Ni, and Zn, *v.* R. a. T. (*C. R.* 114, 1184); Riban (*C. R.* 114, 1357); and Werner (*C. R.* 115, 169); (*abstracts* in *C. J.* 62, 1156, 1157, 1276 [1892]).

NITRIC ACID (vol. iii. p. 517). Regarding the colours produced by diluting red fuming HNO_3Aq *v.* Marchlewski (*B.* 24, 3271 [1891]). For revised tables showing the composition of HNO_3Aq of different concentrations *v.* Lunge a. Rey (*S. C. I.* 1891. 543). Regarding the magnetic rotations of HNO_3Aq *v.* Perkin (*C. J.* 63, 57 [1893]). Hall (*Am.* 13, 554) has examined the rate of production of H and O, and the effect on the concentration of the acid, by the slow and steady electrolysis of HNO_3Aq (*abstract* in *C. J.* 62, 680 [1892]). The interactions of HNO_3Aq with many metals have been examined by Montemartini (*G.* 22 [1], 250, 277, 384, 397, 426 [1891]; *abstracts* in *C. J.* 62, 1278, 1402 [1892]), Veley (*S. C. I.* 10, 206; and elsewhere), and others; the results are noted under various metals. Pickering (*C. J.* 63, 436 [1893]) has isolated the hydrates $HNO_3.H_2O$ and $HNO_3.3H_2O$; the freezing-points of HNO_3Aq, from 1·82 to 86·19 p.c. HNO_3, are given by P.

NITROGEN (vol. iii. p. 556). S.G. of N (air = 1) = ·97209; 1 litre weighs 1·25749 g. (Rayleigh, *P. R.* 53, 134 [1893]). $\mu_D = 1{\cdot}2053$ at −190° (liquid N, containing 5 p.c. O) (Liveing a. Dewar, *P. M.* [5] 36, 928 [1893]). Absorption coefficient in alcohol, *v.* Henrich (*Z. P. C.* 9, 435 [1892]). Diffusion in water, *v.* Duncan a. Hoppe-Seyler (*Zeit. physiol. Chemie*, 17, 147 [1893]).

Preparation of pure nitrogen. Threlfall (*P. M.* [5] 35, 1 [1893]) gives minute directions for preparing pure N by passing air and NH_3 over hot Cu, and absorbing traces of O by $CrCl_2Aq$; exact directions for preparing the $CrCl_2Aq$ are given, and the paper contains numerous details regarding the purifications of the reagents used in the process.

Supposed allotropic form of nitrogen. Threlfall (*l.c.*) has repeated experiments on sparking extremely pure N (*v.* vol. iii. p. 557); no condensation occurred down to −10° and c. 8 mm.

pressure, but when Hg is present a compound of N and H is formed (probably Hg_3N_2, v. vol. iii. p. 221). Regarding the *fixation of nitrogen by growing plants*, v. Beyerinck, also Schloesing a. Laurent (*abstracts* in *C. J.* 62, 1019, 1021 [1892]).

Nitrogen, hydrides of (vol. iii. p. 559). *Hydrazoic acid* N_3H. For new methods of preparing N_3H v. Curtius (*B.* 24, 3341; 26, 1263; *abstracts* in *C. J.* 62, 112; 64 [11], 463 [1892-3]). Wislicenus (*B.* 25, 2084 [1892]) has obtained N_3H by the interaction of NH_3 and N_2O. From $\frac{1}{4}$ g. to $\frac{1}{2}$ g. Na is heated in a stream of NH_3 until all is converted into $NaNH_2$; a current of dry N_2O is then passed over the $NaNH_2$ at 150°–250° as long as NH_3 is given off ($2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3$). By dissolving the product in water, filtering, decomposing by dilute H_2SO_4Aq, and distilling, N_3HAq is obtained.

The following salts are described by Curtius (*B.* 24, 3341; *abstract* in *C. J.* 62, 112 [1892]): $(NH_4)N_3$, $Pb(N_3)_2$, HgN_3, NaN_3.

Nitrogen, iodides of (vol. iii. p. 560). Diiodamine, NHI_2, is the product of adding excess of NH_3Aq to a conc. solution of I in conc. KIAq; by suspending NHI_2 in water, and adding an ammoniacal solution of $AgNO_3$ or Ag_2O, a black compound $NAgI_2$ is obtained which explodes when dry (Szuhay, *B.* 26, 1933; *abstract* in *C. J.* 64 [11], 568 [1893]; *cf.* Selivanoff, *B.* 27, 1012; *abstract* in *C. J.* 66 [11], 312 [1894]).

Nitrous oxide (vol. iii. p. 561). Ramsay a. Shields (*C. J.* 63, 833 [1893]) give the m.p. of N_2O as −102·3°, and the b.p. as −89·8°. Villard (*C. R.* 118, 1096 [1894]) gives the following data for the S.G. of liquid N_2O: ·9105 at 0°, ·885 at 5°, ·856 at 10°, ·804 at 17·5°, ·720 at 26·5°, ·640 at 32·9°, ·605 at 34·9°, ·572 at 36·3°. Liveing a. Dewar (*P. M.* [5] 34, 205 [1892]) give

$$\frac{\mu_D - 1}{d} = ·2634, \text{ and } \frac{\mu^2 - 1}{(\mu^2 + 2)d} = ·163 \text{ at } -90°.$$

Smith (*S. C. I.* 11, 867; 12, 10 [1893]) says that a regular stream of N_2O is obtained by heating to 240°–250° a mixture of 1 pt. dry $NaNO_3$ with c. $1\frac{3}{4}$ pt. dry $(NH_4)_2SO_4$. By passing N_2O, mixed with a little H, over Pd black, the H is entirely converted to H_2O, with formation of N (Montemartini, *Real. Acad. Lincei*, 7 [11], 219 [1892]).

Nitric oxide (vol. iii. p. 562). Very pure NO is obtained, according to Emich (*M.* 13, 73 [1892]), by the interaction of copper and a mixture of H_2SO_4 and HNO_3Aq. Emich (*l.c.*, p. 78) finds that NO is completely decomposed to N and O by passing over nets of Pt or Pd wire kept very hot by an electric current. Emich (*l.c.* p. 86) says that NO and O unite after being dried by long contact with P_2O_5; but Baker (*C. J.* 65, 611 [1894]) finds that *dry* NO and *dry* O do not combine at the ordinary temperature. Regarding the reactions between NO and metals and metallic oxides, v. Sabatier a. Senderens (*C. R.* 114, 1429; 1476; *abstracts* in *C. J.* 62, 1151, 1271 [1892]; results are noted under the different metals and oxides in *Addenda*).

Nitrogen dioxide (vol. iii. p. 565). For the reactions of NO_2 with various metals and oxides v. S. a. S. (*C. R.* 115, 236; *abstract* in *C. J.* 62, 1390 [1892]; results are noted under the different metals and oxides in *Addenda*).

Nitrogen tetroxide (vol. iii. p. 565). For preparation of N_2O_4, v. Cundall (*C. J.* 59, 1076 [1891]). C. (*l.c.*) has measured the dissociation of liquid N_2O_4 in $CHCl_3$ up to c. 25°; Ostwald (*C. J.* 61, 242 [1892]) shows that the dissociation follows van't Hoff's law for dilute solutions.

Nitrous acid (vol. iii. p. 567). Regarding the formation of HNO_2 in solution in HNO_3, v. Veley (*Pr.* 52, 27; *abstract* in *C. J.* 64 [11], 413 [1893]).

Hyponitrous acid (vol. iii. p. 568). Tanatar (*J. R.* 25, 342; *abstract* in *C. J.* 66 [11], 186 [1894]) prepared $Ag_2N_2O_2$ by adding CaO to fairly conc. KNO_2Aq in the ratio $CaO:KNO_2$, then an equivalent of solid $NH_2OH.HCl$, heating to 50°, letting stand for a few days at the ordinary temperature, filtering, acidifying with acetic acid, ppg. by $AgNO_3Aq$, dissolving $Ag_2N_2O_2$ in HNO_3Aq (which leaves AgCl), and ppg. again by Na acetate.

OSMIUM (vol. iii. p. 641). Os fuses readily in the electric arc in a carbon capsule; when fused it has a crystalline fracture, and scratches quartz, but is scratched by topaz (Joly a. Vèzes, *C. R.* 116, 577 [1893]).

Osmic acid (vol. iii. p. 646). Moraht a. Wischin (*Zeit. f. anorg. Chemie*, 3, 153; *abstract* in *C. J.* 64 [11], 380 [1893]) say that the black powder obtained by the interaction of acids and K_2OsO_4Aq (vol. iii. p. 645), when dried over P_2O_5 *in vacuo* till it ceases to lose weight, is osmic acid H_2OsO_4. M. a. W. describe the compound as a sooty-black powder, smelling of OsO_4 in moist air, but unchanged under water containing alcohol. By passing H_2S over H_2OsO_4 a violent reaction occurs, and $Os_2O_2S_3.H_2O$ is formed. Heated with conc. HClAq for many hours with a little alcohol, and evaporated, $Os_2Cl_7.7aq$ was obtained; an alcoholic solution of this substance with KClAq gave K_2OsCl_6 and the filtrate yielded $OsCl_3.3aq$; the substance Os_2Cl_7 is therefore supposed by M. a. W. to be a mixture of $OsCl_4$ and $OsCl_3$. By heating H_2OsO_4 with HIAq, violet-black crystals, probably OsI_4, were obtained. No action occurs when Os is heated with I, or with Br.

Potassium osmiamate (vol. iii. p. 645). Joly (*C. R.* 112, 1442 [1891]) prepares this salt by dissolving 100 pts. OsO_4 in a solution of 100 pts. KOH in 50 pts. H_2O, keeping the solution at c. 40°, and adding 40 c.c. NH_3Aq; after a time the brown liquid becomes colourless, and a yellow crystalline pp. is formed. J. gives the formula $KNOsO_3$ to this salt. Heated *in vacuo* it is rapidly decomposed above 200°, and at 440° almost all the N is given off, the solid products being K_2OsO_4, OsO_2, and $KOsO_3$ (*v. abstract* in *C. J.* 60, 1433 [1891]).

OXIDES (vol. iii. p. 658). Regarding the connections between the stability of oxides when heated and the periodic classification of the elements, *v.* Bailey (*C. J.* 65, 106, 321 [1894]).

OXYGEN (vol. iii. p. 703). *Atomic weight of oxygen* (vol. iii. p. 705). Dittmar a. Henderson (*C. N.* 67, 127, 139, 151, 164; *abstract* in *C. J.* 64 [11], 410 [1893]), from careful determinations made by passing H over hot CuO, and weighing the water and Cu produced, adopt the value 15·87 for the at. w. of O. By measurements of the combining volumes of O and H, combining the results with Rayleigh's determination of the S.G. of O, Scott (*T.* 184, 543 [1893]) got the value 15·862. The following values summarise the most recent determinations (*v.* D. a. H., *l.c.*), Cooke a. Richards, 15·868; Noyes, 15·885; Rayleigh (*Pr.* 45, 425 [1890]), 15·89; Keiser, 15·949; Leduc (*C. R.* 116, 1248 [1893]), 15·88; D. a. H., 15·87; Scott, 15·862. The value adopted in this *Dictionary*, 15·96, is almost certainly too high; the mean of the values obtained by C. a. R., N., R., D. a. H., and S., is 15·875.

The ratio of the combining volumes of O and H was determined by Scott (*l.c.*) to be 2·00245 : 1 (*v.* WATER, this vol. p. 861). S.G. of O referred to H = 15·882 (Rayleigh, *Pr.* 50, 448 [1892]). For an examination of the whole of the spectrum of O, *v.* Eisig (*W.* 51, 747: *abstract* in *C. J.* 66 [ii], 265 [1894]). Liveing a. Dewar (*P. M.* [5] 34, 205 [1892]) determined $\frac{\mu_D - 1}{d}$ to be ·1989, and $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ to be ·1265, at −182° (*cf.* Olszewski a. Witkowski; *abstract* in *C. J.* 64 [ii], 353 [1893]). For diffusion of O in water, *v.* Duncan a. Hoppe-Seyler (*Zeit. physiol. Chemie*, 17, 147 [1892]).

Regarding the division of O between H and CO when mixtures of these gases are exploded, *v.* Harker (*Z. P. C.* 9, 673 [1892]). *Dry* O does not combine with *dry* NO at the ordinary temperature (Baker, *C. J.* 65, 611 [1894]); nor with *dry* K or Na, even when these metals are distilled in the gas (Holt a. Sims, *C. J.* 65, 440 [1894]).

OZONE (vol. iii. p. 788). Regarding the conditions of ozonification of oxygen, *v.* Shenstone a. Priest (*C. J.* 63, 938 [1893]). Baker (*C. J.* 65, 611 [1894]) confirms the observation of Shenstone a. Cundall (*C. J.* 81, 610 [1887]) that *dry* O is ozonised as rapidly as moderately dry O.

PALLADIUM (vol. iii. p. 792). The at. w. of Pd has been re-determined (1) by Bailey a. Lamb (*C. J.* 61, 745 [1892]), by analyses of $Pd(NH_3Cl)_2$; (2) by Keller a. Smith (*Am.* 14, 423 [1892]), by ppg. Pd electrolytically from a solution of $Pd(NH_3Cl)_2$ in NH_3Aq; (3) by Joly a. Leidié (*C. R.* 116, 146 [1893]), by electrolysing K_2PdCl_4 in HClAq; (4) by Keiser a. Breed (*Am.* 16, 20 [1894]), by determining the ratio of Pd to Cl in $Pd(NH_3Cl)_2$. B. a. L. obtained the value 105·459; K. a. S. the value 106·35; J. a. L. the value 105·665; and K. a. B. the value 106·27 (Cl = 35·37; Ag = 107·66; N = 14·01; O = 15·96). The molecule of Pd in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Regarding the preparation of pure Pd, *v.* the memoirs referred to *supra.* Pd absorbs O at 450°, forming Pd_2O (Neumann, *M.* 13, 40 [1892]), but when Pd sponge is heated in dry O till the weight is constant PdO is formed (Wilm, *B.* 25, 220 [1892]). Heated to 200° in NO, Pd sponge that has been saturated with H becomes incandescent and the NO is completely changed to H_2O and NH_3, but oxidation of the Pd does not occur (Sabatier a. Senderens (*C. R.* 114, 1429 [1892]). Regarding *palladium sulphides*, *v.* Petrenko-Kritschenko (*Zeit. f. anorg. Chemie*, 4, 247; *abstract* in *C. J.* 64 [ii], 475 [1893]). *Phosphopalladous compounds*, $PdCl_2.PCl_3$ and $PdCl_2.P(OH)_3$, are described by Fink (*C. R.* 115, 176; *abstract* in *C. J.* 62, 1285 [1892]). Vèzes (*C. R.* 115, 111) describes *potassium palladosochloronitrite* $K_2Pd(NO_2)_2Cl_2$ (*abstract* in *C. J.* 62, 1284 [1892]).

PHOSPHATES (vol. iv. p. 106). Rossel a. Frank (*B.* 27, 52) say that P is obtained by heating $NaPO_3$, or any phosphate of Ca or Mg, with Al in a current of H.

Dipotassium-hydrogen orthophosphate (vol. iv. p. 111). According to Standenmaier (*Zeit. f. anorg. Chemie*, 5, 383 [1893]), K_2HPO_4 cannot be isolated. S. (*l.c.*) describes *acid salts*, $K_5H_4(PO_4)_3.aq$, $K_7H_5(PO_4)_4.2aq$, and $KH_5(PO_4)_2$.

Thorium orthophosphates (vol. iv. p. 112). Volck (*Zeit. f. anorg. Chemie*, 6, 161 [1894]) obtained $Th(HPO_4)_2.aq$ by adding dilute H_3PO_4Aq to $ThCl_4Aq$.

Sodium pyrophosphate (vol. iv. p. 114). For a study of the reaction of HClAq with $Na_4P_2O_7$, *v.* Watson (*S. C. I.* 11, 224; *abstract* in *C. J.* 64 [ii], 272 [1893]).

ORTHOPHOSPHORIC ACID (vol. iv. p. 125). According to Watson (*C. N.* 68, 199 [1893]), H_3PO_4 is changed completely to $H_4P_2O_7$ at 255°–260°, and HPO_3 begins to form at 290°–300°.

PHOSPHORUS (vol. iv. p. 129). Regarding the action of light and heat on *ordinary phosphorus*, *v.* Retgers (*Z. P. C.* 5, 211; *abstract* in *C. J.* 66 [ii], [1894]).

Phosphorus hydride (vol. iv. p. 136). PH_3 and O react at a low pressure to form H_3PO_3 ($2PH_3 + 3O_2 = 2H_3PO_3$); when the gases are allowed to diffuse with one another at less than 50 mm. pressure, the reaction is $PH_3 + O_2 = H_2 + HPO_2$; slow oxidation at greater pressures proceeds approximately according to the equation $4PH_3 + 5O_2 = 2HPO_2 + 2H_3PO_3 + 2H_2$ (H. J. van de Stadt, *Z. P. C.* 12, 322 [1893]). According to van de S., explosion occurs at a certain low pressure, and this pressure depends much on the amount of moisture present, the moisture preventing and retarding the explosion. Kooij (*Z. P. C.* 12, 155 [1893]) has examined the rate of decomposition of PH_3 by heat. For the reaction of PH_3 with $AgNO_3Aq$ *v.* Vitali (*abstract* in *C. J.* 64 [ii], 206 [1893]).

Phosphoric oxide (vol. iv. p. 141). For details regarding the preparation of pure P_2O_5, and for methods of detecting traces of P in P_2O_5, *v.* Threlfall (*P. M.* [5] 35, 14 [1893]).

Phosphorus suboxide (vol. iv. p. 139). [illegible] (*B.* 27, 1257 [1894]) thinks that P_4O is formed by the interaction of P_2O_5 and NH_3.

Phosphorus, sulphides of (vol. iv. p. 145). Helff (*Z. P. C.* 12, 190 [1893]) confirms the statement that there are no definite compounds P_4S and P_2S; by heating together red P and S, he obtained P_4S_3, P_4S_7, P_3S_6, and P_2S_5.

Phosphorus, sulphoiodide of. Ouvrard (*C. R.* 115, 1301; *abstract* in *C. J.* 64 [ii], 164 [1893]) obtained P_2S_3I by heating PI_2 in H_2S at 110°–120°; also by evaporating a solution of the three elements in the proper proportion in CS_2 and heating the residue to 120° in an inert gas; also by dissolving I in a solution of P_2S_3 in CS_2. The compound crystallises from CS_2 in golden-yellow prisms; it is unchanged in dry air, but slowly decomposed in moist air, giving off H_2S; sl. sol. $CHCl_3$, C_6H_6, EtOH, or Et_2O; burns at c. 300°, giving P_2O_5, SO_2, and I; at c. 300° *in vacuo* it separates into I and P_2S_4; decomposed by hot water, and explosively by fuming HNO_3.

Potassium hypophosphates (vol. iv. p. 153). Bansa (*Zeit. f. anorg. Chemie*, 6, 128 [1894]) describes many *double salts* of $K_2H_2P_2O_6$ with $MH_2P_2O_6$, where M = Cd, Co, Cu, Mn, Ni, or Zn; also double salts $MK_2P_2O_6$, where M = Co or Ni. The double salt $K_2Na_2P_2O_6.2aq$ is also described (*abstract* in C. J. 66 [11], 279 [1894]).

Thallium hypophosphates. Joly (*C. R.* 118, 649 [1894]) obtained the *normal salt* $Tl_4P_2O_6$, and the *acid salt* $Tl_2H_2P_2O_6$ (*abstract* in *C. J.* 66 [11], 282 [1894]).

PLATINATES (vol. iv. p. 281).

Sodium thioplatinates. Schneider has obtained the salts Na_2PtS_2 and $Na_2S.PtS.2PtS_2$ (*J. pr.* [2] 48, 411 [1894]).

Platino-oxalates (vol. iv. p. 285). Regarding the constitutional formulæ of the K salts, *v.* Werner (*Zeit. f. anorg. Chemie*, 3, 267), and Söderbaum (*ibid.* 6, 45 [1894]).

PLATINUM-AMMONIUM COMPOUNDS (vol. iv. p. 292). Petersen (*Z. P. C.* 10, 580 [1892]) finds, from cryoscopic determinations, that most of the formulæ generally used for these compounds are molecular. For a discussion of the constitutions of several classes of these compounds, and for measurements of the electrical conductivities of aqueous solutions of some of them, *v.* Werner a. Miolati (*Z. P. C.* 12, 35 [1893]).

POTASSIUM (vol. iv. p. 297). Holt a. Sims (*C. J.* 65, 432 [1894]) found that K became soft at 54·5°, and remained soft to 60·5°, whereat it became brittle; complete melting occurred at 62·5°. H. a. S. say that dry K may be distilled in dry O without the formation of any compound of the two elements. They found the products of the oxidation of K to be K_2O_2, K_2O_3, and finally K_2O_4 (*v. Oxides, infra*). Mixtures of KNO_2 and KNO_3 were formed by oxidising K in NO and in the red oxides of N.

Potassium amide (vol. iv. p. 299). Titherley (*C. J.* 65, 504 [1894]) says that KNH_2 is white and wax-like, melting at 270°–272°. It may be distilled without change in H at 400°–500°. T. says that KNH_2 is not decomposed by heating at c. 400° in a silver boat; if a glass vessel is used, NH_3 is given off with some N and H, and K silicate is formed; a small amount of decomposition occurs in a silver boat at c. 500°, and at a full red heat the amide distils with partial splitting up into its elements. For other reactions of KNH_2, *v.* T. (*l.c.*).

Potassammonium (vol. iv. p. 299). Joannis (*C. R.* 118, 713 [1894]) finds that there is no reaction between N and $N_2H_6K_2$; he says that N_2O produces KNH_2, NH_3, KOH, and N. For the action of O, *v.* J. (*C. R.* 116, 1370; *abstract* in *C. J.* 64 [11], 462 [1893]).

Potassium bromide (vol. iv. p. 299). The melting-point is given as 715° by V. Meyer a. Riddle (*B.* 26, 2443 [1893]).

Potassium chloride (vol. iv. p. 300). Melts at 766°, according to M. a. R. (*l.c.*).

Potassium hydroxide (vol. iv. p. 302). Melts at 1045° (M. a. R., *l.c.*).

Potassium iodide (vol. iv. p. 303). Melts at 623° (M. a. R., *l.c.*). Regarding the interaction of KIAq and $FeCl_3Aq$, *v.* FERRIC CHLORIDE, *Addenda*, p. 913.

Potassium tri-iodide (vol. iv. p. 304). Jakovkin (*Z. P. C.* 13, 539 [1894]) has made an examination of the dissociation of KI_3 in aqueous solution to KIAq and IAq (*abstract* in *C. J.* 66 [11], 271 [1894]).

Potassium nitride (vol. iv. p. 304). The experiments of Titherley (*C. J.* 65, 51[illegible] [1894]) show that K_3N does not exist.

Potassium oxides (vol. iv. p. 304). Holt a. Sims (*C. J.* 65, 432 [1894]) failed to obtain the *monoxide* K_2O by any of the methods said to give this compound, but they say that when K_2O_4 is kept at a red heat it loses O and gives a substance the composition of which approaches that of K_2O. By heating K in a fairly dry mixture of O and N, oxidation proceeded until K_2O_4 was formed (*dry* O is without action on K); when kept in water-vapour K_2O_4 gave off O, and formed K_2O_2; and by heating K in N_2O, H. a. S. obtained K_2O_3, which on exposure to air became K_2O_4.

RUBIDIUM.

Rubidium haloid compounds (vol. iv. p. 413). Wheeler (*Am. S.* [3] 46, 88 [1893]) has prepared *double compounds* of the forms $3RbX.AsX_3$ and $RbX.As_2O_3$; and (*l.c.* p. 269) various compounds of RbX with SbX_3. For physical properties of various salts of Rb, *v.* Erdmann, *Ar. Ph.* 232, 3 (*abstract* in *C. J.* 66 [11], 351 [1894]).

SELENATES (vol. iv. p. 43[illegible]). *Basic salts* of Co and Cu are described by Bogdan (*Bl.* [3] 9, 584; *abstract* in *C. J.* 66 [11], 16 [1894]); the compositions given are $4CoO.3SeO_3.aq$ and $3CuO.2SeO_3.4aq$.

SILICON CHLORIDES (vol. iv. p. 458). In *B.* 27, 1943 [1894] Gattermann a. Weinlig detail the best conditions for preparing $SiCl_4$, $SiHCl_3$, and Si_2Cl_6, from crude Si obtained by the interaction of SiO_2 and Mg powder (*v.* vol. iv. p. 455). Si_2Cl_6 melts at $-1°$; with NH_3Aq it gives off H and forms $SiO_2.xH_2O$ (G. a. W., *l.c.*).

Silicon octochloride Si_4Cl_8. Mol. w. 366·9. V.D. 187·7. Obtained by G. a. W. (*l.c.*) by fractionating crude Si chlorides; boils from 210° to 215°; does not solidify at $-12°$.

SILVER (vol. iv. p. 464). The molecule of Ag in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). According to Lüdtke (*W.* 50, 678; *abstract* in *C. J.* 66 [11], 92 [1894]), thin deposits of Ag on glass, mica, &c., are allotropic forms of the metal. Regarding *alloys* of Ag with *cadmium*, *v.* Heycock a. Neville (*C. J.* 65, 65 [1894]); *v.* also Mylius a. Fromm (*B.* 27, 630 [1894]).

Silver chloride (vol. iv. p. 468). By the action of $HgCl_2Aq$ on pulverulent silver, Jones (*S. C. I.* 12, 983; *abstract* in *C. J.* 66 [11], 138 [1894]) obtained the compound $AgHgCl_2$.

SODIUM (vol. iv. p. 473). The molecule of sodium in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Holt a. Sims (*C. J.* 65, 440 [1894]) found that *dry* sodium may be distilled unchanged in *dry* O; in ordinary O the products are Na_2O and Na_2O_2. Heating to 180°–200° in a limited volume of N_2O forms Na_2O; heating in NO or the red oxides of N produces a mixture of $NaNO_2$ and $NaNO_3$ (H. a. S., *l.c.*).

Sodium amide (vol. iv. p. 475). Titherley (*C. J.* 65, 504 [1894]) describes $NaNH_2$ as a white, transparent solid, with a crystalline structure; softens at 149°, and is completely melted at 155° to a colourless liquid. $NaNH_2$ is obtained in transparent, crystalline needles by heating Na in NH_3 at c. 400°, allowing the product to sublime through a narrow tube, and again subliming by warming gently. $NaNH_2$ decomposes at a red heat into Na, N, and H. It does not give NaN_3, as generally stated (T., *l.c.*); no decomposition occurs at 300°-400°.

Sodium bromide (vol. iv. p. 476). Panfilov (*J. R.* 25, 272 [1893]) obtained NaBr. 5aq by exposing conc. NaBrAq out of doors in winter in Russia; decomposed at −25° to the dihydrate and water.

Sodium iodide (vol. iv. p. 481). NaI. 5aq separates from a solution of 100 g. NaI in 50 c.c. water at −14°; at −10° it gives NaI. 2aq and water (P., *l.c.*).

Sodium nitride (vol. iv. p. 482). NaN_3 is not formed by the interaction of Na or Na_2O and NH_3, or Na and N, according to Titherley (*C. J.* 65, 507; *cf. Sodium amide, supra*).

Sodium monoxide (vol. iv. p. 482). Na_2O is formed by heating Na in a limited volume of O at a temperature below 180°; also by heating Na in a limited volume of N_2O at 180°-200° (Holt a. Sims, *C. J.* 65, 442 [1894]). Heated in excess of O, the peroxide Na_2O_2 is formed. H. a. S. say Na_2O is greyish white. NH_3 reacts with gently heated Na_2O to form $NaNH_2$ and H_2O (Titherley, *C. J.* 65, 510).

Sodium dioxide (vol. iv. p. 483). Na_2O_2 does not combine with O when heated therein (H. a. S., *l.c.*). Regarding the interaction of Na_2O_2 and an alcoholic solution of HCl, *v.* Tafel (*B.* 27, 816 [1894]). For reactions of Na_2O_2, *v.* Poleck, *B.* 27, 2051 (*abstract* in *C. J.* 66 [11], 816).

STRONTIUM. For *Strontium carbide*, *v.* Moissan, *C. R.* 118, 683 (*abstract* in *C. J.* 66 [11], 318 [1894]).

SULPHATES (vol. iv. p. 567).

Chromium sulphates (vol. iv. p. 570). *Double salts* of $Cr_2(SO_4)_3$ and $(NH_4)_2SO_4$ are described by Klobb (*Bl.* [3] 9, 663; *abstract* in *C. J.* 66 [11], 95 [1894]).

Vanadium sulphates (*v.* this vol. pp. 847, 848, 850).

OXY-IMIDO SULPHONATES (vol. iv. p. 602). Divers a. Haga have published a lengthy communication on these salts in *C. J.* 65, 523 [1894].

SULPHUR (vol. iv. p. 606). For measurements of the viscosity of molten S at different temperatures, *v.* Brunhes a. Dussy, *C. R.* 118, 1045 (*abstract* in *C. J.* 66 [11], 343 [1894]).

THALLIUM (vol. iv. p. 674). The molecule of Tl in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]).

Thallium tri-iodide TlI_3. Wells a. Penfield (*Zeit. f. anorg. Chemie*, 6, 312; *abstract* in *C. J.* 66 [11], 318 [1894]) obtained this compound, in rhombic crystals, $a:b:c = \cdot6828:1:1\cdot1217$, by digesting TlI and I with alcohol and evaporating over H_2SO_4.

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